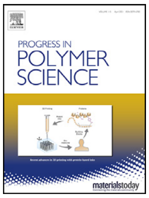
Progress in Polymer Science 162 (2025) 101935

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/progpolymsci



Recyclable fire-retardant bio-based thermosets: From molecular engineering to performances and applications

Yong Guo[a], Qingshan Yang[a], Siqi Huo[a,b,*], Juan Li[c], Pooya Jafari[a], Zhengping Fang[c], Pingan Song[a,d,*], Hao Wang[a,b,*]

[a] Centre for Future Materials, University of Southern Queensland, Springfield 4300, Australia
[b] School of Engineering, University of Southern Queensland, Springfield 4300, Australia
[c] Institute of Fire Safety Materials, NingboTech University, Ningbo 315100, China
[d] School of Agriculture and Environmental Science, University of Southern Queensland, Springfield 4300, Australia

ARTICLE INFO

Article history:
Received 19 September 2024
Revised 21 February 2025
Accepted 26 February 2025
Available online 4 March 2025

Keywords:
Bio-based thermosets
Flame retardancy
Recyclability
Degradability
Applications

ABSTRACT

Thermosets play a critical role in aerospace, automotive, electronics, and construction industries due to their mechanical strength, thermal stability, and chemical resistance. Advanced thermoset materials, such as epoxy resins, phenolic resins and unsaturated polyester resins, have significantly contributed to industrial innovation. However, these traditional thermosets heavily rely on petroleum-based resources and suffer non-recyclability and even high flammability. Last years have witnessed the use of many renewable chemicals for developing advanced bio-based thermosets with tunable physical properties, such as recyclability and reprocessability enabled by dynamic covalent chemistries, fire retardancy, mechanical and thermal properties. This review aims to summarize recent advances in recyclable, flame-retardant, bio-based thermosets, and highlights their molecular structures and design strategies for achieving high performances. We also discuss intrinsic flame-retardant modes of action, and degradation/recycling mechanisms based on dynamic covalent chemistry. Following discussions on their applications, some key challenges and opportunities are also proposed for the development of next-generation advanced thermosets. This work is expected to expedite the creation of high-performance recyclable thermosets and to advance the sustainability transition of traditional thermosets.

1. Introduction

Thermosets are a class of polymers with three dimensional crosslinking networks [1]. Representative examples of thermosetting resins include phenolic resins, melamine formaldehyde resins, unsaturated polyesters, vinyl esters, polyimides, and thermosetting epoxy resins. Thermosetting resins exhibit great mechanical properties, electrical insulation, chemical resistance, and dimensional stability, which allow them to find extensive applications in various industries, such as aerospace, transportation, construction, and electronics [2–4]. The current annual production of thermosetting resins is about 65 million tons, accounting for ~20 % of total polymer production [5,6]. At present, thermosetting resins are mainly synthesized from petroleum-based chemicals. Despite ubiquitous applications, these petroleum-based thermosets encounter significant challenges, primarily stemming from three major drawbacks: (i) Their mass production leads to excessive consumption of petroleum resources and a series of environmental issues [7,8]; (ii) Their intrinsic flammability poses a fire threat to the environment and human beings [9–11]; and (iii) Their non-degradability/recyclability causes the generation of abundant plastic waste and great damage to the ecological system [12,13]. Hence, it is of vital importance to create advanced bio-based thermosets to meet the needs of modern industry as well as sustainable development.

The concerns about over-consumption of petroleum resources, which account for the highest global energy consumption at 53,620 TWh [14], have stimulated the development of bio-based materials. Many bio-based feedstocks have been applied in the fabrication of high-performance thermosets, such as lignin-derived chemicals, vegetable oils, bio-based acids, and furan-based organics [15]. Obviously, the structural diversity of these renewable feedstocks offers a unique opportunity to develop sustainable, advanced thermosets, which are expected to find ubiquitous applica-

---

[*] Corresponding authors at: Centre for Future Materials, University of Southern Queensland, Springfield 4300, Australia.

E-mail addresses: Siqi.Huo@unisq.edu.au, sqhuo@hotmail.com (S. Huo), pingan.song@usq.edu.au, pingansong@gmail.com (P. Song), hao.wang@unisq.edu.au (H. Wang).

https://doi.org/10.1016/j.progpolymsci.2025.101935

Nomenclature

σ_{fl}	Flexural strength
σ_t	Tensile strength
2-EHA	2-Ethylhexylamine
APDS	4-Aminophenyl disulfide
CA	1,4-Cyclohexanedicarboxylic acid
CANs	Covalent adaptable networks
CCT	Cone calorimetry test
CFRPs	Carbon fiber-reinforced polymers
D230	O, O'-Bis(2-aminopropyl) polypropyleneglycol
DA	Diels-Alder
DCA	Dodecanedioic acid
DCBs	Dynamic covalent bonds
DDM	4,4-Diaminodiphenylmethane
DFA	5'-Methylenedifurfurylamin
DGEBA	Bisphenol A- diglycidyl ether
DGEBA/DDM	DDM-cured DGEBA
DHH	6-(2,5-Bis(2-hydroxyethoxy) phenyl)dibenzo[c,e] [1,2]oxaphosphinine 6-oxide
DMA	Dynamic mechanical analysis
DMF	Dimethyl formamide
DOPO	9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
DSC	Differential scanning calorimetry
EP	Epoxy resin
EV	Citric acid-cured DGEBA
ESO	Epoxidized soybean oil
GDE	Glycerol diglycidyl ether
GTE	Glycerol triglycidyl ether
HCl	Hydrochloric acid
HDA	Hexamethylenediamine
HEMAP	2-Hydroxyethyl methacrylate phosphate
HRC	Heat-release capacity
IS	Impact strength
LOI	Limiting oxygen index
MHHPA	Methylhexahydrophthalic anhydride
NA	Not applicable
NaOH	Sodium hydroxide
BMI	N,N'-(4,4′-methylenediphenyl)dimaleimide
N	Nitrogen
P	Phosphorus
PA	Phytic acid
PACM	4,4-Diaminodicyclohexylmethane
PCNs	Permanent cross-linked networks
pHRR	Peak of heat release rate
reverse Diels–Alder	r-DA
S	Sulfur
TA	Tannic acid
TBD	1,5,7-Triazabicyclo [4,4,0] dec-5-ene
T_g	Glass transition temperature
THF	Tetrahydrofuran
THR	Total heat release
TREN	Tris(2-aminoethyl) amine
$T_{r\text{-}DA}$	Temperature of r-DA
TSP	Total smoke production
T_v	Topological freezing transition temperature
UL-94	Vertical burning test
ΔpHRR	pHRR variation compared to control sample
ΔTHR	THR variation compared to control sample
ΔTSP	TSP variation compared to control sample

tions in various industries and meet environmental needs (Fig. 1). To address the flammability issue, many flame-retardant structures have been built into the cross-linked networks of bio-based thermosets, including phosphorus (P)-containing [16], bio-based nitrogen (N)-containing [17], and bio-based benzene/$C{=}C$-rich [18]. The dynamic covalent chemistry, *e.g.,* transesterification [19–22], Diels-Alder (DA) exchange [23], imine metathesis [24], and disulfide exchange [25], has been widely utilized to create recyclable and degradable thermosets [26].

Research on bio-based flame-retardant and recyclable thermosetting materials has made certain progress [27–30], but there is still a lack of comprehensive review articles covering the entire field, especially from the perspective of molecular engineering to deeply explore the performance of these materials. Existing studies mostly focus on flame-retardant properties, recyclability, and the basic characteristics of the materials, while systematic explanations of the relationship between material structure and performance remain insufficient. Additionally, there is a lack of exploration and summary of the practical applications of bio-based flame-retardant and recyclable thermosetting materials.

In this review, the recent development of bio-based, fire-retardant, recyclable thermosets is thoroughly introduced, and the internal relationship between their chemical structure, flame retardancy and recyclability is carefully analyzed. Moreover, the term "bio-based content" refers to the ratio of carbon derived from biomass to the total carbon in the product, as defined by ISO 16620-2:2019 [31–33]. In this review, the bio-based content of the reported bio-based thermosets is calculated and compared. Additionally, the flame-retardant properties, as well as the recycling and degradation mechanisms, are comprehensively discussed. Therefore, this review is mainly focused on the exploration of the structure-performance relationships and practical applications of bio-based, fire-retardant, recyclable thermosets [34]. Finally, this review presents some key challenges associated with these bio-based, fire-retardant, recyclable thermosets, and proposes their future development directions and opportunities for industrial applications.

2. Bio-based feedstocks for recyclable fire-retardant bio-based thermosets

Various chemicals can be derived from biomass through different biological, physical, and chemical processes, and bio-based chemicals used to manufacture advanced thermosets primarily come from lignin, cellulose, bio-based acids, vegetable oils, and similar sources [35]. These chemicals are environmentally friendly and renewable. Utilizing these bio-based feedstocks for recyclable flame-retardant thermosets not only helps mitigate the oil crisis but also reduces environmental pollution, and thus they show great potential in replacing petroleum-based raw materials in the production of thermosets. A summary of bio-based feedstocks for recyclable flame-retardant thermosets is shown in Fig. 2.

2.1. Lignin-derived chemicals

Lignin is a biopolymer with a three-dimensional network structure formed by three phenylpropane units linked *via* ether and carbon-carbon bonds, which is primarily derived from wood herbaceous plants and agricultural by-products [36]. Lignin contains a

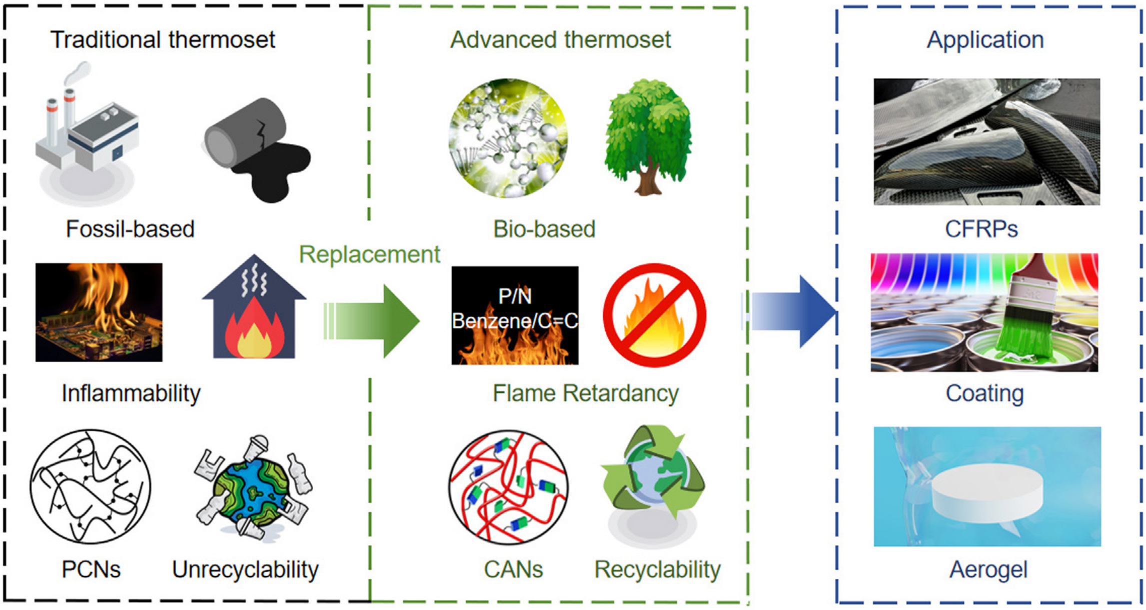


Fig. 1. Illustration of the transition from traditional thermosets to advanced thermosets [26], Copyright 2022. Adapted with permission from Royal Society of Chemistry.

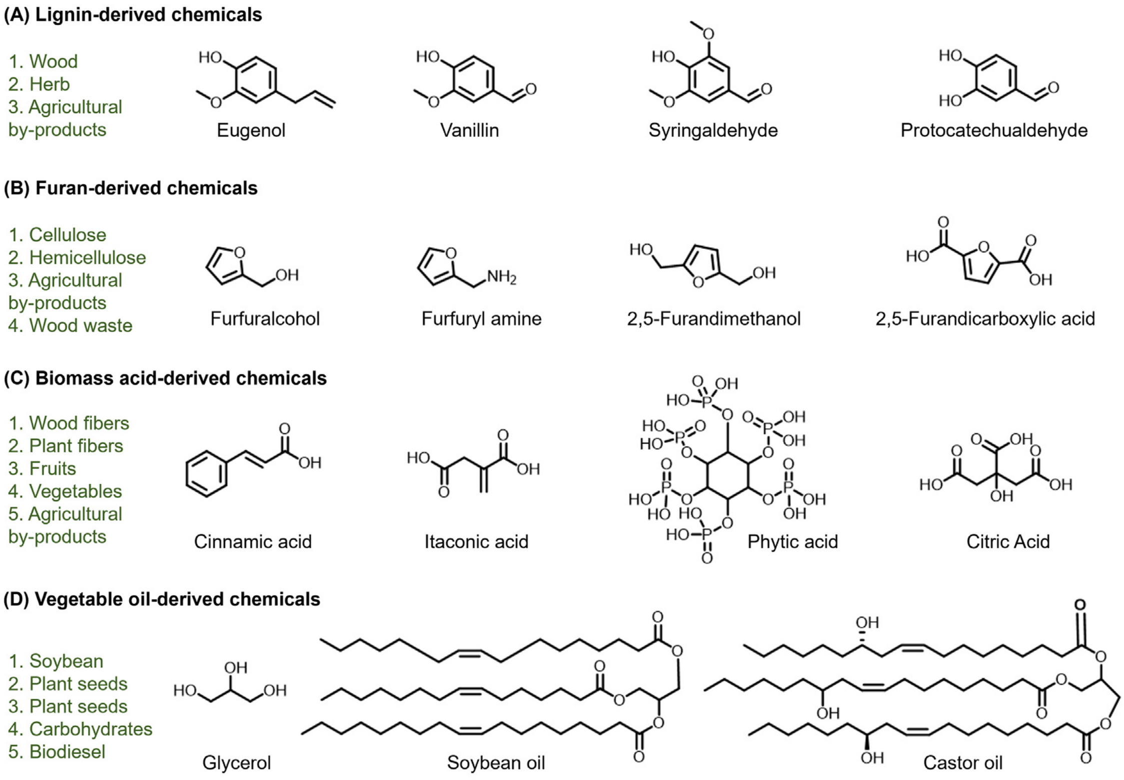


Fig. 2. Sources and representatives of (A) lignin-derived, (B) furan-derived, (C) biomass acid-derived, and (D) vegetable oil-derived chemicals.

rich array of aromatic rings, as well as aliphatic and aromatic hydroxyl, aldehyde, and amino groups. Common lignin derivatives used to fabricate recyclable flame-retardant thermosets include vanillin [37], syringaldehyde [38], protocatechualdehyde [39], and eugenol [40]. Eugenol, containing reactive phenolic hydroxyl and allyl groups, offers potential for chemical modification. The allyl group can undergo "click chemistry" [41] with reagents and epoxidation reactions [42], enabling the introduction of functional groups. Vanillin, syringaldehyde, and protocatechualdehyde structures contain two reactive groups: phenolic hydroxyl and aldehyde. The aldehyde group can react with amines to form Schiff bases, which show certain flame-retardant effect due to the high-temperature self-crosslinking characteristic and impart recyclability and antibacterial properties [43–45]. Additionally, the phenolic hydroxyl groups in lignin-derived compounds can undergo epoxidation [46], ring-opening reactions with epoxides [47], and substitution reactions to incorporate flame-retardant groups [48]. Obviously, the lignin-based chemicals with different reactive groups can be applied in the production of bio-based thermosets by various chemical reactions, making lignin an excellent bio-based platform compound.

2.2. Furan-derived chemicals

Furan derivatives are also widely used bio-based chemicals, which are derived from cellulose, hemicellulose, agricultural by-products, and wood waste. The chemical structure of the furan ring is similar to that of the benzene ring, and thus the furan-derived thermosets exhibit comparable properties to traditional thermosets [49]. Furfuryl alcohol, furfuryl amine, 2,5-furandimethanol, and 2,5-furandicarboxylic acid can undergo epoxidation due to their hydroxyl, amino, and carboxyl groups [50–52], and thus they can be used in the fabrication of bio-based epoxy thermosets. Meanwhile, a variety of bio-based amine curing agents are synthesized by using furfuryl amine as a raw material and utilized to prepare advanced thermoserts [53–55]. Additionally, the DA reaction between furan (as a diene) and maleimide (as a dienophile) provides an efficient pathway for synthesizing high-performance, recyclable thermosets [23].

2.3. Biomass acid-derived chemicals

Biomass acid-derived chemicals produced from wood fibers, plant fibers, fruits, vegetables, and agricultural by-products can be used as the precursor or curing agent to prepare recyclable flame-retardant epoxy thermosets. The common biomass acid-derived chemicals include cinnamic acid, itaconic acid, phytic acid (PA) and citric acid.

Itaconic acid, phytic acid and citric acid have hydroxyl or carboxyl groups, which can react with epoxy resins (EPs) to form a cross-linked network with abundant ester groups [56–58], thereby achieving recyclability through transesterification. In addition, the high content of hydroxyl groups in these structures can be epoxidized to produce bio-based epoxy resins [59], and the corresponding bio-based epoxy thermosets prepared after curing usually have good mechanical strength due to high crosslinking density. In addition, these bio-based resins have lots of ester groups in their structures, which have the potential for recycling due to the transesterification [60]. Cinnamic acid and itaconic acid have not only carboxyl groups, but also carbon-carbon double bonds, which allow other functional groups to be introduced [61].

2.4. Vegetable oil-derived chemicals

Vegetable oil-derived chemicals applied to manufacture bio-based, recyclable, fire-retardant thermosets mainly include soybean oil, castor oil, and glycerin, which are derived from soybean, castor, plant seeds, carbohydrates, and biodiesel.

Natural glycerin is primarily extracted from plant and animal fats. Glycerol contains three hydroxyl groups, and they can be epoxidized to produce glycerol diglycidyl ether (GDE) and glycerol triglycidyl ether (GTE), which are both suitable for the fabrication of high-performance thermosets [37,62]. During curing, these compounds can form two-dimensional chain and three-dimensional network structures, endowing the obtained thermosets with superior mechanical properties.

Soybean oil, as a renewable, biodegradable, and soybean seed-derived material, can serve as an alternative to petroleum-derived raw materials for fabricating thermosets. Soybean oil is a highly unsaturated oil with an average of 4-5 non-conjugated double bonds per molecular chain, but it usually suffers from low reactivity. However, it can be modified by epoxidation to produce epoxidized soybean oil (ESO), which can be applied in high performance thermosets [63–65]. Compared to conventional epoxy resins, ESO has a higher degree of epoxidation, offering enhanced film formation, chemical resistance, and heat resistance.

Castor oil, extracted from castor seeds, contains a high concentration of ricinoleic acid and includes olefinic double bonds, ester groups, hydroxyl groups, and other reactive sites, allowing it to undergo various chemical modifications to produce bio-based thermosets, such as esterification, hydrogenation, epoxidation, dehydrogenation, dehydration, alcoholysis, and transesterification [66–68]. The uniform distribution of hydroxyl groups along its main chain facilitates the formation of a consistent cross-linked structure within the bio-based thermosets, thus realizing high toughness.

3. Flame-retardant structures for recyclable fire-retardant bio-based thermosets

Thermosets are highly flammable, posing risks to the environment, humans, and property [69–71]. Improving their flame-retardant properties can expand their use in specialized fields. Flame retardant modifications include (i) additive and (ii) intrinsic methods [72,73]. Additive flame retardants often reduce mechanical properties and may leach over time [74]. In contrast, intrinsic modification integrates flame-retardant structures into the cross-linked networks, addressing the limitations of additive methods [75]. The structures and mechanisms of recyclable bio-based flame-retardant thermosets are shown in Fig. 3. Additionally, commonly used flame-retardant tests include: (a) limiting oxygen index (LOI), which measures the minimum oxygen concentration required to sustain combustion under specified conditions; (b) vertical burning test (UL-94), which evaluates the flammability of materials by assessing their self-extinguishing ability when ignited vertically; and cone calorimetry test (CCT), which evaluates the fire behavior of materials by measuring their heat release, smoke production, and mass loss under controlled heat exposure. In the CCT, △pHRR, △THR, and △TSP refer to the reduction in peak of heat release rate (pHRR), the reduction in total heat release (THR), and the reduction in total smoke production (TSP), compared to control samples.

3.1. Phosphorus-containing structures

Phosphorous-containing structures are the most commonly introduced flame-retardant components into cross-linked network of thermoset (Fig. 3A). The phosphorus is a multivalent element and can exist in any valance from -3 to 5. The flame-retardant mechanisms of P-containing structures are usually determined by the oxidation states of phosphorus in the flame retardants. The structures with P in a higher oxidation state, such as trimethyl phosphate [76,77], triazatriphosphinine [78], and dimethyl phenoxyphosphate [4,79,80], exhibit a condensed-phase mechanism *via* promoting the carbonization of the thermoset matrix (Fig. 3F). The structures with P in a lower oxidation state, such as dimethyl phenylphosphonate [81,82], methyldiphenylphosphine oxide [83–85], and phosphaphenanthrene [86–91], primarily display a gaseous-phase mechanism through producing PO·, HPO· and HPO_2· radicals to capture high-energy radicals from the matrix [92] during the combustion. For many P-containing structures, both gaseous- and condensed-phase mechanisms coexist.

3.2. Bio-based nitrogen-containing structures

Chemically introducing bio-based N-containing structures (Fig. 3B) into the cross-linked network is another effective method to enhance fire retardancy of bio-based thermosets. Curing bio-based N-containing epoxy resins (An) with furan/aromatic amine hardeners (Cm, Fig. 3D) can obtain fire-retardant bio-based

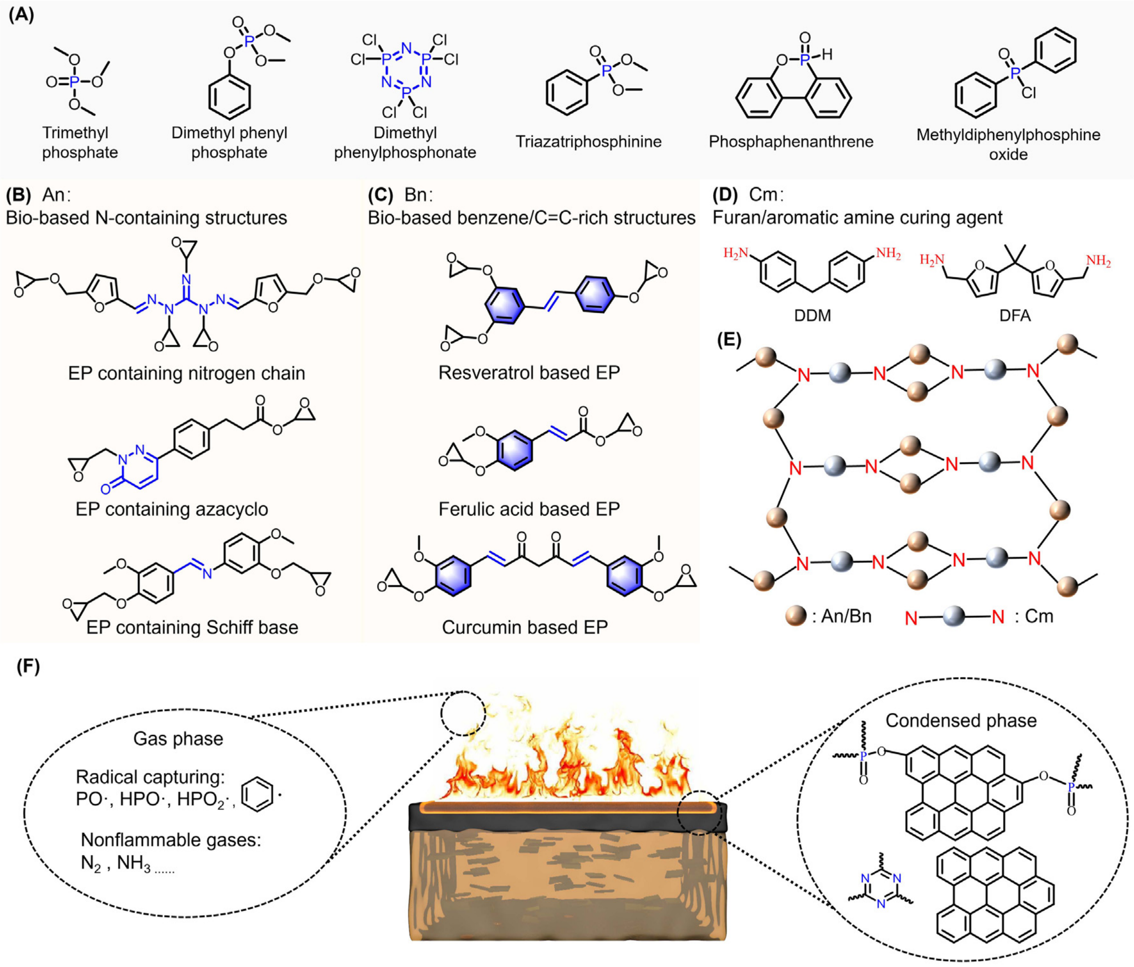


Fig. 3. Flame-retardant structures and mechanisms for recyclable fire-retardant bio-based thermosets. (A) Phosphorus-containing structures, (B) bio-based N-containing structures, (C) bio-based benzene/C=C-rich structures, and (D) furan/aromatic amine curing agent structures. Schematic of (E) the cross-linked (An/Bn + Cm) network, and (F) flame-retardant mechanisms for different structures (phosphorus-containing, bio-based nitrogen-containing, and benzene/C=C-rich).

thermosets (An+Cm, Fig. 3E) [93–95]. The -C=N- bonds within the cross-linked network of bio-based thermoset can generate N-containing six-membered heterocyclic compounds by rearrangement and cyclizing at high temperatures, which leads to the formation of stable char layers to inhibit heat-oxygen exchange. Furthermore, the nitrogen-containing structures can produce inert nitrogen-derived gases to exert diluting effect in the gas phase.

3.3. Bio-based benzene/C=C-rich structures

Curing bio-based benzene/C-C-rich epoxy resins (Bn, Fig. 3C) with rigid hardeners (Cm) can also produce the fire-retardant bio-based thermosets (Bn+Cm, Fig. 3E). During combustion, the phenol radicals derived from the benzene/C-C-rich structures can interrupt the free radical chain reaction in the gas phase [96–98]. Besides, the benzene/C=C-rich structures can form stable and compact char layers on the thermoset surface, thus suppressing the heat release and smoke generation in the condensed phase [99–101].

4. Dynamic covalent chemistry for recyclable fire-retardant bio-based thermosets

Covalent adaptable networks (CANs) with dynamic covalent bonds endow thermosets with recyclability and degradation under external stimuli [102–104]. Additionally, the topological transformation of CANs enables thermosets to reprocess [105–109]. Based on the reaction mechanisms, CANs can be broadly categorized into two types: dissociative exchange and associative exchange (Fig. 4A and B) [110–113].

For dissociative exchange [114], the dynamic covalent bonds are initially broken and then reformed within the CANs (Fig. 4A). During dissociative exchange, the crosslink density of thermosets decreases because the breakage and reformation of dynamic covalent bonds occur separately, potentially causing a loss of network connectivity and even complete depolymerization. The best-known examples of dissociative dynamic linkages are thermally reversible DA adducts. The DA addition reaction, as a typical dissociative exchange, generally occurs between electron-deficient dienophiles and electron-rich conjugated dienes, forming cyclohexene adducts *via* [4+2] cycloaddition (Fig. 4A_1) [115–117]. This reaction is favorable under mild conditions, while the reverse Diels–Alder (r-DA) reaction can occur at high temperatures [118]. Bio-based flame-retardant recyclable thermosets based on DA cycloadducts between furan and maleimide have been widely explored. As previously mentioned, the CANs with DA adducts may result in gel-to-sol transitions or reduced crosslink density during reprocessing, potentially impacting mechanical properties and recyclability [119].

For associative exchange, dynamic bond breakage and regeneration occur simultaneously, thus the CANs can maintain a constant

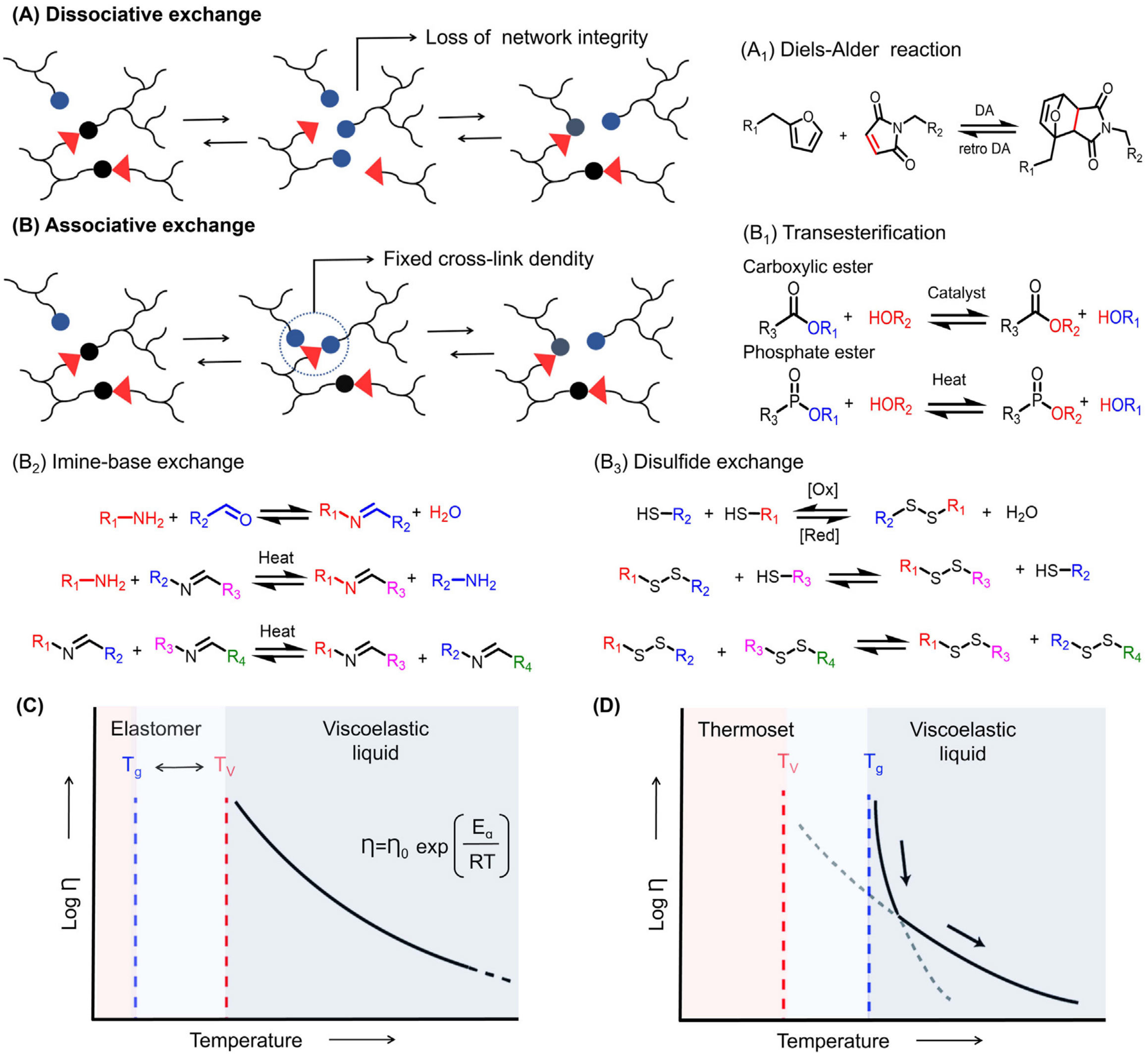


Fig. 4. Dynamic covalent chemistry for recyclable fire-retardant bio-based thermosets. Schematic of (A) dissociative exchange [35], Copyright 2022. Adapted with permission from Elsevier Science Ltd, and (A_1) Diels-Alder addition. Illustration of (B) associative exchange [35], Copyright 2022. Adapted with permission from Elsevier Science Ltd, (B_1) transesterification, (B_2) imine-base exchange, and (B_3) disulfide exchange. Representation of the viscoelastic behavior of vitrimers with (C) T_g lower than T_v, and (D) T_v well below T_g [35], Copyright 2022. Adapted with permission from Elsevier Science Ltd.

crosslink density under external stimuli (Fig. 4B) [120]. Unlike dissociative CANs, the associative CANs (named vitrimers) exhibit a constant crosslink density. Under external stimuli, their network topology can be rearranged through dynamic bond exchange, enabling a transition from viscoelastic solid to viscoelastic liquid. This allows vitrimers to flow when heated, enabling reshaping without compromising material integrity [121]. Representative associative exchanges include transesterification (Fig. 4B_1), Schiff base exchange (Fig. 4B_2), and disulfide bond exchange (Fig. 4B_3).

Ester groups are common groups within the cross-linked network of thermosets, typically formed through the reactions between epoxy/hydroxy groups and carboxyl/phosphoric acid groups [122]. Under external stimuli, the transesterification within the cross-linked network allows vitrimer to realize topology rearrangement but maintain a constant crosslink density. Notably, the carboxylate-based transesterification vitrimers usually require a catalyst to induce the associative exchange, but the phosphate-based transesterification vitrimers do not.

Schiff base is usually formed through the dehydration condensation between aldehyde and amino groups [123], and it can be hydrolyzed into aldehyde and amino groups. The degradation of Schiff base-containing thermosets primarily relies on the hydrolysis of Schiff base. Additionally, Schiff bases can undergo substitution reactions with amino groups in anhydrous conditions, and exchange reactions can occur between Schiff bases, thus the Schiff base-containing vitrimers can be reshaped through hot-pressing.

Disulfide bonds can be broken into thiols and exchanged under external stimuli [124], and thus they can be applied in the manufacture of recyclable thermosets. Notably, due to the relatively low bond energy of disulfide bonds (251 kJ/mol, approximately 40 % lower than C–C/H bonds), the topology rearrangement of disulfide-containing vitrimers can be stimulated under mild conditions [125].

The viscoelastic characteristics of vitrimers are governed by two critical temperatures: the glass transition temperature (T_g) and the topological freezing transition temperature (T_v) [126–128]. The significance of these two transition temperatures, which are fundamental to vitrimers, can be effectively illustrated through two specific examples. In the first case, the vitrimer exhibits a T_g that is lower than T_v (Fig. 4C). When heated to a temperature between T_g and T_v, the glassy vitrimer first transitions into a rubbery state, behaving as an elastomer. At this temperature, the exchange reactions are relatively slow, allowing the network to remain largely intact. When the temperature rises further to above T_v, the exchange reactions accelerate and become significant, resulting in the conversion of the elastomer into the viscoelastic liquid, where the flow is primarily governed by the kinetics of exchange reaction, leading to a typical Arrhenius decrease in viscosity. In the second case, a rapid exchange reaction is integrated within a rigid thermoset matrix that has a T_g higher than T_v (Fig. 4D). In this situation, T_v can be estimated through the extrapolation of stress-relaxation or creep tests, rendering this transition theoretical. The network remains constrained not by the reaction kinetics but by the absence of segmental motion linked to T_g. Below T_g, segmental motion does not occur, preventing any exchange reactions and thus fixing the network (this relates to the diffusion limit). As the material is heated beyond its T_g, segmental motion begins to occur gradually, while the exchange reactions are already occurring at a fast rate. Initially, the kinetics of network rearrangement are diffusion-controlled, with segmental motions predominating the topology changes, which yields Williams–Landel–Ferry equation viscosity behavior [129,130]. As heating continues, the exchange kinetics transition from being diffusion-controlled to being governed by the exchange reactions, adhering to Arrhenius behavior [131].

4.1. Diels-Alder reaction

The bio-based furan and maleimide groups readily undergo DA reaction, enabling the construction of flame-retardant, recyclable bio-based thermosets. For instance, Zhao *et al.* [132] fabricated a recyclable flame-retardant DA-based thermoset (re-CP-co-BMI) using a bio-based eugenol/cyclotriphosphazene-containing monomer (CP-3AF, Fig. 5A) and N,N'-(4,4′-methylenediphenyl)dimaleimide (BMI). The resulting re-CP-co-BMI demonstrated a high bio-based carbon content (56.3 %, Fig. 5J) and desirable flame retardancy due to the incorporation of eugenol- and cyclotriphosphazene-containing structures. Moreover, re-CP-co-BMI can maintain its structural stability in trichlorobenzene at room temperature for 48 h, but it can be fully degraded in high temperatures because of the r-DA reaction (Fig. 5E). However, re-CP-co-BMI suffered from poor thermal stability, with low T_g of 82.9 °C and temperature of r-DA ($T_{r\text{-}DA}$) of 125 °C. The tensile strength of re-CP-co-BMI was 7.5 MPa, indicative of unsatisfied mechanical properties. Bio-based amines are rare in type and quantity, and furfuryl amine stands out for its high application value. Its amino group can be epoxidized to produce diglycidyl furfurylamine (DGFA, Fig. 5B), which contains reactive furan and epoxy groups. Based on DGFA, Chen *et al.* [133,134] synthesized two phosphorus-containing DA adducts (Fig. 5C and D), which were respectively cured with methylhexahydrophthalic anhydride (MHHPA) for the preparation of flame-retardant recyclable bio-based thermosets (BMP-EP and DOPO-TMP-EP). The bio-based carbon contents of BMP-EP and DOPO-TMP-EP were 28.6 % and 22.0 %, respectively. BMP-EP exhibited great thermal stability, flame retardancy, and reprocessability (Fig. 5F), attributed to the electron-withdrawing phosphonate group. Meanwhile, DOPO-TMP-EP, containing a phosphate spacer with a low rotational energy barrier [135], showed improved segment mobility and dynamic reversibility, leading to excellent self-healing capability and reprocessability. The flame-retardant effect of phosphate spacer also enhanced the fire safety of DOPO-TMP-EP (Fig. 5G). As shown in Fig. 5H and I, compared to re-CP-co-BMI and BMP-EP, DOPO-TMP-EP exhibited better overall performance. DOPO-TMP-EP showed high T_g of 121°C and $T_{r\text{-}DA}$ of 168 °C, demonstrating great thermal stability. Its LOI and UL-94 classification was up to 29.8 % and V-0, with 79.8 %, 57.4 %, and 77.2 % reductions in pHRR, THR and TSP relative to control sample. DOPO-TMP-EP showed a tensile strength of 92.1 MPa, and its tensile strength retention reached 94.5 % after recycling. The phosphorus atom with high oxidation state of +5 mainly functioned in the condensed phase during combustion, and the DA cycloaddition structures played a synergistic role. In addition, the phosphorus atom with an oxidation state of +3 in the 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) contributed to gas-phase flame retardancy through interrupting the combustion reaction of the polymer matrix by the capturing effect of its P-containing radicals, and to condensed-phase flame retardancy through promoting the formation of compact char layers on the matrix surface by the catalyzing effect of its pyrophosphate derivatives [136–138]. These findings suggest that constructing DOPO-containing neighboring group in the DA-based epoxy resins contributes to achieving high-performance, flame-retardant, bio-based recyclable thermosets.

In summary, re-CP-co-BMI mainly achieves cross-linking through DA reaction, and thus it suffers from poor thermal and mechanical properties due to the existence of abundant DA crosslinking points. Although it has high recyclability, its unsatisfied overall performance limits its practical applications. In contrast, BMP-EP and DOPO-TMP-EP, with limited DA groups, show better comprehensive performances. Meanwhile, due to the presence of ester and tertiary amine groups, both BMP-EP and DOPO-TMP-EP can undergo transesterification at high temperatures, thus they exhibit great reprocessability and recyclability. To enhance the performances of DA/bio-based thermosets, more research should be focused on controlling the content of DA adducts within the crosslinked network. One promising strategy is to introduce DA adducts into the prepolymer, such as epoxy resin, prior to crosslinking [139,140]. Another approach involves synthesizing curing agents containing DA adducts and using them in the preparation of DA-based thermosets [141–143]. These strategies offer new approaches for developing recyclable, flame-retardant, bio-based thermosets. In addition, considering the low bio-based carbon contents of these three systems, using bio-based furan compounds and bio-based unsaturated compounds to create DA/fully bio-based, recyclable thermosets can further support sustainable development.

4.2. Transesterification

Transesterification is commonly applied in the fabrication of flame-retardant, recyclable bio-based vitrimers, typically involving β-hydroxyl ester exchange and phosphate ester exchange (Fig. 6A and B). Many bio-based monomers containing ester bonds (Fig. 6A_1) and bio-based curing agents to form β-hydroxyl ester (Fig. 6A_2) had been reported for the preparation of fire-retardant, bio-based vitrimers based on β-hydroxyl ester exchange. For the vitrimers based on phosphate ester exchange, using the phosphate ester-containing curing agents is a common approach (Fig. 6B).

For β-hydroxyl ester-based vitrimer, using bio-based ingredients to synthesize ester-containing resin monomers contributes to enhancing the bio-based carbon content of the vitrimer, as these monomers make up a significant proportion of vitrimer. Furthermore, chemically incorporating flame-retardant structures, such as nitrogen-containing, phosphorus-based, and benzene/C=C-rich, can impart excellent intrinsic flame-retardant properties to the resulting vitrimer. However, a major drawback is the use of numerous toxic solvents in the synthesis of resin monomers, which poses significant risks to human health and the environment. Moreover, since the ester bond is located on the main chain, it negatively impacts recyclability, particularly in mechanical recycling, which often exhibits low recovery efficiency.

In addition to introducing ester units into resin monomers, the β-hydroxyl ester units can also be formed when the bio-based carboxylic acids are used as hardeners to cure epoxy resins. Furthermore, anhydrides are frequently employed alongside bio-based carboxylic acids as curing agents, and this process is typically solvent-free. Due to the high β-hydroxyl ester content, the resulting vit-

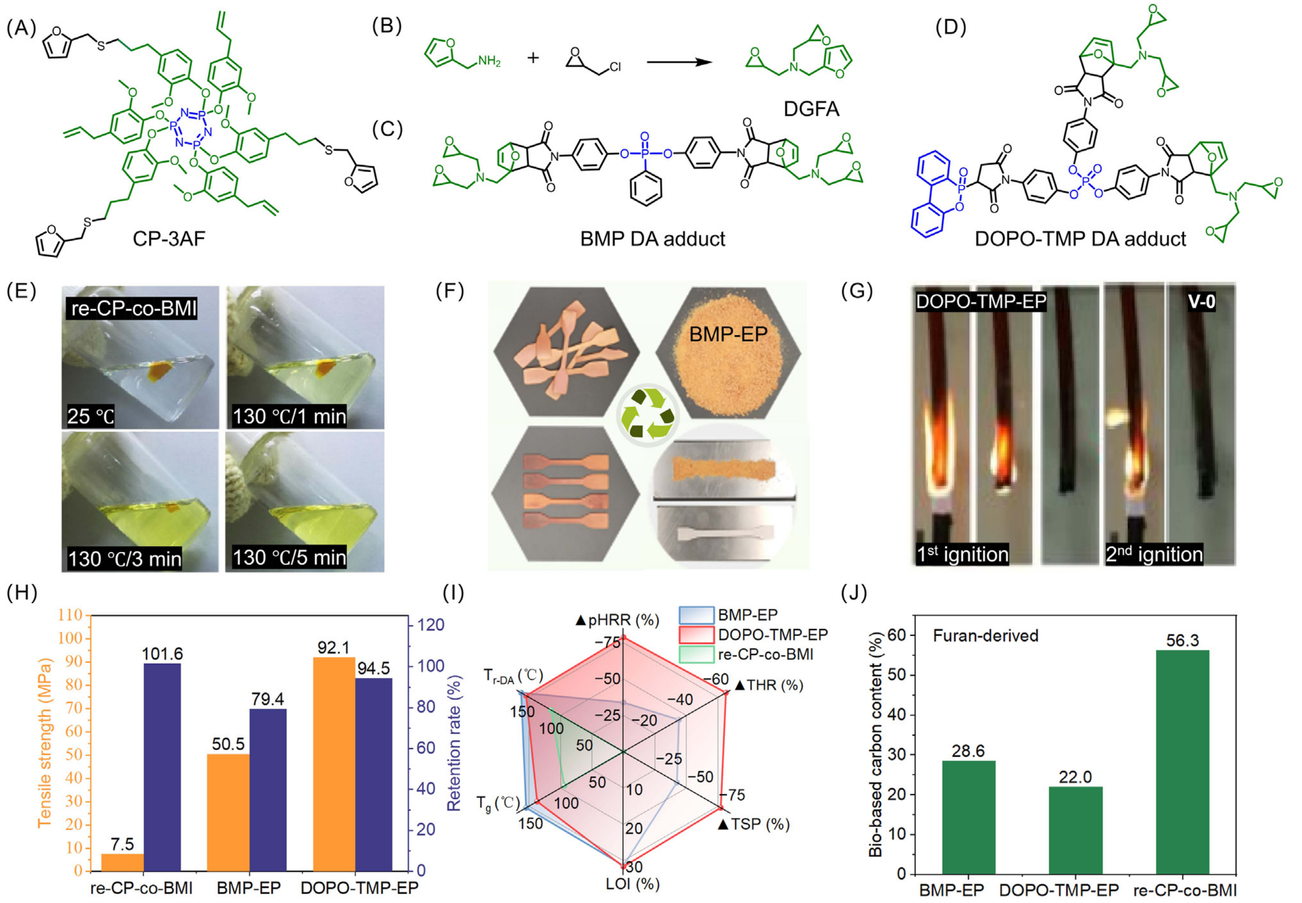


Fig. 5. DA/bio-based, fire-retardant thermosets and their comprehensive performances. Chemical structures of (A) re-CP-co-BMI [132], Copyright 2021. Adapted with permission from Elsevier Science Ltd, (C) BMP DA adduct [133], Copyright 2023. Adapted with permission from John Wiley & Sons Inc, and (D) DOPO-TMP DA adduct [134], Copyright 2023. Adapted with permission from John Wiley & Sons Inc. (B) Synthesis of bio-based DGFA [133], Copyright 2023. Adapted with permission from John Wiley & Sons Inc. (E) Degradation behaviors of re-CP-co-BMI [132], Copyright 2021. Reproduced with permission from Elsevier Science Ltd. (F) Reprocessing procedure of BMP-EP [133], Copyright 2023. Reproduced with permission from John Wiley & Sons Inc. (G) Burning process of DOPO-TMP-EP during UL-94 test [134], Copyright 2023. Reproduced with permission from John Wiley & Sons Inc. (H) Tensile strength of three DA-based thermosets and their tensile strength retention after recycling. (I) Performance comparison of three DA-based thermosets. (J) Bio-based carbon content of three DA-based thermosets.

rimers have high recycling efficiency. However, when curing EP with carboxylic acid, a catalyst, such as zinc acetate and imidazole, is necessary to facilitate the ring-opening reaction of the epoxy group, thus improving both the reaction rate and curing efficiency [144]. However, during prolonged use, external catalysts may leach from the vitrimer matrix, potentially resulting in irreversible damage to both the environment and human health [106]. Besides, due to the incorporation of acids and anhydrides, which often introduce a substantial quantity of aliphatic chains, the resulting vitrimers tend to be highly flammable. Typically, a phosphorus content of over 2 wt% is necessary to attain satisfactory flame retardancy [19,21,145,146].

Finally, phosphate esters can undergo transesterification and thus many phosphate ester-based vitrimers have been developed. Notably, the transesterification of phosphate esters occurs at a faster rate with a lower activation energy compared to those of β-hydroxyl esters, even in the absence of a catalyst. The formation of phosphate esters typically takes place through a ring-opening reaction between P-OH and epoxy groups without the usage of solvent. In addition, due to the high content of phosphate, the resulting vitrimers exhibit excellent flame retardancy. However, due to the inherent instability of phosphate ester bonds, the phosphate ester-based vitrimers usually exhibit poor solvent resistance, leading to degradation under both weak alkaline and neutral conditions. This instability significantly restricts their practical applications.

4.2.1. Bio-based monomer containing ester bond

Wei *et al.* [147] fabricated ester-containing recyclable flame-retardant bio-based thermosets (FREPs, Fig. 7A) using bio-based itaconic acid-derived hyperbranched EP (IA-EHBP) and bisphenol A- diglycidyl ether (DGEBA) as prepolymers and (1,3,5-hexahydro-s-triazine-1,3,5-triyl) benzyl mercaptan as a curing agent. FREP10 (IA-EHBP: 10 wt%, bio-based carbon content: 20 wt%) demonstrated excellent flame-retardant performance, as indicated by an LOI of 33.4 % and a UL-94 V-0 rating. The self-extinguishing behavior of FREP10 during UL-94 test is presented in Fig. 7B, demonstrating the significant role of DOPO group. Furthermore, the FREP specimen can be chemically recycled in the tetrahydrofuran (THF) solution (Fig. 7C) due to the presence of hexahydro-s-triazine and ester structures in its network. Both P-containing and N-containing building blocks can be recycled and reused to reform FREP10. As shown in Fig. 7F, the reformed FREP10 (r-FREP10) exhibited similar flame retardancy and mechanical properties to original FREP10, with retention of tensile strength (σ_t), impact strength (IS), and flexural strength (σ_{fl}) reaching 99.9 %, 77.2 %, and 95.9 %, respectively.

Cao *et al.* [95] developed an aromatic N-heterocycle-derived, ester-containing, bio-based epoxy monomer and cured it with 4,4-diaminodiphenylmethane (DDM) to construct recyclable flame-retardant bio-based thermosets (CSPZ-EP/DDM, Fig. 7D). The bio-based carbon content of CSPZ-EP/DDM reached 62.1 % (Fig. 7H).

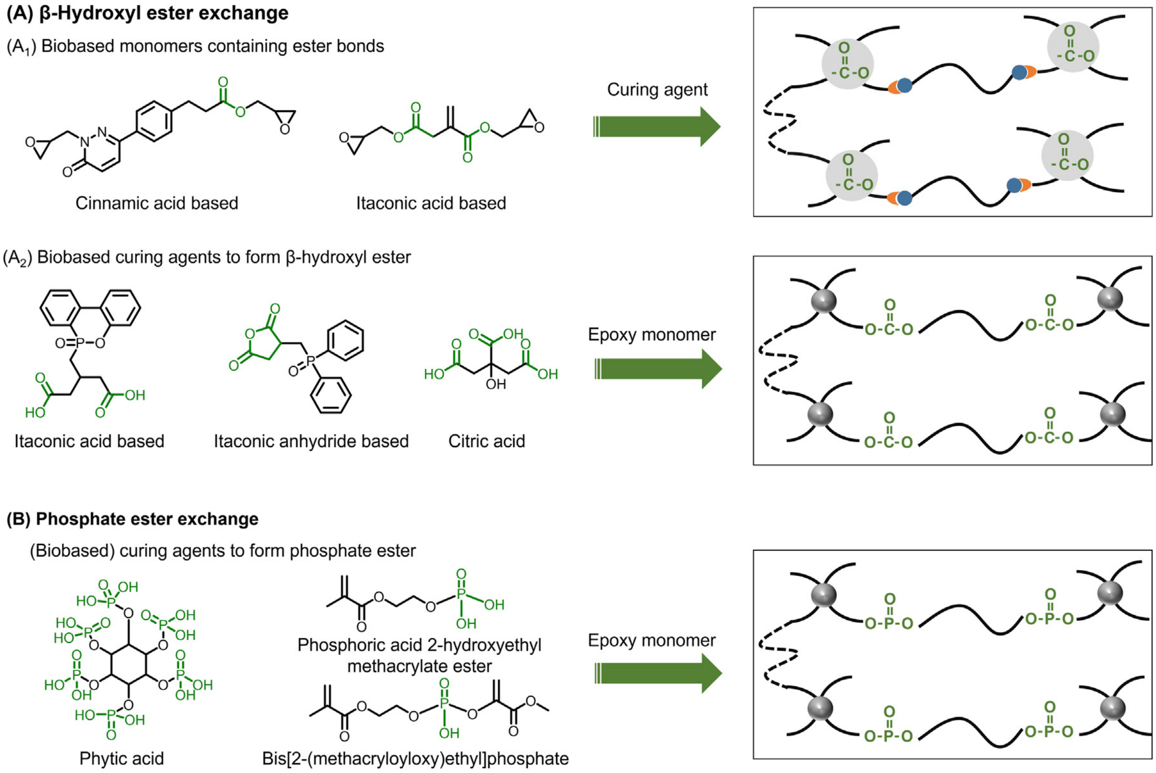


Fig. 6. Design of fire-retardant bio-based transesterification vitrimers. (A) β-Hydroxyl ester exchange: Chemical structures and curing mechanism of (A$_1$) bio-based monomers containing ester bonds, and (A$_2$) bio-based curing agents to form β-hydroxyl ester. (B) Phosphate ester exchange: chemical structures and reaction mechanism of (bio-based) curing agents to from phosphate ester.

Because the stiff aromatic pyridazinone structure contributes to carbonization at high temperatures, CSPZ-EP/DDM exhibited excellent flame retardancy, achieving a UL-94 V-0 rating. Additionally, it showed remarkable acid/base resistance (Fig. 7E) due to the low content of ester group. CSPZ-EP/DDM can be chemically degraded by ethylene glycol, and the resulting chemicals can be repolymerized into CSPZ-EP/DDM. As presented in Fig. 7G, the recycled CSPZ-EP/DDM possessed similar hardness and Young's modulus (398 and 5088 MPa) to original CSPZ-EP/DDM (412 and 5176 MPa), demonstrating its outstanding recyclability.

4.2.2. Bio-based curing agents to form β-hydroxyl ester

Huang *et al.* [148] fabricated a recyclable flame-retardant bio-based vitrimer with β-hydroxyl ester groups (EV IADPPO 3P, Fig. 8A) by using partially bio-based diphenylphosphine oxide itaconic anhydride (IADPPO) and citric acid to cure DGEBA. The phosphorus and bio-based carbon contents of EV IADPPO 3P were 3 and 31.2 wt%, respectively. EV IADPPO 3P achieved a UL-94 V-0 classification (Fig. 8B) with an LOI of 27.0 %. The combustion behavior of EV IADPPO 3P was further investigated by CCT. The pHRR and THR of EV IADPPO 3P were reduced by 33.4 % and 33.2 %, respectively, relative to those of citric acid-cured DGEBA (EV). Additionally, the recycled EV IADPPO 3P presented a higher flexural strength than the original EV IADPPO 3P (Fig. 8C), reaching 58 MPa, and its flexural modulus was well preserved.

Zhang *et al.* [149] synthesized a bio-based epoxy monomer (E) containing phosphonate groups from magnolol and cured it with 1,4-cyclohexanedicarboxylic acid (CA) and dodecanedioic acid (DCA) to fabricate a flame-retardant recyclable bio-based thermoset (E/1C/2D, Fig. 8B, the mole ratio of CA to DA = 1:2). The bio-based carbon content of E/1C/2D was up to 51.8 wt%. Compared to EV IADPPO 3P, E/1C/2D exhibited superior flame-retardant efficiency, attributed to its higher phosphorus content. E/1C/2D achieved a UL-94 V-0 rating and an LOI of 31.0 %. The pHRR and THR of E/1C/2D were reduced by 54.0 % and 56.2 %, respectively, compared to those of DCA-cured E (E/DCA). E/1C/2D can form dense and continuous char layers during combustion (Fig. 8E), which led to great flame retardancy. However, duo to the long aliphatic chain in the network of E/1C/2D, it possessed a lower T_g (67 °C) than EV IADPPO 3P (107 °C). The tensile strength and elongation at break of E/1C/2D were 97 MPa and 6.3 %, which were both higher than those of E/DCA, demonstrating superior mechanical property. The E/1C/2D debris can be reconstructed into a complete sheet by heat pressing at 170 °C (Fig. 8F) because of the transesterification at high temperatures. The tensile strength and elongation at break of the recycled E/1C/2D reached 110 MP and 6.2 %, respectively, confirming great recyclability (Fig. 8I).

4.2.3. Bio-based curing agents to form phosphate ester

Liu *et al.* [57] utilized a bio-based epoxy monomer synthesized from itaconic acid to crosslink with phytic acid to generate flame-retardant recyclable bio-based thermosets (EIA-PA, Fig. 9A) with phosphate ester groups. When the molar ratio of epoxy group to P-OH was 1:1, the resultant EIA-PA-1 exhibited a high bio-based carbon content of 100 % (Fig. 9F), and it featured great flame retardancy with a UL-94 V-0 rating and an LOI of 33.5 % (Fig. 9E), attributing to the formation of high-quality char layers during combustion (Fig. 9B). Furthermore, the retention of tensile strength of EIA-PA-1 after one reprocessing cycle was 83.9 % (Fig. 9C) due to the rapid phosphate exchange (Fig. 9D). Additionally, Liu *et al.*[150] developed a flame-retardant recyclable bio-derived thermoset (EHPT, Fig. 9G) based on dynamic phosphate exchange by reacting ESO with 2-hydroxyethyl methacrylate phosphate (HEMAP) and tannic acid (TA). When the contents of HEMAP and TA both reached 24.1 wt%, the bio-based carbon content of EHP$_{0.7}$T$_{0.7}$ was 58.9 % (Fig. 9F). As presented in Fig. 9E, EHP$_{0.7}$T$_{0.7}$

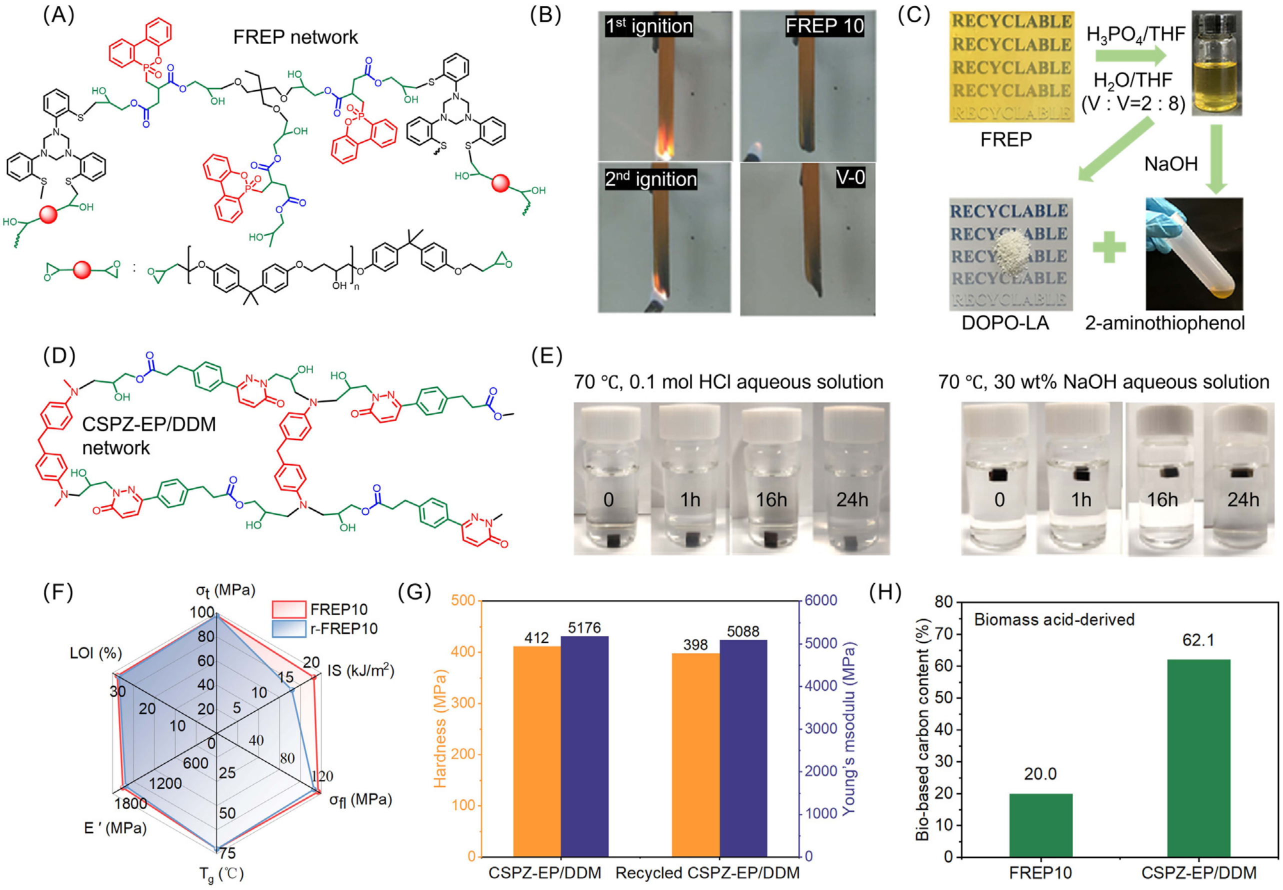


Fig. 7. Two fire-retardant vitrimers based on bio-based monomers containing ester bonds and their comprehensive properties. Illustration of cross-linked network of (A) FREP [147], Copyright 2023. Adapted with permission from the American Chemical Society, and (D) CSPZ-EP/DDM [95], Copyright 2023. Adapted with permission from Elsevier Science Ltd. (B) Burning process of FREP10 during UL-94 test [147], Copyright 2023. Reproduced with permission from the American Chemical Society. (C) Chemical recycling process of FREP10 [147], Copyright 2023. Reproduced with permission from the American Chemical Society. (E) Acid/base resistance of CSPZ-EP/DDM [95], Copyright 2023. Reproduced with permission from Elsevier Science Ltd. (F) Performance (T_g, LOI, storage modulus, tensile strength, impact strength and flexural strength) comparison between FREP and r-FREP. (G) Hardness and Young's modulus of CSPZ-EP/DDM and recycled CSPZ-EP/DDM. (H) Bio-based carbon content of two transesterification-based vitrimers.

achieved a UL-94 V-0 rating and an LOI of 26.7 %. Additionally, the pHRR, THR, and TSP of $EHP_{0.7}T_{0.7}$ were decreased by 54.0 %, 10.6 %, and 18 %, respectively, compared to $EHP_{0.7}T_0$ (HEMAP content: 21.9 wt%, and TA content: 0 wt%). Furthermore, the compact char layer of $EHP_{0.7}T_{0.7}$ after CCT test (Fig. 9H) indicated that the phosphorus with a high oxide state in $EHP_{0.7}T_{0.7}$ played a significant role in the condensed phase. Due to the flexible segments and low crosslinking density, EIA-PA-1 and $EHP_{0.7}T_{0.7}$ both had low T_g values of 69.0 and 68.6 °C, respectively (Fig. 9E). Furthermore, $EHP_{0.7}T_{0.7}$ can be applied as a reusable adhesive due to the dynamic phosphate exchange under external stimuli, and its shear strength can be restored to 75 % of its original value after one recycling cycle.

Table 1 summarizes the comprehensive performances of the bio-based fire-retardant transesterification vitrimers. For bio-based monomer containing ester bond, the resulting vitrimers (CSPZ-EP/DDM and FREP10) possessed abundant rigid structures, leading to outstanding flame retardancy and mechanical properties. However, due to the steric hindrance and low ester content, the transesterification was hindered, making mechanical recycling unprocurable, but chemically recycling can be achieved. Thus, increased attention should be given to incorporate a higher concentration of ester bonds or synergize with other dynamic covalent bonds (DCBs) to further regulate dynamic behavior, achieving a balance among flame retardancy, mechanical performance, and recyclability in the resulting vitrimers. Additionally, introducing other flexible constructions such as DCBs with lower bond energies (S-S) or chain structures into the rigid network, which work together with high bond-energy ester bonds and rigid structures, could effectively enhance recyclability. For instance, by combining dynamic non-covalent interactions with covalent bonds, our group [151] developed self-healing, strong, recyclable, and fire-safe epoxy vitrimers. This was achieved by curing a commercial epoxy monomer containing ester groups, bis(2,3-epoxypropyl) cyclohex-4-ene-1,2-dicarboxylate, with a phosphorus/silicon-containing polyethyleneimine.

For bio-based curing agents to form β-hydroxyl ester, the resultant systems (EV IADPPO 3P and E/1C/2D) contained flexible carboxylic acid curing agents and rigid resin monomers, thus effectively balancing overall performance. The primary limitation is the requirement for 1,5,7-triazabicyclo [4,4,0] dec 5-ene (TBD) as a transesterification catalyst. Firstly, designing the prepolymer monomers with tertiary amines for self-catalysis is an effective solution. For example, Xu *et al.* [152] prepared a catalyst-free, self-healing bio-based vitrimer (EMDA–AA) by curing menthane diamine-based epoxy monomers with adipic acid. Due to the autocatalytic effect of tertiary amines in the EMDA–AA vitrimer, the vitrimer network achieved topological rearrangement through dynamic transesterification reactions without the need for additional catalysts. The resulting vitrimer demonstrated excellent self-healing, shape memory, and reprocessing properties. Besides, the incorporation of a suitable 'modifier' containing abundant primary

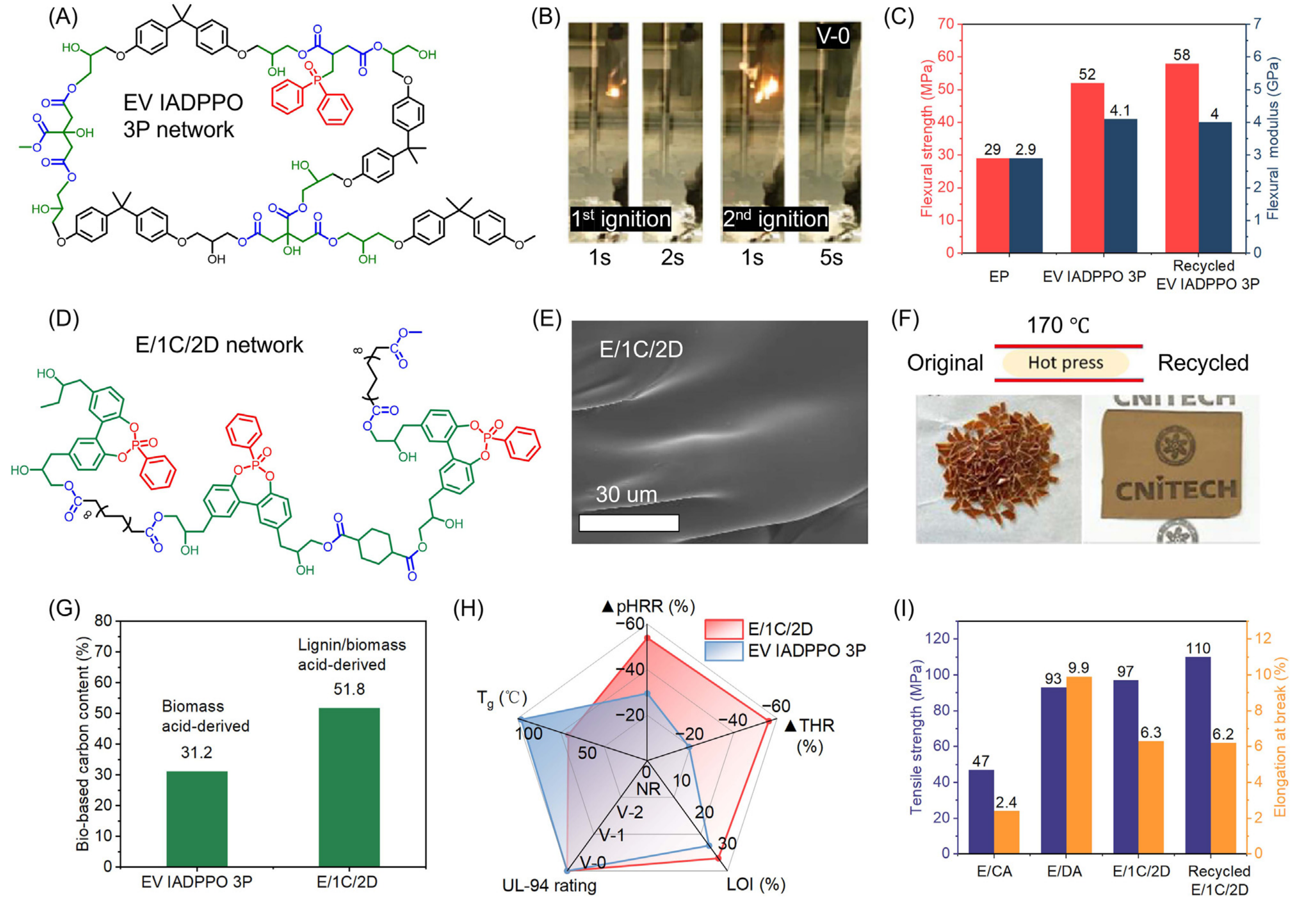


Fig. 8. Two recyclable fire-retardant vitrimers based on bio-based curing agents to form β-hydroxyl ester and their overall performances. Schematic of cross-linked network of (A) EV IADPPO 3P [148], Copyright 2024. Adapted with permission from Elsevier Science Ltd, and (D) E/1C/2D [149], Copyright 2023. Adapted with permission from Elsevier Science Ltd. (B) Burning process of EV IADPPO 3P during UL-94 test [148], Copyright 2024. Reproduced with permission from Elsevier Science Ltd. (C) Flexural strength and modulus of EP, EV IADPPO 3P and recycled EV IADPPO 3P. (E) SEM image of E/1C/2D char residue after UL-94 test [149], Copyright 2023. Reproduced with permission from Elsevier Science Ltd. (F) Recycling procedure of E/1C/2D [149], Copyright 2023. Reproduced with permission from Elsevier Science Ltd. (G) Bio-based carbon content of EV IADPPO 3P and E/1C/2D. (H) Comparison between T_g, LOI, UL-94, △pHRR, △THR and △TSP of EV IADPPO 3P and E/1C/2D. (I) Tensile strength and elongation at break of E/CA, E/DA, E/1C/2D and recycled E/1C/2D.

hydroxyl groups or tertiary amines is another effective solution, which can chemically link to the cross-linked network and catalyze dynamic transesterification reactions under external stimuli. For example, Chen *et al.* [145] utilized DHH as a multifunctional transesterification modifier to develop a fire-safe, catalyst-free epoxy vitrimer. This approach effectively achieved “two goals with one solution,” as the resulting epoxy vitrimer demonstrated both recyclability and fire safety. Through incorporating a rationally designed tertiary amine/phosphorus-containing reactive oligomer into EP, our group [153] had also developed a catalyst-free, closed-loop recyclable transesterification vitrimer, which exhibited superior mechanical properties, durability, and fire retardancy. Besides, amino acids are abundant biological resources, primarily derived from protein hydrolysis, with amino and carboxyl groups that can serve as latent curing agents. The ester bonds and tertiary amines in the cross-linked network offer extensive potential for degradation and recyclability, marking a promising direction for future development of bio-based, flame-retardant, and recyclable thermosets [154,155].

For phosphate ester-based vitrimers, the transesterification of phosphate esters demonstrates high reactivity, providing EIA-PA-1 and $EHP_{0.7}T_{0.7}$ with excellent overall performance. However, the primary challenges of these phosphate ester-based vitrimers include low thermal stability, poor solvent resistance, and susceptibility to degradation. Future research should be thus focused on improving the solvent resistance of phosphate ester-based vitrimers, with partial modification of phosphate groups as a potential solution. For instance, Song *et al.* [156] prepared a curing agent (ammonium hydrogen phytate), by modifying PA with urea, to cure melamine-urea-formaldehyde resin and applied the resultant thermoset as a wood coating. The resulting coating exhibited comparable T_g, hardness, adhesion, and water resistance. Yu *et al.* [157] developed a bio-based latent curing agent through the reaction of PA and imidazole, which was then used to cure DGEBA. The resulting thermosets exhibited high thermal stability and flame retardancy.

4.3. Imine exchange

Due to their dynamic and flame-retardant properties, the imine bonds are widely utilized in the preparation of flame-retardant recyclable bio-based thermosets through the strategies of (i) bio-based monomers containing Schiff base (Fig. 10A), (ii) bio-based curing agents containing Schiff base (Fig. 10B), and (iii) polyimides: polyaldehydes (P) + diamines (D) (Fig. 10C).

The advantages and disadvantages of prepolymer monomers containing Schiff bases are like those of prepolymer monomers with ester groups, primarily because the properties of the resulting thermosets are significantly influenced by structural elements beyond the dynamic covalent bonds. It has a high bio-based carbon content, and due to the flame-retardant effect of the Schiff base,

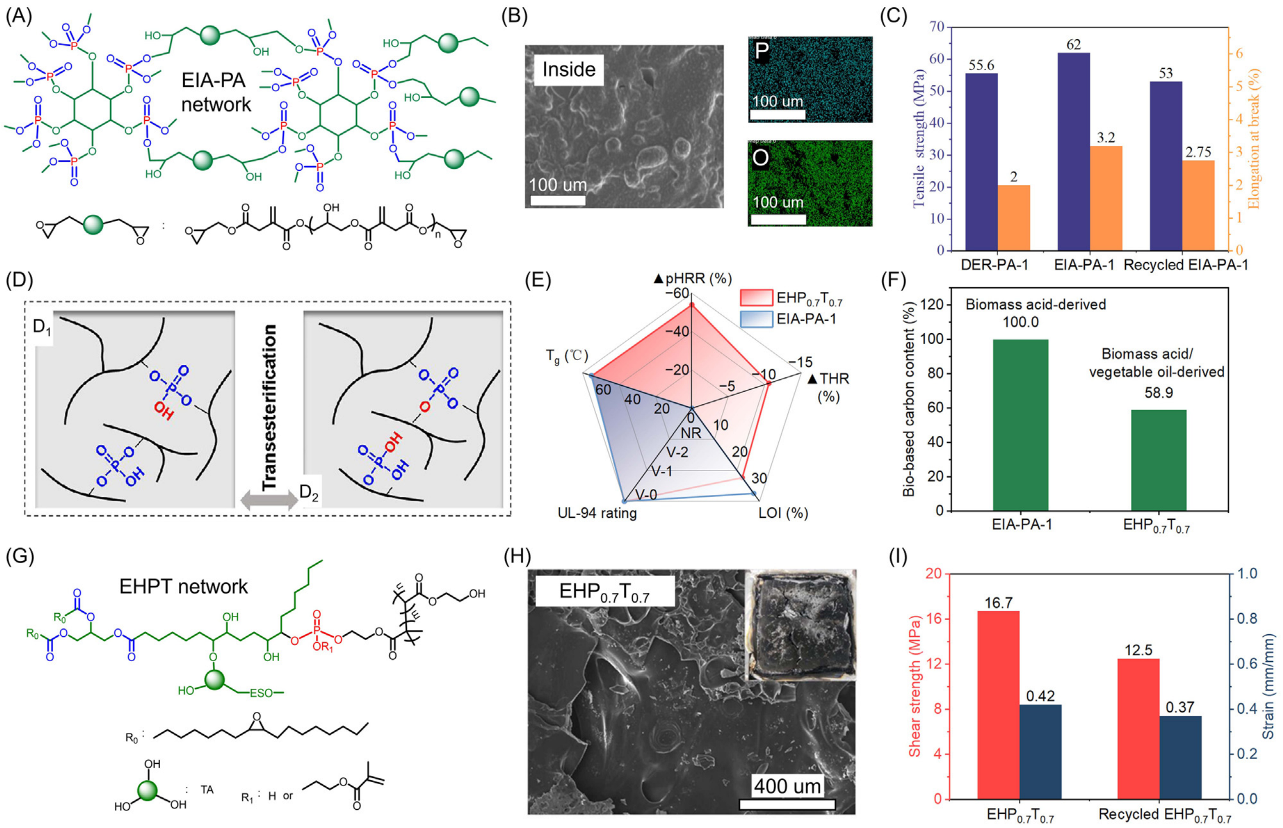


Fig. 9. Two recyclable fire-retardant bio-based thermosets based on phosphate ester exchange and their comprehensive properties. Illustration of cross-linked network of (A) EIA-PA [57], Copyright 2020. Adapted with permission from Elsevier Science Ltd, and (G) EHPT [150], Copyright 2023. Adapted with permission from the American Chemical Society. (B) SEM image and EDS spectra of the interior of EIA-PA-1 residue after LOI test [57], Copyright 2020. Reproduced with permission from Elsevier Science Ltd. (C) Tensile strength and elongation at break of DER-PA-1, EIA-PA-1, and recycled EIA-PA-1. (D) Proposed transesterification of dynamic phosphate esters [150], Copyright 2023. Reproduced with permission from the American Chemical Society. (E) Comparison of T_g, LOI, UL-94, △pHRR and △THR between EIA-PA-1 and $EHP_{0.7}T_{0.7}$. (F) Bio-based carbon content of EIA-PA-1 and $EHP_{0.7}T_{0.7}$. (H) Digital and SEM images of $EHP_{0.7}T_{0.7}$ char obtained from CCT [150], Copyright 2023. Reproduced with permission from the American Chemical Society. (I) Shear strength and strain of $EHP_{0.7}T_{0.7}$ and recycled $EHP_{0.7}T_{0.7}$.

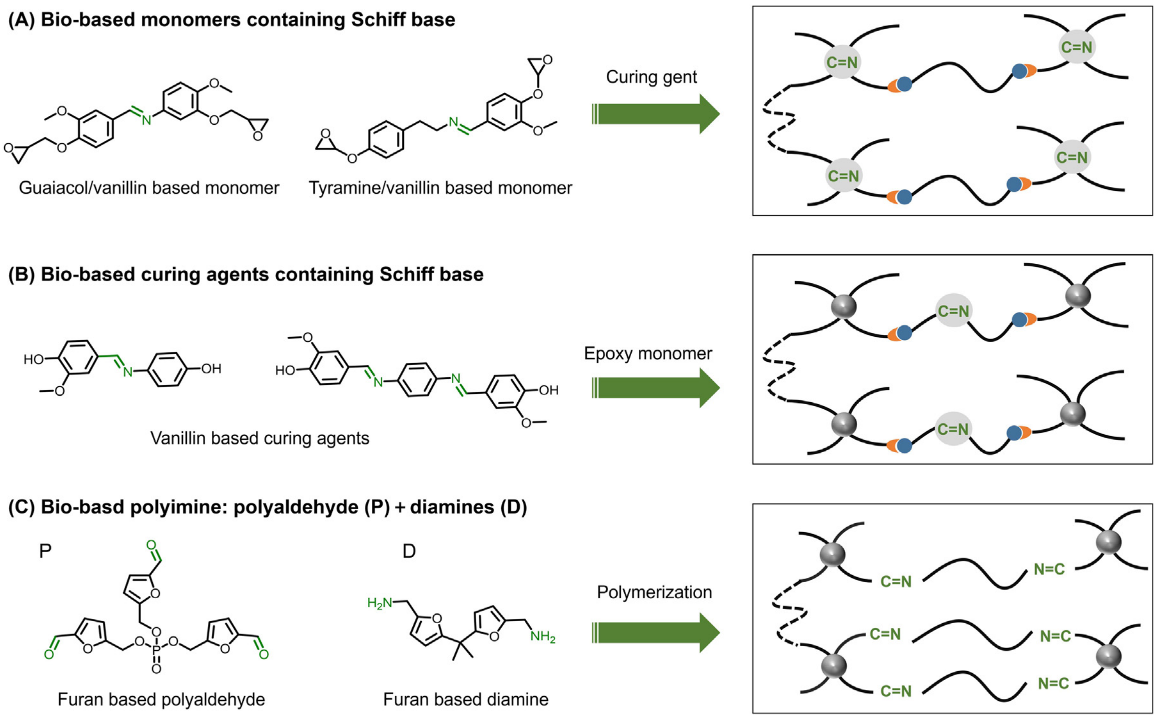


Fig. 10. Design of recyclable fire-retardant bio-based thermosets based on imine exchange. Chemical structures and curing mechanisms of (A) bio-based monomers containing Schiff base, (B) bio-based curing agent containing Schiff base, and (C) polyaldehyde + diamines.

Table 1
Summary of comprehensive performances of the bio-based fire-retardant transesterification vitrimers.

Specimens	Bio-based carbon content (%)	Exchange reaction	T_g (°C)	Flame-retardant performance					Mechanical properties		Recyclability
				Flame-retardant structure	LOI (%)	UL94 rating	△pHRR (%)	△THR (%)	σ_t (MPa)	σ_{fl} (MPa)	Retention of mechanical properties (%)
EV IADPPO 3P [148]	31.2	β-Hydroxyl ester exchange	107 (DSC)	Diphenylphosphine oxide	27.0	V-0	-33.4	-33.2	NA	52	115 (σ_{fl})
E/1C/2D [149]	62.9	β-Hydroxyl ester exchange	67 (DSC)	Phenylphosphoyl	31.0	V-0	-54.0	-56.2	97.0	NA	113.4 (σ_t)
CSPZ-EP/DDM [95]	62.1	β-Hydroxyl ester exchange	205 (DMA)	N-containing heterocycles, DDM	NA	V-0	NA	NA	NA	NA	96.6 (Hardness)/98.3 (Young's modulus)
FREP10 [147]	20.0	β-Hydroxyl ester exchange	72 (DMA)	DOPO	33.4	V-0	-23.8	-6.4	97.6	131.0	99.9 (σ_t)
EIA-PA-1 [57]	100.0	Phosphate ester exchange	69 (DSC)	Phosphate	32.0	V-0	NA	NA	62.0	NA	83.9 (σ_t)
$EHP_{0.7}T_{0.7}$ [150]	58.9	Phosphate ester exchange	68.6 (DMA)	Phosphate, TA	26.1	V-0	-54.0	-10.6	NA	NA	75 (Shear strength)

the thermosets, typically cured by rigid aromatic curing agents, exhibits excellent flame retardancy without requiring the presence of other flame-retardant elements. Meanwhile, this design involves the use of toxic solvents, and recycling efficiency is relatively low, typically relying on solvent degradation to achieve recycling.

Similarly, the preparation process for Schiff base-containing curing agents involves green solvents, facilitating an environmentally friendly approach. Additionally, the rapid stress relaxation enabled by imine bond exchange reactions endows the resulting thermosets with excellent reprocessability. Simultaneously, its primary drawback is the low reactivity between the phenolic hydroxyl group and the epoxy group, necessitating the addition of a catalyst to enhance the reaction rate and accelerate the curing process.

The cross-linking of polyimides relies solely on the imide bonds formed through the condensation of aldehydes and amines, eliminating the need for a catalyst. At the same time, because polyimides have multiple cross-linking sites, the content of Schiff base is high, which makes polyimides have good recyclability.

To achieve a polyaldehyde structure, it is common to introduce a flame-retardant component, typically a phosphorus-containing structure. However, the production of a polyaldehyde structure usually requires a toxic solvent. Consequently, the resulting polyimide exhibits strong flame-retardant properties due to the presence of phosphorus-based flame-retardant structures and Schiff bases. However, due to the relatively low cross-linking density, the mechanical properties are often undesirable.

4.3.1. Bio-based monomers containing Schiff base

Yang *et al.* [158] prepared a flame-retardant recyclable bio-based thermoset (A_7P_3-D230, Fig. 11A) from vanillin-based epoxy monomer (VAD-EP), vanillin/DOPO-containing epoxy monomer (VDP-EP), and O, O'-bis(2-aminopropyl) polypropyleneglycol (D230, curing agent). A_7P_3-D230 with a bio-based carbon content of 40.3 % (Fig. 11I) exhibited outstanding flame retardancy due to the synergistic effect between DOPO and Schiff base groups. The blow-off effect observed during UL-94 test (Fig. 11B) demonstrated the gas-phase flame-retardant effects of DOPO and Schiff base groups in A_7P_3-D230. Additionally, A_7P_3-D230 possessed excellent reprocessability due to the high content of Schiff base and the flexible chain structure from D230, which enhanced the segment mobility. Due to outstanding recyclability, the tensile strength of the recycled A_7P_3-D230 reached 86.1 % and 66.8 % of the original value after one and two reprocessing cycles, respectively (Fig. 11C).

Furthermore, Li *et al.* [93] synthesized an imine-based epoxy monomer from a guaiacol derivative and vanillin, and cured it with DDM to fabricate a flame-retardant recyclable bio-based thermoset (GV-EP/DDM, Fig. 11D). The bio-based carbon content of GV-EP/DDM was up to 76.4 % (Fig. 11I). In comparison to A_7P_3-D230 in Fig. 11E, GV-EP/DDM exhibited higher T_g and greater flame-retardant performance due to the higher phenyl content and crosslinking density. GV-EP/DDM achieved an LOI of 35.5 % (calculated based on char yield), and a UL-94 V-0 rating. According to CCT results, the pHRR and THR of GV-EP/DDM were reduced by 86.4 % and 48.1 %, respectively. The rigid configuration may hinder the dynamic exchange of imine bonds, adversely affecting the recycling performance of GV-EP/DDM. However, due to the high crosslinking density of GV-EP/DDM, the material demonstrated high acid resistance. In Fig. 11F, the hardness and Young's modulus of the recycled GV-EP/DDM R-GV-EP/DDM increased by 53.7 % and 24.8 % compared to those of the original one, which was attributed to self-crosslinking reactions between Schiff base groups at high temperatures.

The GV-EP/DDM system demonstrates high mechanical strength and excellent char-forming capability due to its robust main chain with conjugated imine bonds on benzene rings; however, it exhibits limited dynamic performance. Conversely, A_7P_3-D230 incor-

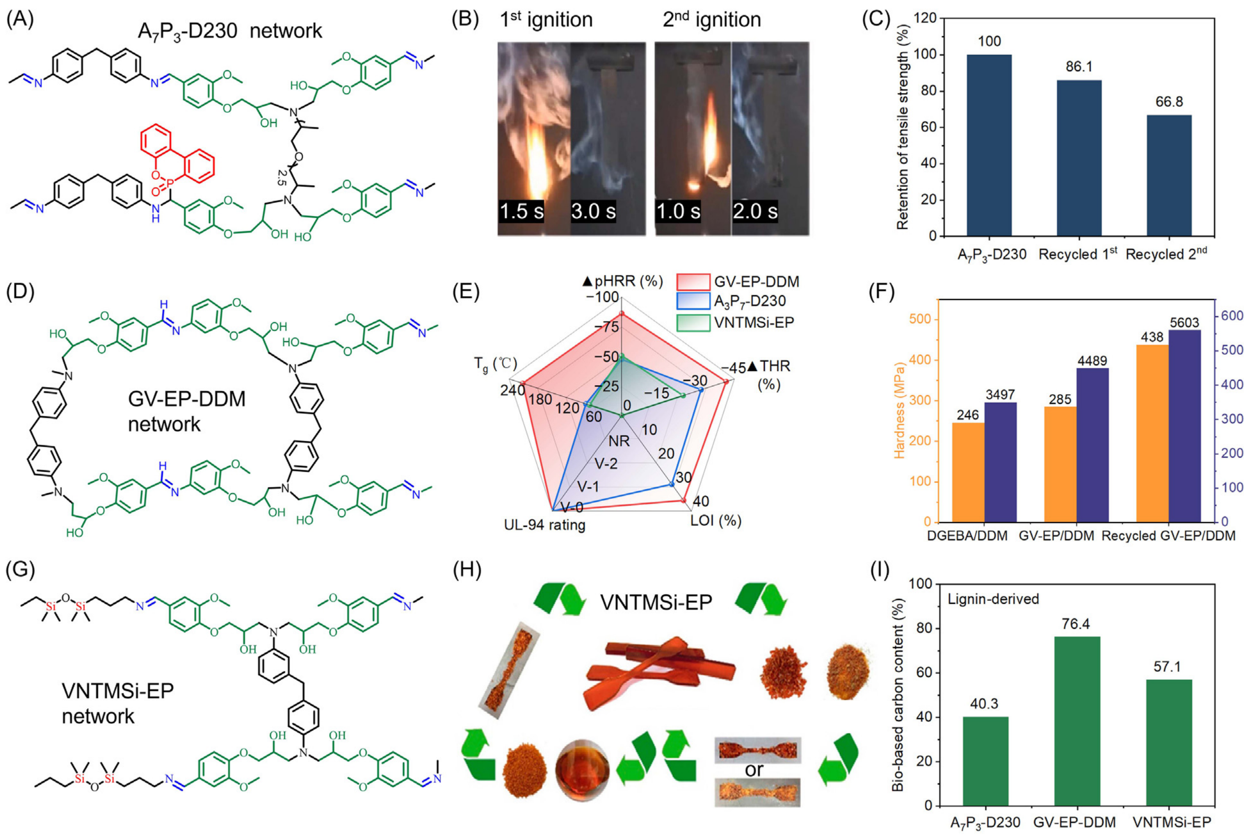


Fig. 11. Three recyclable fire-retardant thermosets based on bio-based monomers containing Schiff base and their comprehensive properties. Illustration of cross-linked network of (A) A$_7$P$_3$-D230 [158], Copyright 2022. Adapted with permission from Elsevier Science Ltd. (D) GV-EP-DDM [93], Copyright 2022. Adapted with permission from Elsevier Science Ltd, and (G) VNTMSi-EP [159], Copyright 2023. Adapted with permission from the American Chemical Society. (B) Burning process of A$_7$P$_3$-D230 during UL-94 test [158], Copyright 2022. Reproduced with permission from Elsevier Science Ltd. (C) Retention of tensile strength for A$_7$P$_3$-D230 after different recycling cycles. (E) Comparison of T_g, LOI, UL-94, △pHRR and △THR between GV-EP-DDM, A$_7$P$_3$-D230 and VNTMSi-EP. (F) Hardness and Young's modulus of DGEBA/DDM, GV-EP/DDM and recycled GV-EP/DDM. (H) Reprocessing procedure of VNTMSi-EP [159], Copyright 2023. Reproduced with permission from the American Chemical Society. (I) Bio-based carbon content of GV-EP-DDM, A$_7$P$_3$-D230 and VNTMSi-EP.

porates an excess of flexible segments, necessitating the addition of phosphorus-containing components to achieve adequate flame retardancy, which compromises its originally phosphorus-free flame-retardant characteristics. Ding *et al.* [159] proposed a strategic design that incorporated rigid vanillin with flexible siloxane spacers to synthesize a monomer achieving an optimal balance of rigidity and flexibility. Upon curing with DDM, a novel, robust, imine-based EP trimer (VNTMSi-EP/DDM, bio-based carbon content: 57.1 %) was formed, as shown in Fig. 11G. Due to the presence of the siloxane segments and the aromatic Schiff base structures, the pHRR and THR values of VNTMSi-EP/DDM were reduced by 51 % and 25 %, respectively, compared to DDM-cured (DGEBA/DDM), as shown in Fig. 11E. Additionally, the flexible siloxane segments within the thermosetting network provided high segmental mobility and enabled rapid imine bond exchange, endowing VNTMSi-EP/DDM with efficient chemical and physical recyclability, as illustrated in Fig. 11H. After 1–3 hot-pressing cycles, the retention of tensile strength and modulus remained above 98 %. This integrated rigid-flexible design strategy enables the development of high-performance, recyclable, flame-retardant bio-based thermosets.

4.3.2. Bio-based curing agents containing Schiff base

To fabricate recyclable flame-retardant thermosets using bio-based imine-containing curing agents, Tian *et al.* [160] synthesized a vanillin-derived Schiff base-containing hardener to cure bio-based GTE, and introduced a catalyst and DOPO as a flame retardant to produce a flame-retardant bio-based recyclable system (BEVs, Fig. 12A). The resulting BEV-6 containing 6 wt% of DOPO and 69.6 wt% of bio-based carbon (Fig. 12G) exhibited excellent flame retardancy (Fig. 12B), degradability (Fig. 12C), and recyclability (Fig. 12I). Additionally, in another study, Tian *et al.* [161] utilized the same hardener to cure DGEBA with a catalyst and DOPO-HQ as a flame retardant to construct recyclable flame-retardant bio-based thermosets (EVHQ, Fig. 11D). Compared to BEV-6 in Fig. 12H, the obtained EVHQ2.0 (DOPO-HQ content: 22 wt%, and bio-based carbon content: 27.6 wt%) demonstrated higher T_g and better flame retardancy, which was attributed to the presence of the phenyl structure in DGEBA. The blow-off phenomenon observed during UL-94 tests (Fig. 12B and E) for both EVHQ2.0 and BEV-6 can be attributed to the gas-phase flame-retardant effect of DOPO group. The ΔpHRR and ΔTHR of EVHQ2.0 reached -54.0 % and -43.2 %, respectively, and the dense char layer surface in Fig. 12C after CCT of EVHQ2.0 further confirmed that the aromatic imine structures formed stable char residues through cross-linking and rearrangement reactions at elevated temperatures. Moreover, from Fig. 12I, both thermosets exhibited high tensile strength, with negligible changes in tensile strength observed after three reprocessing cycles, which was attributable to the rapid imine exchange at high temperatures.

4.3.3. Bio-based polyimides

To prepare recyclable flame-retardant bio-based polyimides, the biomass vanillin derivatives and 5-hydroxymethyl-2-furanaldehyde were utilized to synthesize phosphorus-containing multi-aldehydes

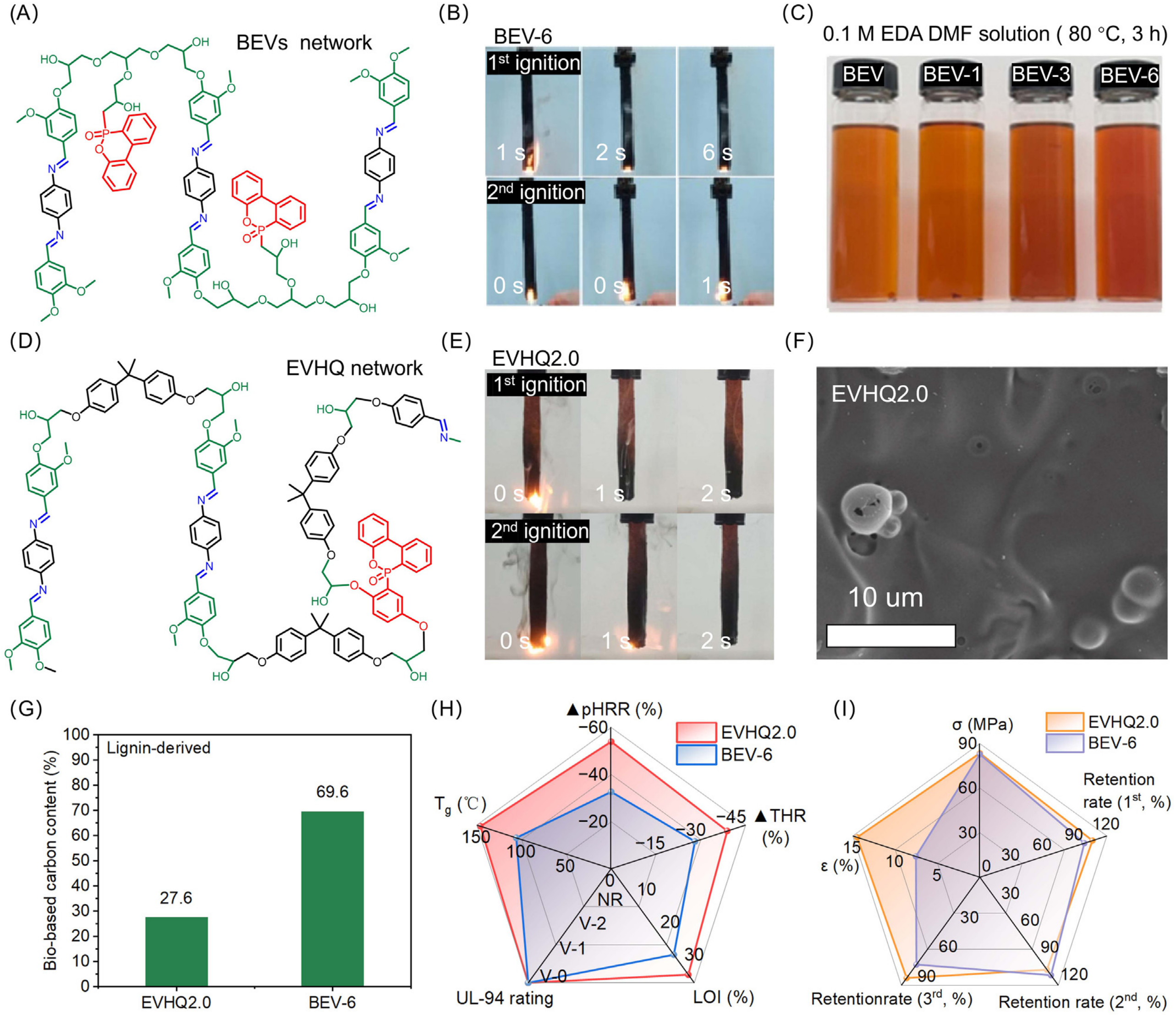


Fig. 12. Two recyclable fire-retardant thermosets based on bio-based curing agent containing Schiff base and their overall performances. Schematic of cross-linked network of (A) BEVs [160], Copyright 2023. Adapted with permission from Elsevier Science Ltd, and (D) EVHQ [161], Copyright 2024. Adapted with permission from Elsevier Science Ltd. (B) Burning process of BEV-6 during UL-94 test [160], Copyright 2023. Reproduced with permission from Elsevier Science Ltd. (C) Degradation behavior of BEV-6 [160], Copyright 2023. Reproduced with permission from Elsevier Science Ltd. (E) Burning process of EVHQ2.0 during UL-94 test [161], Copyright 2024. Reproduced with permission from Elsevier Science Ltd. (F) SEM photo of char for EVHQ2.0 after CCT [161], Copyright 2024. Reproduced with permission from Elsevier Science Ltd. (G) Bio-based carbon content of EVHQ2.0 and BEV-6. (H) Comparison of T_g, LOI, UL-94, △pHRR and △THR between EVHQ2.0 and BEV-6. (I) Tensile strength, flexural strength and retention of tensile strength for different recycling cycles of EVHQ2.0 and BEV-6.

(TMP, HVP, and TMFP), which subsequently reacted with diamines to yield polyimides (Fig. 13A). Among various TMP-based polyimides, the TMP-DDM (T_g: 178 °C, LOI: 30.9 %) and TMP-PACM (T_g: 128 °C, LOI: 30.4 %) exhibited higher T_g and LOI values (Fig. 13B). This indicates that the rigid diamines significantly improve the thermal stability and flame retardancy of polyimides. As presented in Fig. 13C, due to the high cross-linking density, the tensile strengths of HVP-D230, TMP-PACM, and TMP-DDM reached 57.9, 54.3, and 69.2 MPa, respectively. However, an excessively rigid configuration may hinder the dynamic imine exchange. Consequently, the retention rate of tensile strength for HVP-D230 (97.2 %) surpassed those for TMP-PACM (95.8 %) and TMP-DDM (94.2 %) after physical recycling. Furthermore, after two physical recycling cycles, the tensile strength retention rates of TMP-PACM and TMP-DDM only had 106.8 % and 91.3 %, but that of TMP-HDA reached 148.7 % due to the presence of flexible segments and self-crosslinking of Schiff bases. The chemical recycling rate of different polyimides in Fig. 13D further supports this observation. The polyimides with flexible diamines, such as HVP-D230 and HVP-DFDA, exhibited HVP recycling rates of 100 % and 91.4 %, respectively. In contrast, TMP-PACM and TMP-DDM only achieved TMP recycling rates of 76.6 % and 69.3 %. Thus, more attention should be directed toward incorporating flexible structures to modulate the overall performance of bio-based polyimides.

Additionally, a furan-derived polyimide was prepared by the reaction between TMFP and a furan-derived diamine (DFDA) [166]. The resultant TMFP-DFDA vitrimers can be recycled by chemical decomposition in hydrochloric acid (HCl)/THF solution. Moreover, the 1st- recycled and 5th- recycled vitrimers exhibited LOI values of 35.0 % and 33.5 %, respectively, and both achieved a UL-94 V-0 rating (Fig. 13F) due to their excellent char-forming abilities, stemming from the Schiff base/furan/phosphorus-rich structures. As shown in Fig. 13E, the 1st- recycled and 5th- recycled vitrimers displayed low tensile strength and elongation at break (approximately 2 MPa and 0.4 %), which may be attributed to the low cross-linking density of the original TMFP-DFDA.

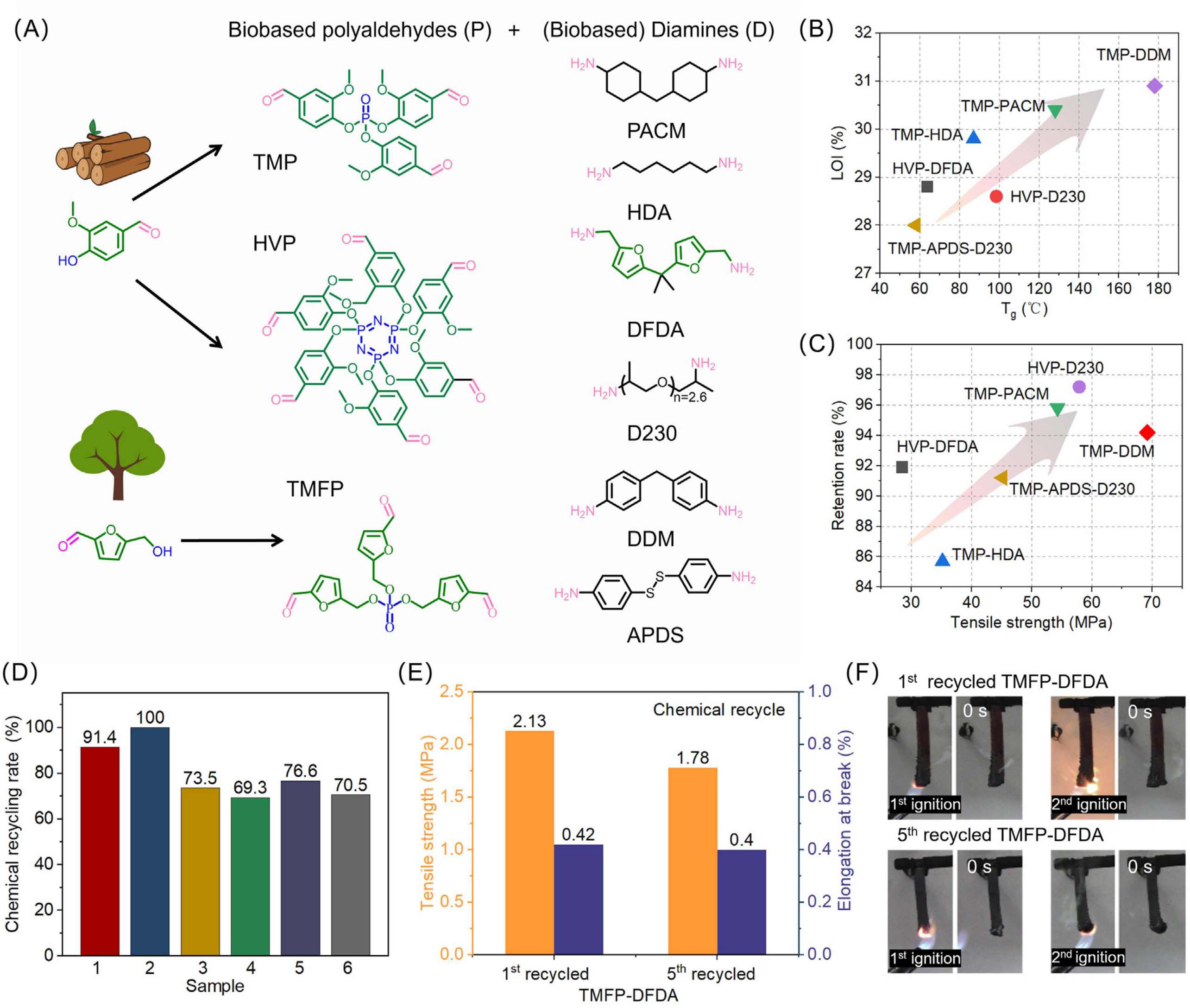


Fig. 13. Polyimides prepared by bio-based polyaldehyges and (bio-based) diamines, and their comprehensive performances. (A) Chemical structures of bio-based polyaldehyges and (bio-based) diamines. (B) Comparison of T_g and LOI for different polyimides. (C) Tensile strength and retention of tensile strength after physical reprocessing for different polyimides. (D) Chemical recycling rate (building block recycling efficiency) of different polyimides (from 1 to 6, HVP-DFDA, HVP-D230, TMP-HDA, TMP-PACM, TMP-DDM, TMP-APDS-D230). (E) Tensile strength and elongation at break for 1st and 5th-recycled TMFP-DFDA. (F) Burning process of 1st and 5th recycled TMFP-DFDA during UL-94 test [166], Copyright 2024. Reproduced with permission from Elsevier Science Ltd.

Table 2 summarizes the comprehensive performances of the recyclable bio-based fire-retardant thermosets based on imine metathesis. For bio-based monomers containing Schiff base, due to the dense rigid structures and high crosslinking density, GV-EP/DDM exhibited excellent flame-retardant properties without the need for additional flame-retardant groups. However, the rigid structures also impacted dynamic exchange, making degradation and recycling challenging. To address this issue, the A_7P_3-D230 system was constructed based on flexible D230 curing agent, but it needed the introduction of additional flame retardants. Consequently, greater emphasis should be placed on exploring flexible flame-retardant structures as curing agents or incorporating them into the main chain of the matrix.

For bio-based curing agents containing Schiff base, these findings demonstrate that these curing agents, when catalyzed by 4-dimethylaminopyridine, can cure EPs to yield high-performance recyclable thermosets. However, the low chemical reactivity of phenolic hydroxyl groups and the high melting points of these curing agents (usually solid) resulted in poor processability. Additionally, the imine-containing chemicals are prone to hydrolysis and challenging to purify and store, significantly limiting their practical applications. Future research should therefore focus on developing imine-containing curing agents with high curing activity and enhanced hydrolysis resistance. Utilizing secondary amines as curing agents in non-catalytic systems presents a promising approach. For instance, Dağlar *et al.* [167] designed a liquid imine monomer with secondary amine functionality to address these issues, which then reacted with commercially available epoxy monomers to produce high-performance thermosets. Peng *et al.* [168] synthesized a secondary amine curing agent for the catalyst-free curing of GDE. The resulting thermosets exhibited excellent thermal stability, mechanical properties, flame retardancy, and reprocessability.

For bio-based polyimides, current research on obtaining polyaldehyde structures primarily involved substitution reactions with phosphorus-containing compounds. Therefore, greater emphasis should be placed on developing environmentally friendly synthesis and achieving phosphorus-free intrinsic flame retardancy. Additionally, the diamines currently selected are predominantly derived from petroleum sources, highlighting the need to explore bio-based diamines. For instance, the rigidity of bio-based

Table 2
Summary of comprehensive performances of the bio-based, recyclable, fire-retardant thermosets based on imine exchange.

Specimens	Bio-based carbon content (%)	Strategy	T_g (°C)	Flame-retardant performance					Mechanical properties		Recycling efficiency after different cycles		
				Flame-retardant structure	LOI (%)	UL-94 rating	△pHRR (%)	△THR (%)	σ_t (MPa)	σ_{fl} (MPa)	One (%)	Two (%)	Three (%)
GV-EP-DDM [93]	76.4	Monomer containing Schiff base	220.0 (DSC)	Schiff base, DDM	35.5	V-0	-86.4	-48.1	NA	NA	153.6 (Hard-ness)	NA	NA
A_7P_3-D230 [158]	40.3	Monomer containing Schiff base	80.3 (DSC)	DOPO, Schiff base	28.7	V-0	-48.0	-32.0	75.5	NA	86.1 (σ_t)	66.8 (σ_t)	NA
VNTMSi-EP [159]	57.1	Monomer containing Schiff base	72.0 (DSC)	Siloxane, aromatic Schiff base	NA	NA	-51.0	-25.0	54.9	111.0	97.8 (σ_t)	99.1 (σ_t)	102.6 (σ_t)
EVHQ2.0 [161]	27.6	Curing agent containing Schiff base	146 (DMA)	DOPO	32.5	V-0	-54.0	-43.2	83.5	NA	106.4 (σ_t)	102.6 (σ_t)	102.6 (σ_t)
BEV-6 [160]	69.6	Curing agent containing Schiff base	105 (DMA)	DOPO	26.4	V-0	-32.7	-31.2	82.8	NA	98.8 (σ_t)	108.8 (σ_t)	88.9 (σ_t)
TMP-HDA [165]	72.7	Polyimide	87 (DSC)	Trimethyl phosphate	29.8	V-1	NA	NA	35.2	NA	85.7 (σ_t)	148.7 (σ_t)	NA
TMP-PACM [165]	55.2	Polyimide	128 (DSC)	Trimethyl phosphate	30.4	V-1	NA	NA	54.3	NA	95.8 (σ_t)	106.8 (σ_t)	NA
TMP-DDM [165]	55.2	Polyimide	178 (DSC)	Trimethyl phosphate	30.9	V-0	NA	NA	69.2	NA	94.2 (σ_t)	91.3 (σ_t)	NA
TMP-APDS-D230 [162]	62.7	Polyimide	58 (DSC)	Trimethyl phosphate	28.0	V-0	NA	NA	45.2	NA	91.2 (σ_t)	NA	NA
HVP-DFDA [169]	92.9	Polyimide	63.8 (DSC)	Triazatriphosphinine	28.8	NA	NA	NA	28.5	NA	91.9 (σ_t)	NA	NA
HVP-D230 [163]	69.6	Polyimide	98.4 (DSC)	Triazatriphosphinine	28.6	NA	NA	NA	57.9	NA	97.2 (σ_t)	NA	NA
HVP-HDA [164]	72.7	Polyimide	96.7 (DSC)	Triazatriphosphinine	27.5	V-0	NA	NA	40.9	NA	53.0 (σ_t)	NA	NA
TMFP-DFDA [166]	92.9	Polyimide	NA	Trimethyl phosphate	35.0	V-0	NA	NA	2.13	NA	NA	NA	NA

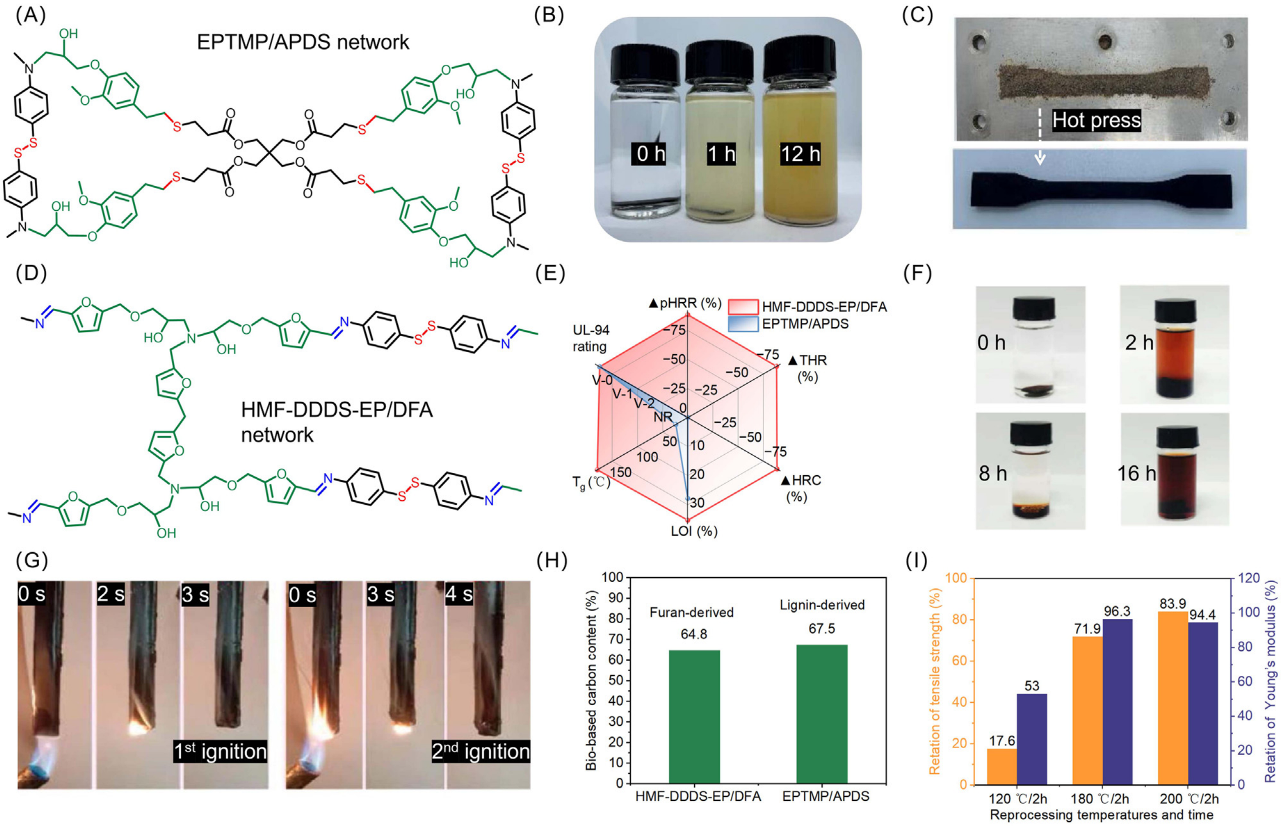


Fig. 14. Two recyclable fire-retardant thermosets based on disulfide exchange and their comprehensive properties. Illustration of cross-linked network of (A) EPTMP/APDS [40], Copyright 2024. Adapted with permission from Elsevier Science Ltd, and (D) HMF-DDDS-EP/DFA [171], Copyright 2023. Adapted with permission from Elsevier Science Ltd. (B) Degradable behavior of EPTMP/APDS [40], Copyright 2024. Reproduced with permission from Elsevier Science Ltd. (C) Reprocessing procedure of EPTMP/APDS [40], Copyright 2024. Reproduced with permission from Elsevier Science Ltd. (E) Comparison of T_g, LOI, UL-94, △pHRR, △HRC and △THR between EPTMP/APDS and HMF-DDDS-EP/DFA. (F) Degradable behavior of HMF-DDDS-EP/DFA [171], Copyright 2023. Reproduced with permission from Elsevier Science Ltd. (G) Burning process of HMF-DDDS-EP/DFA during UL-94 test [171], Copyright 2023. Reproduced with permission from Elsevier Science Ltd. (H) Bio-based carbon content of EPTMP/APDS and HMF-DDDS-EP/DFA. (I) Retention of mechanical properties (tensile strength and Young's modulus) for EPTMP/APDS after physical recycling at different reprocessing temperatures for 2 h.

menthane diamine lies between that of phenylcycloamines and aliphatic amines, which may help balance flame retardancy, mechanical properties, and recyclability of polyimides.

4.4. Disulfide exchange

Although sulfur (S) is recognized for its potential role in flame retardancy, the inherent instability of disulfide bonds within cross-linked thermoset networks significantly compromises the thermal stability. This instability poses a challenge in improving the flame retardancy of thermosets. Despite its promise, only limited studies have reported on flame-retardant recyclable bio-based thermosets based on disulfide exchange, which primarily introduced disulfide bonds into the thermoset network using curing agents such as 4-aminophenyl disulfide (APDS) and cystamine [170].

Li *et al.* [40] synthesized a novel disulfide-containing bio-based flame-retardant epoxy vitrimer (EPTMP/APDS, Fig. 14A), and its bio-based carbon content was 67.5 % (Fig. 14H). EPTMP/APDS exhibited excellent flame retardancy, with an LOI of 28.4 % and a UL-94 V-0 rating, which was probably because of the synergistic effect between N and S. Due to the low crosslinking density and the presence of flexible groups such as thioether, ester, and disulfide in EPTMP/APDS, it demonstrated low T_g, reduced mechanical properties, degradability (Fig. 14B) and recyclability (Fig. 14C). Moreover, the recycled EPTMP/APDS showed tensile strength/Young's modulus recovery rates of 17.6 %/53.0 % and 83.92 %/94.4 % after physical reprocessing at 120 and 200 °C for 2 h, respectively (Fig. 14F). However, the tensile strength and elongation at break of the recycled EPTMP/APDS could not be fully restored to their original levels after physical reprocessing, which was mainly due to the thermal decomposition occurred at high reprocessing temperatures.

Nabipour *et al.* [171] reported the fabrication of a bio-based epoxy thermoset (HMF-DDDS-EP/DFA, Fig. 14D) by using a furan-derived epoxy monomer (HMF-DDDS-EP) and 5'-methylenedifurfurylamin (DFA), and its bio-based carbon content was 64.8 % (Fig. 14H). Compared to EPTMP/APDS, HMF-DDDS-EP/DFA exhibited higher T_g and better flame retardancy, owing to the abundance of phenyl and furan structures (Fig. 14E). The HMF-DDDS-EP/DFA system achieved a UL-94 V-0 rating and an LOI of 36.0 %, with pHRR and THR reductions of 88.5 % and 71.9 % relative to those of DGEBA/DDM. The self-extinguishing behavior of HMF-DDDS-EP/DFA during UL-94 test (Fig. 14G) was due to the gas-phase fire-retardant effects of Schiff base and sulfur-containing structures. Furthermore, due to the presence of Schiff base and disulfide bonds, the HMF-DDDS-EP/DFA system demonstrated excellent chemical degradability (Fig. 14F). Notably, the high-purity raw materials can be recycled after the chemical degradation of HMF-DDDS-EP/DFA.

Based on the findings presented above, it is evident that an excessive number of disulfides and relatively flexible chains contribute to the poor flame retardancy, thermal stability, mechanical properties, and weather resistance of the thermosets. Conversely, an overly rigid configuration may impede the dynamic interchange of disulfide bonds. Therefore, careful consideration must be given to the selection and proportion of flexible segments to achieve a balance between the flame retardancy and other performances of the disulfide-based thermosets. Furthermore, by utilizing low bond energy disulfide bonds in conjunction with certain high bond energy DCBs, a synergistic effect can be achieved, resulting in recyclable thermosets with enhanced overall properties. For example, Cui *et al.* [172] applied flexible thioctic acid as a curing agent to cure rigid 4,4′-methylene bis(N,N-diglycidylaniline), allowing the disulfide/ester-containing thermosets to achieve excellent mechanical properties, self-repair capabilities, recyclability, and geometric stability. Similarly, Ma *et al.* [173] combined flexible thioctic acid and rigid bis(p-aminocyclohexyl) methane as curing agents for commercial bis(p-aminocyclohexyl)methane, producing disulfide/ester-containing, recyclable thermosets that exhibited exceptional thermal, mechanical, and dynamic properties. However, the flame-retardant properties of these materials have not been thoroughly investigated, and thus, it is necessary to introduce additional flame-retardant groups and achieve a balance among the overall properties.

4.5. Overview of the CANs

In this section, the advantages and disadvantages of CANs are summarized in Table 3. The advantages of bio/DA-based thermosets include ease of preparation, accessibility to bio-based sources, and certain flame retardancy. The advantages of bio-based recyclable transesterification thermosets include easy construction and abundant potential bio-based ingredients. Imine exchange benefits from abundant potential bio-based ingredients, intrinsic flame retardancy, and mild reaction conditions. Lastly, disulfide exchange is advantageous due to its presence in natural compounds and mild recycling conditions.

However, the bio/DA-based thermosets usually show relatively low crosslinking density, which diminishes thermal and mechanical performances, limits stability at elevated temperatures, and increases susceptibility to hydrolysis in humid environments. Although the dynamic nature of DA bonds facilitates recyclability, it compromises heat resistance, but high crosslinking density may restrict reprocessability. For transesterification, the ester bonds generally exhibit low thermal stability, contributing to flammability and susceptibility to hydrolysis, thereby reducing their applicability in high-temperature and moisture-rich settings. The transesterification-based thermosets commonly present low-density networks and often require catalysts to induce exchange reaction, potentially compromising long-term performance. Imine bonds are highly sensitive to hydrolysis, especially in humid or acidic/alkaline conditions, and exhibit limited thermal stability, which constrains their utility in the materials that may face high temperatures. Imine-containing networks also tend to have low crosslinking density and are vulnerable to environmental fluctuations, adversely affecting durability over time. For disulfide exchange, its low thermal stability and slower exchange rate limit reprocessability in complex network structures. Disulfide bonds are moisture-sensitive and prone to hydrolysis, impacting durability in wet conditions. Moreover, these bonds form low-density networks that may lack sufficient strength for high-stress applications.

5. Potential applications of recyclable fire-retardant bio-based thermosets

5.1. Carbon fiber-reinforced polymer composites

Carbon fiber-reinforced polymers (CFRPs) are extensively used in various industries due to their superior strength and lightweight properties [174–178]. However, most CFRPs are composed of thermosetting resins, which, once cured, cannot be remelted or reshaped [179]. Conventional recycling methods (mechanical, thermal, and chemical) require harsh conditions, such as high temperature, pressure, and cutting. Mechanical recycling reduces CFRP size to 50–100 mm but compromises the structural integrity of the recycled CFs, leading to performance loss [180]. Thermal recycling degrades the polymer matrix at high temperatures, causing CF loss [181]. Chemical recycling uses acids, bases, or solvents to break down the polymer matrix, reducing the mechanical properties of the recycled CFs [182]. By incorporating dynamic covalent bonds, such as ester bonds, Schiff base bonds, and DA bonds, the resin matrix can be effectively degraded by chemical methods, allowing for high-quality recovery of CF (Fig. 15A) [183–185]. Furthermore, the fire safety is a critical requirement in CFRPs for applications, *e.g.*, wind turbines, automotive, and aerospace [186–188]. As a result, there is an increasing focus on introducing flame-retardant structures containing nitrogen and phosphorus into CFRPs due to their proven high efficacy. Given the depletion of fossil fuel resources, the use of bio-based materials instead of petroleum-derived alternatives is of growing significance for developing flame-retardant, recyclable CFRPs [189,190].

Bio/polyimide-based CFRPs (CV/HEXA-CF [191] and HVP/D230-CF [163]) were prepared by utilizing vanillin, and they exhibited LOI values of 28.8 % and 34.2 %, respectively, with a UL-94 V-0 rating. The self-extinguishing behavior of HVP/D230-CF during

Table 3
Overview of the CANs with their corresponding advantages and shortcomings.

CANs	Advantages	Limitations
DA reaction	√ Ease of preparation √ Accessible bio-based sources √ Certain flame retardancy	✧ Hydrolysis sensitivity ✧ Low thermal stability ✧ Low crosslinking density ✧ Limited tunability
Transesterification	√ Ease of preparation √ Abundant potential bio-based ingredient	✧ Low thermal stability ✧ Low crosslinking density ✧ Sensitivity to hydrolysis ✧ Catalyst required
Imine exchange	√ Abundant potential bio-based ingredient √ Intrinsic flame retardancy √ Mild reaction conditions	✧ Hydrolysis sensitivity ✧ Low crosslinking density ✧ Low heat resistance
Disulfide exchange	√ Exist in natural compounds √ Mild recycling conditions	✧ Hydrolysis sensitivity ✧ Poor thermal stability ✧ Low crosslinking density ✧ Poor mechanical properties

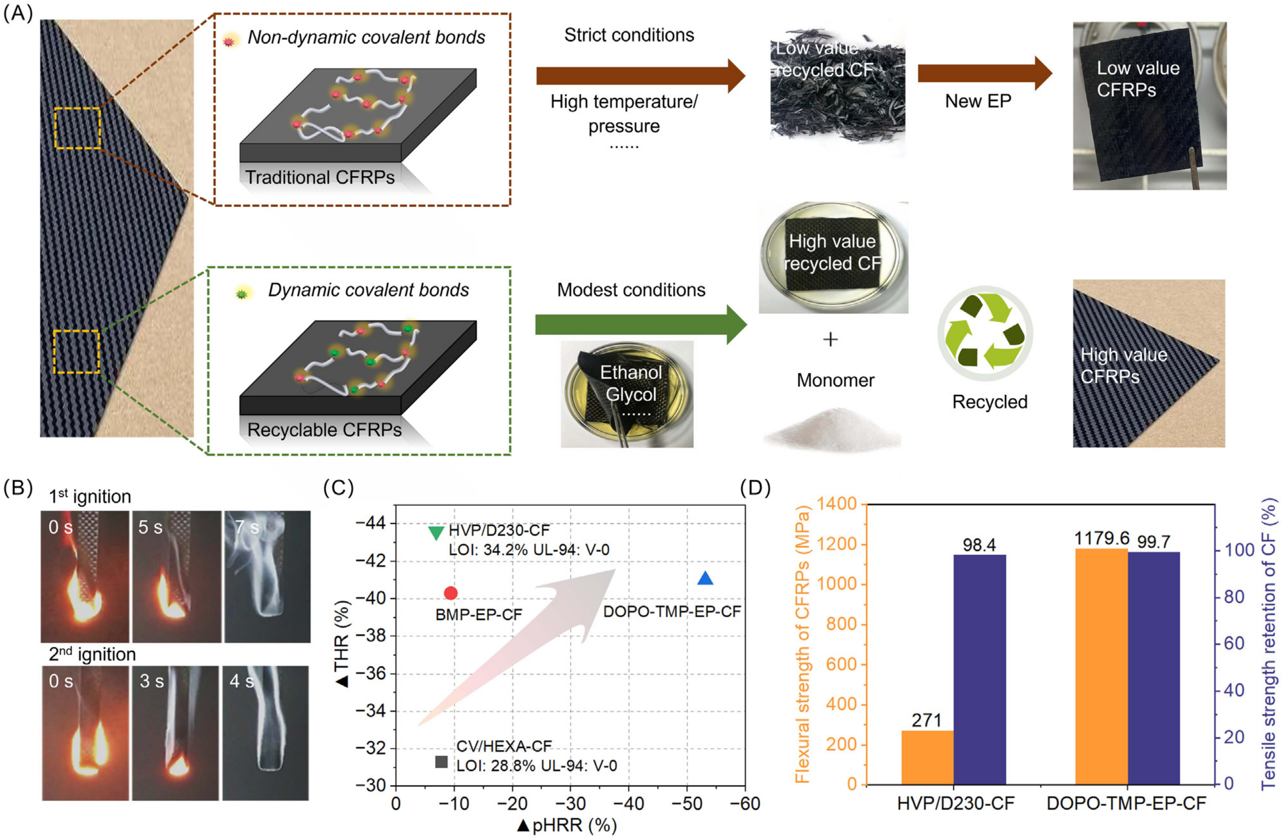


Fig. 15. Application of recyclable fire-retardant bio-based thermosets on carbon fiber-reinforced polymer (CFRP) composites. (A) Comparison between traditional and recyclable CFRPs [163], Copyright 2021. Reproduced with permission from Elsevier Science Ltd. (B) Burning process of HVP/D230-CF during UL-94 test [163], Copyright 2021. Reproduced with permission from Elsevier Science Ltd. (C) Comparison of LOI, UL-94, △pHRR, and △THR for different recyclable CFRPs. (D) Flexural strength of HVP/D230-CF and DOPO-TMP-EP-CF and tensile strength retention of the recycled CF after chemical recycling.

combustion, as shown in Fig. 15B, was primarily attributed to its Schiff base structures. Additionally, the DA/bio-based CFRPs, such as BMP-EP-CF [133] and DOPO-TMP-EP-CF [134], demonstrated low heat release during combustion. Notably, as presented in Fig. 15C, DOPO-TMP-EP-CF achieved a 53.1 % reduction in pHRR and a 43.0 % reduction in THR, outperforming previously reported flame-retardant CFRPs. The synergy between high- and low-oxidation state phosphorus contributed to flame retardancy through the formation of pyrophosphate derivatives and free-radical quenching, effectively acting in both condensed and gas phases during combustion. Furthermore, maleimide derivatives from the retro-DA reaction promoted crosslinking and dehydration in the matrix, generating a high-quality char layer that reduced the release of combustible volatiles and suppressed heat transfer. The flexural strength of HVP/D230-CF and DOPO-TMP-EP-CF and the tensile strength retention of CFs after chemical recycling of these systems are presented in Fig. 15D. Due to the high crosslinking density of the polymer matrix in DOPO-TMP-EP-CF, it exhibited a high flexural strength of 1179.6 MPa. In addition, both systems showed great recyclability, and their tensile strength retentions of CFs were close to 100 %.

5.2. Coatings

Bacterial contamination in food processing, medical equipment, and public facilities presents significant challenges to both industrial operations and public health [192–194]. Due to their hydroxyl groups, EPs generally exhibit high hydrophilicity, which can promote bacterial growth. Currently, 90 % of traditional commercial thermosets still rely on the extraction of petroleum resources, giving rise to issues such as nonrenewable raw materials, flammability and non-recyclability [195]. Therefore, the development of advanced thermosets with recycling, flame-retardant, and antibacterial properties, has become increasingly important. The Schiff base, known for its potential antibacterial activity, has been explored in various forms to achieve recyclable, flame-retardant, and antibacterial thermoset coatings (Fig. 16A).

Bio-based monomers containing aldehyde groups, such as vanillin, eugenol, and protocatechualdehyde, are commonly used for synthesizing Schiff base-containing recyclable coatings. However, aromatic amines required for the formation of Schiff bases are predominantly derived from non-renewable sources, with bio-based amines being scarce. In one study, GV-EP, synthesized from the reaction of vanillin and 5-amino-guaiacol, was used as a precursor for producing recyclable flame-retardant antibacterial coatings (GV-EP/DDM) [93]. Due to the flame-retardant effect of the Schiff base, the GV-EP/DDM system achieved a UL-94 V-0 rating (Fig. 16F) and demonstrated excellent recyclability by hot-pressing at 230 °C and 10 MPa (Fig. 16D). Additionally, after co-culturing Escherichia coli with the original GV-EP/DDM and recycled GV-EP/DDM (R-GV-EP/DDM), the bacterial population significantly decreased, with antibacterial rates of 75.2 % and 91.5 %, respectively (Fig. 16B and E). This suggests that the integration of the Schiff base and methoxyl groups into the coating network markedly enhances the antibacterial performance. Another promising approach raised by our group [3] involved the development of vanillin-based, Schiff base/phosphorus-containing vitrimer ($CIP_{1.0}$), which similarly exhibited flame retardancy, recyclability, and antibacterial properties, with an antibacterial rate exceeding 82.5 % against Escherichia coli. Compared with the control sample (CI) without phosphorus,

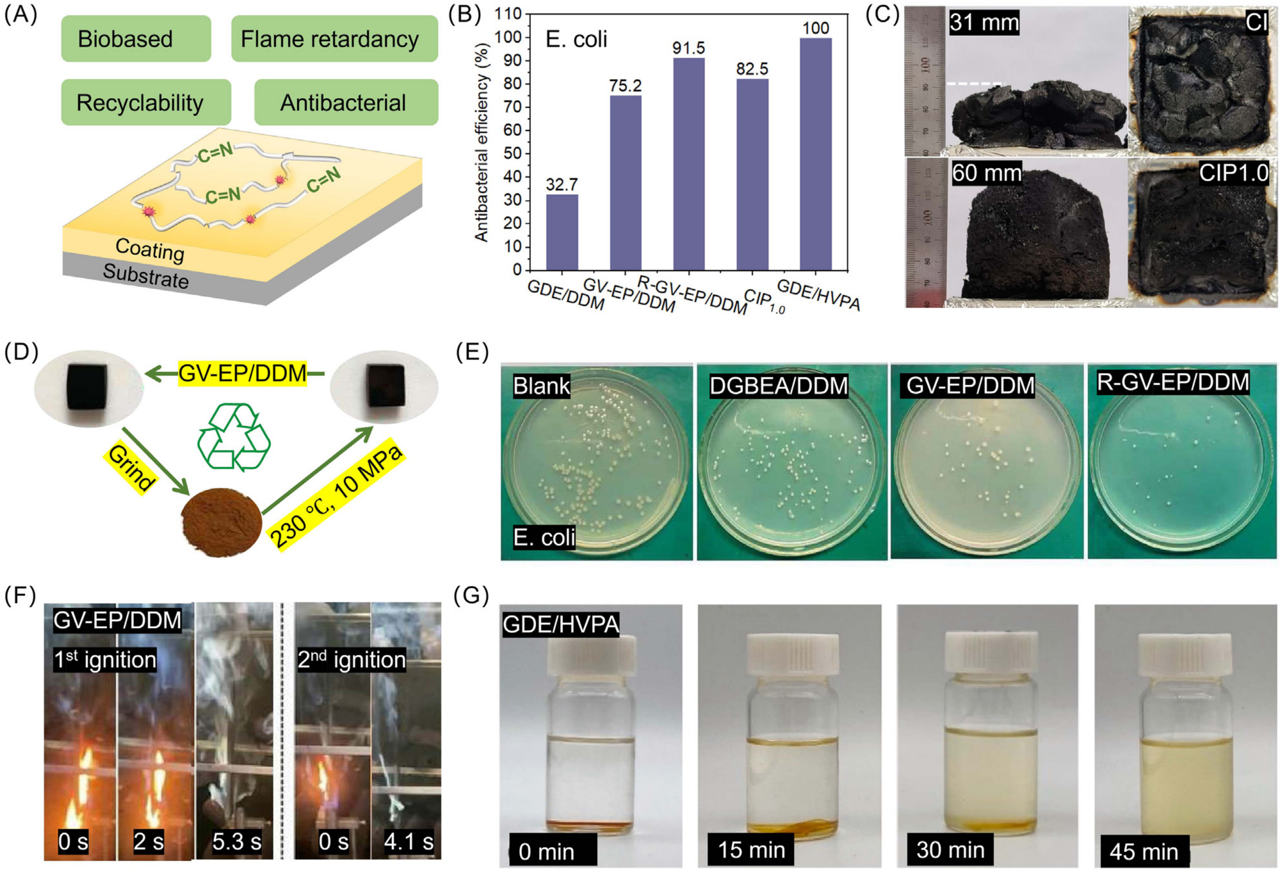


Fig. 16. Application of recyclable fire-retardant bio-based thermosets as antibacterial coatings. (A) Illustration of recyclable fire-retardant bio-based coatings. (B) Comparison of antibacterial efficiency for Escherichia coli among different coatings. (C) Top- and side-view digital images of residual chars for CI and CIP1.0 [3], Copyright 2024. Reproduced with permission from Elsevier Science Ltd. (D) Reprocessing procedure of GV-EP/DDM [93], Copyright 2022. Reproduced with permission from Elsevier Science Ltd. (E) Digital photographs of the antibacterial test results [93], Copyright 2022. Reproduced with permission from Elsevier Science Ltd. (F) Burning process of GV-EP/DDM during UL-94 test [93], Copyright 2022. Reproduced with permission from Elsevier Science Ltd. (G) Chemical degradation procedure of GDE/HVPA in 1 M HCl/THF (2/8, v/v) solution [168], Copyright 2022. Reproduced with permission from Elsevier Science Ltd.

the CIP1.0 formed highly intumescent and dense char layers during combustion (Fig. 16C), which demonstrated the synergist between the Schiff base and phosphorus in the condensed phase. Furthermore, the bio-based HVPA hardener was used to cure GDE to produce a recyclable flame-retardant antibacterial coating (GDE/HVPA) [168]. Due to the synergistic effect of the Schiff base and phosphonitrile structure, the GDE/HVPA system displayed outstanding flame retardancy, chemical recyclability/degradability (Fig. 16G) and antibacterial performance. The antibacterial rate of GDE/HVPA was up to 100 % for Escherichia coli, which was higher than that of previously reported Schiff base-containing antibacterial coatings.

5.3. *Aerogels*

Organic aerogels are an intriguing class of highly porous and ultralight materials with broad applications in thermal insulation, energy storage, and chemical absorption [196–198]. However, traditional organic aerogels, typically made from fossil-based feedstocks, raise environmental concerns since it is difficult to recycle them back to their original monomers [199]. Additionally, they suffer from low thermal stability and pose potential fire hazards [200]. To address these challenges, the bio-based polyimide aerogels with covalent adaptable networks and flame-retardant groups offer a promising alternative for the development of next-generation sustainable and fire-safe aerogels.

Wang *et al.* [201] developed bio-based flame-retardant recyclable polyimide aerogels (PIAs, Fig. 17A) using amines and cyclophosphazene derivatives (HVP and HBP) sourced from bio-based chemicals, including vanillin and 4-hydroxybenzaldehyde. In terms of flame retardancy (Fig. 17C), PIA-A1 (HVP + TREN) and PIA-A2 (HVP + 70 wt% TREN + 30 wt% 2-EHA) extinguished rapidly after ignition due to the formation of dense char layers (Fig. 17D). In contrast, PIA-B1 (HBP + TREN), PIA-B2 (HBP + 70 wt% TREN + 30 wt% 2-EHA), and a reference material continued to burn for slightly longer (9–15 s), as depicted in Fig. 17C. To evaluate recyclability, the samples were cut into small pieces and immersed in a 0.1 M HCl solution at room temperature for 24 h (Fig. 17B). In the acidic conditions, the hydrolysis of imine bonds occurred, leading to the selective breakdown of the polymer networks, with aldehyde monomers precipitating and primary amines dissolving in the solution. Filtration enabled the effective isolation of solid HVP and HBP monomers, achieving recovery yields of 83 % to 95 %. The acidic filtrate was then treated with an ion exchange resin to remove chloride ions, producing neutral amines. Pure TREN was obtained from PIA-A1 and PIA-B1 after water removal, whereas for PIA-A2 and PIA-B2, 2-EHA and water were separated from TREN *via* reduced pressure distillation. Pure 2-EHA was further extracted with ethyl acetate and dried, with recovery rates of 41 % to 51 %, and the recovery rates of TREN ranged from 77 % to 91 %.

The application of flame-retardant bio-based recyclable thermosets in carbon fiber-reinforced polymer composites, antibacterial coatings, and aerogels demonstrates significant advantages, including excellent flame retardancy and recyclability. Furthermore, these materials exhibit multifunctional properties, such as antibac-

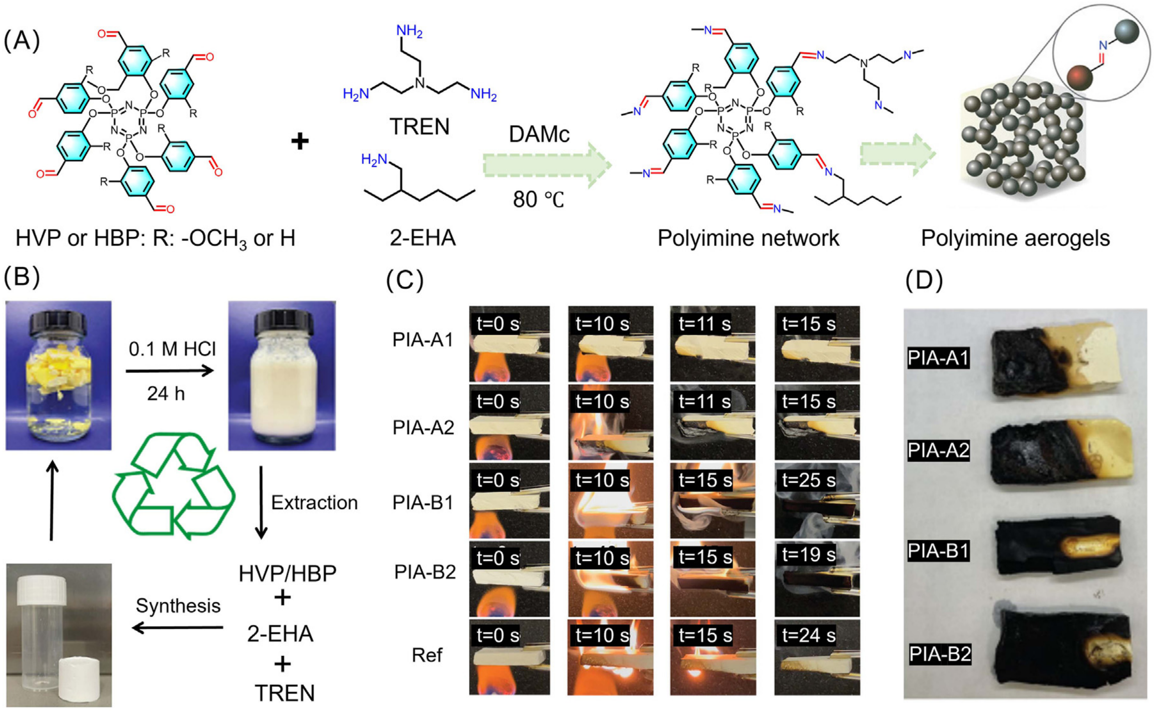


Fig. 17. Application of recyclable fire-retardant bio-based thermosets on aerogels. (A) Synthesis route of polyimide aerogels [201], Copyright 2022. Reproduced with permission from John Wiley & Sons Inc. (B) Chemical recycling procedure of polyimide aerogels [201], Copyright 2022. Reproduced with permission from John Wiley & Sons Inc. (C) Burning process of polyimide aerogels [201], Copyright 2022. Reproduced with permission from John Wiley & Sons Inc. (D) Digital photographs of char residues for PIAs after burning tests [201], Copyright 2022. Reproduced with permission from John Wiley & Sons Inc.

terial activity and thermal insulation, making them highly suitable for fields requiring high performance and sustainable development. Potential future applications encompass high-performance composite materials, such as lightweight flame-retardant structural components for aerospace, automotive, and rail transit. In the construction and building sector, these materials can serve as flame-retardant insulation materials for green buildings, environmentally friendly coatings, and decorative panels. In electronics and electrical applications, they can be used as battery pack protective materials and flame-retardant casings for electronic devices. Additional applications include the medical and healthcare fields, (e.g., flame-retardant and antibacterial medical devices, and recyclable protective equipment), energy and energy storage systems (e.g., thermal management materials for energy storage and protective components for new energy equipment) [202], environmental protection and marine engineering (e.g., degradable fireproof materials and protective materials for marine equipment), and functional textiles (e.g., fire-resistant clothing, industrial protective wear, and household textiles).

Although flame-retardant bio-based recyclable thermosets offer advantages such as flame retardancy, environmental sustainability, and recyclability in practical applications, they still encounter several bottlenecks. These challenges include high production costs, difficulties in achieving large-scale production, complex recycling processes, the lack of standardized industry norms, and insufficient long-term durability and environmental adaptability.

6. Conclusions and perspectives

6.1. Conclusions

Incorporating multifunctional properties such as intrinsic flame retardancy and recyclability into thermosets will significantly expand their application ranges and improve usage safety. In the context of ‘carbon neutrality’ and ‘multifunctionality’, the development of recyclable, flame-retardant, bio-based thermosets not only minimizes environmental impact but also extends their practical applications. This review explores how material selection and structural design influence the flame retardancy, recyclability, and other performance characteristics of bio-based thermosets. The strategies and action modes of different CANs for the construction of recyclable, fire-retardant, bio-based thermosets are summarized. Bio-based thermosetting materials, designed with specialized structures, exhibit unique properties such as high mechanical strength, flame retardancy, degradability, recyclability, and antibacterial activity. Consequently, these materials are well-suited to meet the demands of various fields, including CFRPs, antibacterial coatings, and aerogels. Understanding the relationship between bio-based feedstocks, structures, and performances offers valuable insights for the design of these materials and the promotion of their practical applications.

6.2. Challenges

Despite significant advancements in the field of bio-based recyclable flame-retardant thermosets, several challenges remain:

(1) Low bio-based content and high costs: Currently, most recyclable, bio-based, flame-retardant thermosets exhibit a low bio-based content. Additionally, the high cost of bio-based raw materials, primarily due to the complexity of their extraction, results in elevated production costs for these thermosets.
(2) Trade-off between fire retardancy and other properties: The fire-retardant thermosets reported in many studies are achieved through the introduction of flame-retardant groups or additives. However, this often complicates the preparation process of the

thermosets and leads to reduced performances, such as mechanical strength.

(3) Dependency on petroleum-based curing agents: Most curing agents used in the construction of these recyclable, bio-based, flame-retardant thermosets are derived from petroleum-based chemicals, which hinders the development of entirely bio-based high-performance thermosets.

(4) Weak DCBs: Most DCBs have low bond energy, leading to unsatisfied mechanical properties and durability of these recyclable bio-based thermosets. Furthermore, DCBs, such as Schiff base bonds, are prone to hydrolysis, which negatively impacts the weather resistance of the Schiff base-containing recyclable thermosets.

6.3. Opportunities

(1) Innovative screening methods for bio-based raw materials: Artificial intelligence and machine learning technologies can offer effective and innovative screening methods for bio-based raw materials. Beyond traditional experimental methods, artificial intelligence and machine learning [203–205] employ data-driven approaches to analyze the relationships between feature parameters and material properties. These advanced technologies offer powerful tools for material selection and design, providing predictive insights that can accelerate the discovery of bio-based raw materials that can be applied for fabricating recyclable, fire-retardant thermosets, thereby reducing development costs.

(2) Exploration of intrinsically flame-retardant structures from nature: Further exploration of intrinsically flame-retardant structures from natural sources is crucial. As previously mentioned, the bio-based compounds containing benzene or C=C-rich structures, when incorporated into thermoset network, can provide satisfactory flame retardancy without the need for additional additives. Thus, more benzene or C=C-rich bio-based chemicals should be explored for the preparation of bio-based, recyclable, fire-retardant thermosets.

(3) Utilization of bio-based curing agents: Bio-based curing agents is critical for the fabrication of bio-based thermosets, such as plant oil-based curing agents, amino acid-based curing agents, lignin-based curing agents, chitosan-based curing agents, furfural-based curing agents, and tannin-based curing agents. The performance optimization and functionalization of these curing agents play a pivotal role in the development of fully bio-based thermoset systems, enabling enhanced sustainability and material properties. In addition, amine curing agents are relatively rare in nature, highlighting the significance of developing bio-based amine curing agents. For instance, Wu *et al.* [206] obtained 4,4'-methylenebis(cyclohexylamine) from industrially relevant lignin side streams and demonstrated its effectiveness as a curing agent in the development of high-performance, recyclable thermosets.

(4) Development of stable DCBs: In addition to the mentioned DCBs, more efforts should be put into developing new DCBs that can only undergo bond exchange under specific stimuli, such as light of specific wavelengths and specific chemicals. For example, azobenzene derivatives can undergo a reversible cis-trans isomerization reaction when exposed to light of specific wavelengths [207]. Additionally, the CAN, composed of β-amino amide with a high activation energy, demonstrates excellent structural stability, resistance to hydrolysis and creep, and high temperature-dependent viscoelasticity (activation energy of approximately 230 to 270 kJ mol^{-1}) [208]. With these DCBs, the developed bio-based thermosets can keep stable in daily usage and be recycled in certain conditions.

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.

CRediT authorship contribution statement

Yong Guo: Writing – original draft, Visualization. **Qingshan Yang:** Writing – review & editing. **Siqi Huo:** Writing – review & editing, Supervision, Funding acquisition. **Juan Li:** Writing – review & editing. **Pooya Jafari:** Writing – review & editing. **Zhengping Fang:** Writing – review & editing. **Pingan Song:** Writing – review & editing, Supervision, Funding acquisition. **Hao Wang:** Writing – review & editing, Supervision, Funding acquisition.

Data availability

Data will be made available on request.

Acknowledgements

The authors acknowledge the financial support received from the Australian Research Council (Nos. DP230103008, DE230100616, LP230100278, DP240102628, and DP240102728).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.progpolymsci.2025.101935.

References

[1] Nabavi SF, Dalir H. A review on laser-assisted manufacturing process of thermoset composites: a review of fundamentals, processes, scientific modelling, challenges and prospective. Opt Laser Technol 2025;181:111713. doi:10.1016/j.optlastec.2024.111713.

[2] Chen Q, Huo SQ, Lu YX, Ding MM, Feng JB, Huang GB, et al. Heterostructured Graphene@Silica@Iron Phenylphosphinate for fire-retardant, strong, thermally conductive yet electrically insulated epoxy nanocomposites. Small 2024;20:2310724. doi:10.1002/smll.202310724.

[3] Ye GF, Wang C, Zhang Q, Song PA, Wang H, Huo SQ, et al. Bio-derived Schiff base vitrimer with outstanding flame retardancy, toughness, antibacterial, dielectric and recycling properties. Int J Biol Macromol 2024;278:134933. doi:10.1016/j.ijbiomac.2024.134933.

[4] Wang JS, Wang J, Yang S, Chen X, Chen KW, Zhou G, et al. Multifunctional phosphorus-containing imidazoliums endowing one-component epoxy resins with superior thermal latency, heat resistance, mechanical properties, and fire safety. Chem Eng J 2024;485:149852. doi:10.1016/j.cej.2024.149852.

[5] Klingler WW, Bifulco A, Polisi C, Huang ZY, Gaan S. Recyclable inherently flame-retardant thermosets: chemistry, properties and applications. Compos Part B Eng 2023;258:110667. doi:10.1016/j.compositesb.2023.110667.

[6] Post W, Susa A, Blaauw R, Molenveld K, Knoop RJI. A review on the potential and limitations of recyclable thermosets for structural applications. Polym Rev 2020;60:359–88. doi:10.1080/15583724.2019.1673406.

[7] Wan JT, Zhao JQ, Zhang XW, Fan H, Zhang JH, Hu DD, et al. Epoxy thermosets and materials derived from bio-based monomeric phenols: transformations and performances. Prog Polym Sci 2020;108:101287. doi:10.1016/j.progpolymsci.2020.101287.

[8] Ye GF, Huo SQ, Wang C, Zhang Q, Wang BT, Guo ZH, et al. Fabrication of flame-retardant, strong, and tough epoxy resins by solvent-free polymerization with bioderived, reactive flame retardant. Sustain Mater Technol 2024;39:e00853. doi:10.1016/j.susmat.2024.e00853.

[9] Chen ZW, Guo Y, Chu YP, Chen TT, Zhang QW, Li CX, et al. Solvent-free and electron transfer-induced phosphorus and nitrogen-containing heterostructures for multifunctional epoxy resin. Compos Part B Eng 2022;240:109999. doi:10.1016/j.compositesb.2022.109999.

[10] Huo SQ, Sai T, Ran SY, Guo ZH, Fang ZP, Song PA, et al. A hyperbranched P/N/B-containing oligomer as multifunctional flame retardant for epoxy resins. Compos Part B Eng 2022;234:109701. doi:10.1016/j.compositesb.2022.109701.

[11] Wang C, Huo SQ, Ye GF, Wang BT, Guo ZH, Zhang Q, et al. Construction of an epoxidized, phosphorus-based poly(styrene butadiene styrene) and its application in high-performance epoxy resin. Compos Part B Eng 2024;268:111075. doi:10.1016/j.compositesb.2023.111075.

[12] Ma C, Guo ZH, Fang ZP, Li J. Flame retardancy and chemical degradation of epoxy containing phenylphosphonate group under mild conditions. Compos Part B Eng 2022;239:109967. doi:10.1016/j.compositesb.2022.109967.

[13] Wang C, Ye GF, Zhang Q, Wang H, Huo SQ, Liu ZT. Closed-loop recyclable, self-catalytic transesterification Vitrimer coatings with superior adhesive strength, fire retardancy, and environmental stability. ACS Mater Lett 2024;7:210–19. doi:10.1021/acsmaterialslett.4c02235.

[14] Wang ZJ, Li SY, Jin ZJ, Li ZM, Liu QY, Zhang KQ. Oil and gas pathway to net-zero: review and outlook. Energy Strat Rev 2023;45:101048. doi:10.1016/j.esr.2022.101048.

[15] Zhang CQ, Xue JQ, Yang XY, Ke YZ, Ou RX, Wang Y, et al. From plant phenols to novel bio-based polymers. Prog Polym Sci 2022;125:101473. doi:10.1016/j.progpolymsci.2021.101473.

[16] Huo SQ, Song PA, Yu B, Ran SY, Chevali VS, Liu L, et al. Phosphorus-containing flame retardant epoxy thermosets: recent advances and future perspectives. Prog Polym Sci 2021;114:101366. doi:10.1016/j.progpolymsci.2021.101366.

[17] Cao Q, Li JH, Fan QQ, Liu BT, Kou Y, Jian XG, et al. Flame retardant behavior of bio-based epoxy resin bearing pyridazinone and dynamic ester bond via self-blow-out and vesicular carbon formation. Polym Degrad Stab 2024;222:110707. doi:10.1016/j.polymdegradstab.2024.110707.

[18] Qi Y, Weng ZH, Kou Y, Li JH, Cao Q, Wang JY, et al. Facile synthesis of bio-based tetra-functional epoxy resin and its potential application as high-performance composite resin matrix. Compos Part B Eng 2021;214:108749. doi:10.1016/j.compositesb.2021.108749.

[19] Zhang YR, Gu S, Wang YZ, Chen L. Intrinsically flame-retardant epoxy vitrimers with catalyst-free multi-reprocessability towards sustainable carbon fiber composites. Sustain Mater Technol 2024;40:e00883. doi:10.1016/j.susmat.2024.e00883.

[20] Cui JJ, Liu FK, Lu Z, Feng SW, Liang C, Sun YD, et al. Repeatedly recyclable 3D printing catalyst-free dynamic thermosetting photopolymers. Adv Mater 2023;35:2211417. doi:10.1002/adma.202211417.

[21] Chen JH, Zhang YR, Wang YZ, Chen L. Reprocessable, malleable and intrinsically fire-safe epoxy resin with catalyst-free mixed carboxylate/phosphonate transesterification. Polymer 2023;281:126083. doi:10.1016/j.polymer.2023.126083.

[22] Li GM, Zhang P, Huo SQ, Fu YK, Chen L, Wu YP, et al. Mechanically strong, thermally healable, and recyclable epoxy vitrimers enabled by Zn Al-layer double hydroxides. ACS Sustain Chem Eng 2021;9:2580–90. doi:10.1021/acssuschemeng.0c08636.

[23] Puyadena M, Calafel I, de San Roman EG, Martin L, González A, Irusta L. Recyclable epoxy resin via simultaneous dual permanent/reversible crosslinking based on Diels-alder chemistry. Macromol Chem Phys 2021;222:2100146. doi:10.1002/macp.202100146.

[24] Wang HB, Fu Y, Liu Y, Li JP, Sun XZ, Liu T. Synthesis of facilely healable and recyclable imine vitrimers using biobased branched diamine and vanillin. Eur Polym J 2023;196:112309. doi:10.1016/j.eurpolymj.2023.112309.

[25] Tratnik N, Tanguy NR, Yan N. Recyclable, self-strengthening starch-based epoxy vitrimer facilitated by exchangeable disulfide bonds. Chem Eng J 2023;451:138610. doi:10.1016/j.cej.2022.138610.

[26] Schenk V, Labastie K, Destarac M, Olivier P, Guerre M. Vitrimer composites: current status and future challenges. Mater Adv 2022;3:8012–29. doi:10.1039/D2MA00654E.

[27] Zhao XL, Tian PX, Li YD, Zeng JB. Biobased covalent adaptable networks: towards better sustainability of thermosets. Green Chem 2022;24:4363–87. doi:10.1039/D2GC01325H.

[28] Gu S, Zhao JX, Wang YZ, Chen L. Towards sustainable and fire-safe thermosets using phosphorus-containing covalent adaptable networks. Chempluschem 2024;11:e202400341. doi:10.1002/cplu.202400341.

[29] Rashid MA, Liu WS, Wei Y, Jiang QR. Review on intrinsically recyclable flame retardant thermosets enabled through covalent bonds. J Appl Polym Sci 2022;139:e52493. doi:10.1002/app.52493.

[30] Liu JK, Wang SP, Peng YY, Zhu J, Zhao WW, Liu XQ. Advances in sustainable thermosetting resins: from renewable feedstock to high performance and recyclability. Prog Polym Sci 2021;113:101353. doi:10.1016/j.progpolymsci.2020.101353.

[31] Bu ML, Zhang XQ, Zhou T, Lei CH. Fully bio-based epoxy resins derived from magnolol and varying furan amines: cure kinetics, superior mechanical and thermal properties. Eur Polym J 2022;180:111595. doi:10.1016/j.eurpolymj.2022.111595.

[32] Pan X, Sengupta P, Webster DC. High biobased content epoxy-anhydride thermosets from epoxidized sucrose esters of fatty acids. Biomacromolecules 2011;12:2416–28. doi:10.1021/bm200549c.

[33] Zhang JS, Shang QQ, Hu Y, Zhang F, Huang J, Lu JY, et al. High-biobased-content UV-curable oligomers derived from tung oil and citric acid: microwave-assisted synthesis and properties. Eur Polym J 2020;140:109997. doi:10.1016/j.eurpolymj.2020.109997.

[34] Zhao WW, Liu JK, Wang SP, Dai JY, Liu XQ. Bio-based thermosetting resins: from molecular engineering to intrinsically multifunctional customization. Adv Mater 2024;36:2311242. doi:10.1002/adma.202311242.

[35] Lucherelli MA, Duval A, Avérous L. Biobased vitrimers: towards sustainable and adaptable performing polymer materials. Prog Polym Sci 2022;127:101515. doi:10.1016/j.progpolymsci.2022.101515.

[36] Laurichesse S, Avérous L. Chemical modification of lignins: towards biobased polymers. Prog Polym Sci 2014;39:1266–90. doi:10.1016/j.progpolymsci.2013.11.004.

[37] Zhou MH, Ao X, Islam M, Liu YY, Prolongo SG, Wang DY. Bio-based epoxy vitrimer with inherent excellent flame retardance and recyclability via molecular design. Int J Biol Macromol 2024;262:129363. doi:10.1016/j.ijbiomac.2024.129363.

[38] Xie WQ, Huang SW, Liu SM, Zhao JQ. Imine-functionalized biomass-derived dynamic covalent thermosets enabled by heat-induced self-crosslinking and reversible structures. Chem Eng J 2021;404:126598. doi:10.1016/j.cej.2020.126598.

[39] Yang H, Yuan GM, Liu ZJ, Tao YH, Yang PP, Wu K, et al. Protocatechualdehyde-based epoxy vitrimer with low dielectric, excellent flame retardancy, and recyclability. Prog Org Coat 2024;197:108819. doi:10.1016/j.porgcoat.2024.108819.

[40] Li WB, Xiao LH, Wang YG, Huang JR, Liu ZS, Chen J, et al. Thermal-induced self-healing bio-based vitrimers: shape memory, recyclability, degradation, and intrinsic flame retardancy. Polym Degrad Stab 2022;202:110039. doi:10.1016/j.polymdegradstab.2022.110039.

[41] Li C, Fan H, Aziz T, Bittencourt C, Wu LB, Wang DY, et al. Biobased epoxy resin with low electrical permissivity and flame retardancy: from environmental friendly high-throughput synthesis to properties. ACS Sustain Chem Eng 2018;6:8856–67. doi:10.1021/acssuschemeng.8b01212.

[42] Liu T, Hao C, Wang LW, Li YZ, Liu WC, Xin JN, et al. Eugenol-derived biobased epoxy: shape memory, repairing, and recyclability. Macromolecules 2017;50:8588–97. doi:10.1021/acs.macromol.7b01889.

[43] Niu HX, Nabipour H, Wang X, Song L, Hu Y. Phosphorus-free vanillin-derived intrinsically flame-retardant epoxy thermoset with extremely low heat release rate and smoke emission. ACS Sustain Chem Eng 2021;9:5268–77. doi:10.1021/acssuschemeng.0c08302.

[44] Liu XH, Zhang ED, Feng ZQ, Liu JM, Chen BF, Liang LY. Degradable bio-based epoxy vitrimers based on imine chemistry and their application in recyclable carbon fiber composites. J Mater Sci 2021;56:15733–51. doi:10.1007/s10853-021-06291-5.

[45] Ji JQ, Huang SW, Liu SM, Yuan YC, Zhao JQ, Zhang SJ. A novel biomass-derived Schiff base waterborne epoxy coating for flame retardation and anti-bacteria. Polym Degrad Stab 2022;199:109910. doi:10.1016/j.polymdegradstab.2022.109910.

[46] Savonnet E, Grau E, Grelier S, Defoort B, Cramail H. Divanillin-based epoxy precursors as DGEBA substitutes for biobased epoxy thermosets. ACS Sustain Chem Eng 2018;6:11008–17. doi:10.1021/acssuschemeng.8b02419.

[47] Nabipour H, Wang X, Batool S, Song L, Hu Y. A phosphaphenanthrene-containing vanillin derivative as co-curing agent for flame-retardant and antibacterial epoxy thermoset. Polymer 2021;217:123460. doi:10.1016/j.polymer.2021.123460.

[48] Zhong J, Huang YS, Chen YT, Li LP, Guo CG. Synthesis of eugenol-modified epoxy resin and application on wood flame retardant coating. Ind Crops Prod 2022;183:114979. doi:10.1016/j.indcrop.2022.114979.

[49] Eid N, Ameduri B, Boutevin B. Synthesis and properties of furan derivatives for epoxy resins. ACS Sustain Chem Eng 2021;9:8018–31. doi:10.1021/acssuschemeng.0c09313.

[50] Marotta A, Faggio N, Ambrogi V, Cerruti P, Gentile G, Mija A. Curing behavior and properties of sustainable furan-based epoxy/anhydride resins. Biomacromolecules 2019;20:3831–41. doi:10.1021/acs.biomac.9b00919.

[51] Manarin E, Da Via F, Rigatelli B, Turri S, Griffini G. Bio-based vitrimers from 2,5-furandicarboxylic acid as repairable, reusable, and recyclable epoxy systems. ACS Appl Polym Mater 2023;5:828–38. doi:10.1021/acsapm.2c01774.

[52] Wang S, Sun F, Ni ZB, Lyu Y, Kaneko T, Dong WF, et al. Aromatic epoxy from caffeic acid: mechanical properties and flame retardancy. ACS Sustain Chem Eng 2024;12:10713–26. doi:10.1021/acssuschemeng.4c01107.

[53] Park HW, Toan M, Kim HJ, Lee JH, Shin S. Renewable epoxy thermosets with extremely high biomass content from furan derivatives and their flame retardancy. J Ind Eng Chem 2020;92:184–90. doi:10.1016/j.jiec.2020.09.003.

[54] Nabipour H, Wang X, Song L, Hu Y. A high performance fully bio-based epoxy thermoset from a syringaldehyde-derived epoxy monomer cured by furan-derived amine. Green Chem 2021;23:501–10. doi:10.1039/D0GC03451G.

[55] Wang X, Nabipour H, Kan YC, Song L, Hu Y. A fully bio-based, anti-flammable and non-toxic epoxy thermosetting network for flame-retardant coating applications. Prog Org Coat 2022;172:107095. doi:10.1016/j.porgcoat.2022.107095.

[56] Gonçalves F, Ferreira P, Alves P. Synthesis and characterization of itaconic-based epoxy resin: chemical and thermal properties of partially biobased epoxy resins. Polymer 2021;235:124285. doi:10.1016/j.polymer.2021.124285.

[57] Liu YL, Wang BB, Ma SQ, Xu XW, Qiu JF, Li Q, et al. Phosphate-based covalent adaptable networks with recyclability and flame retardancy from bioresources. Eur Polym J 2021;144:110236. doi:10.1016/j.eurpolymj.2020.110236.

[58] Zhang JH, Gong ZJ, Wu C, Li TC, Tang YY, Wu JD, et al. Itaconic acid-based hyperbranched polymer toughened epoxy resins with rapid stress relaxation, superb solvent resistance and closed-loop recyclability. Green Chem 2022;24:6900–11. doi:10.1039/D2GC01541B.

[59] Kumar S, Samal SK, Mohanty S, Nayak SK. Bio-based tri-functional epoxy resin (TEIA) blend cured with anhydride (MHHPA) based cross-linker: Thermal, mechanical and morphological characterization. J Macromol Sci A 2018;55:496–506. doi:10.1080/10601325.2018.1470468.

[60] Pan XJ, Luo ZY, Liu FQ, Yi QQ, Zeng YN. Construction of robust and fully bio-based epoxy vitrimers with facile malleability, self-healing ability, and recy-

clability from peach gum polysaccharide and itaconic acid. Ind Crops Prod 2024;208:117779. doi:10.1016/j.indcrop.2023.117779.

[61] Sun JH, Wang BT, Guo ZH, Fang ZP, Li J. Flame retardant epoxy resin toughened and strengthened by a reactive compatibilizer. Polymer 2022;248:124798. doi:10.1016/j.polymer.2022.124798.

[62] Luo YH, Wang Y, Xia CL, Ahmad A, Yang R, Li XN, et al. Eco-friendly soy protein isolate-based films strengthened by water-soluble glycerin epoxy resin. Prog Org Coat 2022;162:106566. doi:10.1016/j.porgcoat.2021.106566.

[63] Ding XM, Chen L, Guo DM, Liu BW, Luo X, Lei YF, et al. Controlling cross-linking networks with different imidazole accelerators toward high-performance epoxidized soybean oil-based thermosets. ACS Sustain Chem Eng 2021;9:3267–77. doi:10.1021/acssuschemeng.0c08852.

[64] Liu YY, He J, Li YD, Zhao XL, Zeng JB. Biobased epoxy vitrimer from epoxidized soybean oil for reprocessable and recyclable carbon fiber reinforced composite. Compos Commun 2020;22:100445. doi:10.1016/j.coco.2020.100445.

[65] Zeng RT, Wu Y, Li YD, Wang M, Zeng JB. Curing behavior of epoxidized soybean oil with biobased dicarboxylic acids. Polym Test 2017;57:281–7. doi:10.1016/j.polymertesting.2016.12.007.

[66] Ma YF, Wang R, Li QG, Li M, Liu CG, Jia PY. Castor oil as a platform for preparing bio-based chemicals and polymer materials. Green Mater 2021;10:99–109. doi:10.1680/jgrma.20.00085.

[67] Park SJ, Jin FL, Lee JR. Effect of biodegradable epoxidized castor oil on physicochemical and mechanical properties of epoxy resins. Macromol Chem Phys 2004;205:2048–54. doi:10.1002/macp.200400214.

[68] Fu QH, Tan JH, Han CH, Zhang XX, Fu B, Wang F, et al. Synthesis and curing properties of castor oil-based triglycidyl ether epoxy resin. Polym Adv Technol 2020;31:2552–60. doi:10.1002/pat.4982.

[69] Wang HN, Huo SQ, Wang C, Ye GF, Zhang Q, Song PA, et al. A P/N/Si-containing hyperbranched flame retardant for improving mechanical performances, fire safety, and UV resistance of epoxy resins. Prog Org Coat 2024;193:108562. doi:10.1016/j.porgcoat.2024.108562.

[70] Chen Q, Liu L, Zhang AL, Wang WD, Wang ZZ, Zhang JZ, et al. An iron phenylphosphinate@graphene oxide nanohybrid enabled flame-retardant, mechanically reinforced, and thermally conductive epoxy nanocomposites. Chem Eng J 2023;454:140424. doi:10.1016/j.cej.2022.140424.

[71] Ye GF, Huo SQ, Wang C, Shi Q, Yu LF, Liu ZT, et al. A novel hyperbranched phosphorus-boron polymer for transparent, flame-retardant, smoke-suppressive, robust yet tough epoxy resins. Compos Part B Eng 2021;227:109395. doi:10.1016/j.compositesb.2021.109395.

[72] Su JH, Yang YD, Wan CC, Li XG, Chai YL, Chai HY, et al. A novel flame-retardant, smoke-suppressing, and superhydrophobic transparent bamboo. Research 2024;7:0314. doi:10.34133/research.0317.

[73] Sai T, Ye X, Wang B, Guo Z, Li J, Fang Z, et al. Transparent, intrinsically fire-safe yet impact-resistant poly(carbonates-b-siloxanes) containing Schiff-base and naphthalene-sulfonate. J Mater Sci Technol 2024;225:11–20. doi:10.1016/j.jmst.2024.11.023.

[74] Peng XL, Liu QY, Wang DH, Liu CB, Zhao Y, Wang R, et al. A hyperbranched structure formed by in-situ crosslinking of additive flame retardant endows epoxy resins with great flame retardancy improvement. Compos Part B Eng 2021;224:109162. doi:10.1016/j.compositesb.2021.109162.

[75] Ishak A, Longuet C, Otazaghine B, Sonnier R. Synthesis of novel reactive flame retardant to improve fire resistance and mechanical properties in epoxy resin. Polym Degrad Stab 2024;228:110925. doi:10.1016/j.polymdegradstab.2024.110925.

[76] Lu YX, Feng JB, Chu T, Huo SQ, Xie HY, Xu ZG, et al. A 2D biobased P/N-containing aggregate for boosting fire retardancy of PA6/aluminum diethylphosphinate via synergy. J Mater Sci Technol 2024;198(1):73–82. doi:10.1016/j.jmst.2024.03.001.

[77] Rong H, Guo Y, Chen ZW, Chen TT, Yu Y, He CL, et al. Synergistic effect of phenyl phosphoric acid derivatives and DOPO on multifunctional epoxy resin: fire safety, mechanical properties, transparency and hydrophobicity. Polym Degrad Stab 2023;216:110471. doi:10.1016/j.polymdegradstab.2023.110471.

[78] Hu B, Wang J, Chen X, Wang JS, Yang S, Zhu L, et al. A fire-safe, single-component epoxy resin based on a phosphorus/imidazole-containing latent curing agent and diphenylphosphine. Polym Adv Technol 2024;35:e6238. doi:10.1002/pat.6238.

[79] Hou BY, Wang YN, Li BJ, Li N, Yang D, Liu HC, et al. Bio-based flame-retardant plasticizers derived from l-lactic acid: effects of valence states of phosphorus structure on fire safety, flexibility and transparency of poly(lactic acid). Chem Eng J 2023;474:145563. doi:10.1016/j.cej.2023.145563.

[80] Yang QS, Wang J, Yang S, Huo SQ, Song PA, Fang ZP, et al. A phosphorus-containing aliphatic amine curing agent towards intrinsic flame-retardant and smoke-suppressive epoxy resins. J Polym Res 2023;30:51. doi:10.1007/s10965-023-03437-8.

[81] Huo SQ, Zhou ZX, Jiang JW, Sai T, Ran SY, Fang ZP, et al. Flame-retardant, transparent, mechanically-strong and tough epoxy resin enabled by high-efficiency multifunctional boron-based polyphosphonamide. Chem Eng J 2022;427:131578. doi:10.1016/j.cej.2021.131578.

[82] Xu B, Jia M, Wang D, Zhao SH, Zhu SA, Qian LJ. A discovery for phosphorus valence and unsaturated bonds in polyphosphate/polyphosphonate: promotion or inhibition for its flame-retardant mode of action in PET. Polym Degrad Stab 2024;227:110873. doi:10.1016/j.polymdegradstab.2024.110873.

[83] Yang QS, Wang J, Chen X, Yang S, Huo SQ, Chen QF, et al. A phosphorus-containing tertiary amine hardener enabled flame retardant, heat resistant and mechanically strong yet tough epoxy resins. Chem Eng J 2023;468:143811. doi:10.1016/j.cej.2023.143811.

[84] Huo SQ, Yang S, Wang J, Cheng JW, Zhang QQ, Hu YF, et al. A liquid phosphorus-containing imidazole derivative as flame-retardant curing agent for epoxy resin with enhanced thermal latency, mechanical, and flame-retardant performances. J Hazard Mater 2020;386:121984. doi:10.1016/j.jhazmat.2019.121984.

[85] Zhang TT, Huo SQ, Ye GF, Wang C, Zhang Q, Xue YJ, et al. Phosphorus/boron-containing, flame-retardant polyurethane elastomers with great mechanical, shape-memory, and recycling performances. Polym Degrad Stab 2024;230:111047. doi:10.1016/j.polymdegradstab.2024.111047.

[86] Zhang QQ, Yang S, Wang J, Cheng JW, Zhang QX, Ding GP, et al. A DOPO based reactive flame retardant constructed by multiple heteroaromatic groups and its application on epoxy resin: curing behavior, thermal degradation and flame retardancy. Polym Degrad Stab 2019;167:10–20. doi:10.1016/j.polymdegradstab.2019.06.020.

[87] Huo SQ, Liu ZT, Li C, Wang XL, Cai HP, Wang J. Synthesis of a phosphaphenanthrene/benzimidazole-based curing agent and its application in flame-retardant epoxy resin. Polym Degrad Stab 2019;163:100–9. doi:10.1016/j.polymdegradstab.2019.03.003.

[88] Zhang AL, Zhang JZ, Liu LA, Dai JF, Lu XY, Huo SQ, et al. Engineering phosphorus-containing lignin for epoxy biocomposites with enhanced thermal stability, fire retardancy and mechanical properties. J Mater Sci Technol 2023;167:82–93. doi:10.1016/j.jmst.2023.06.004.

[89] Guo Y, Rong H, Chen ZW, Chen TT, Yu Y, Zhang XD, et al. A novel DOPO derivative containing multifunctional groups aiming to improve fire safety, thermal stability and curing state towards epoxy resin. Polym Degrad Stab 2022;205:110142. doi:10.1016/j.polymdegradstab.2022.110142.

[90] Guo Y, Yang HM, Rong H, Chen ZW, Chen TT, Yu Y, et al. Hydrophobicity, transparency, mechanically excellent and fire safety multifunctional epoxy resin based on a novel DOPO derivative with cyano group. Prog Org Coat 2023;185:107897. doi:10.1016/j.porgcoat.2023.107897.

[91] Zhou J, Guo Y, Chen ZW, Chen TT, Yu Y, Zhang QW, et al. A synthesized P/N/S oligomer flame retardant to construct superior flame-retardant, transparent, and mechanical properties epoxy resin. Mater Today Chem 2024;40:102201. doi:10.1016/j.mtchem.2024.102201.

[92] Feng JB, Ma ZW, Wu JP, Zhou ZZ, Liu Z, Hou BY, et al. Fire-safe aerogels and foams for thermal insulation: from materials to properties. Adv Mater 2024:2411856. doi:10.1002/adma.202411856.

[93] Li JH, Weng ZH, Cao Q, Qi Y, Lu BW, Zhang SH, et al. Synthesis of an aromatic amine derived from biomass and its use as a feedstock for versatile epoxy thermoset. Chem Eng J 2022;433:134512. doi:10.1016/j.cej.2022.134512.

[94] Nabipour H, Wang X, Kandola B, Song L, Kan YC, Chen J, et al. A bio-based intrinsically flame-retardant epoxy vitrimer from furan derivatives and its application in recyclable carbon fiber composites. Polym Degrad Stab 2023;207:110206. doi:10.1016/j.polymdegradstab.2022.110206.

[95] Cao Q, Li JH, Liu BT, Zhao Y, Zhao J, Gu HW, et al. Toward versatile biobased epoxy vitrimers by introducing aromatic N-heterocycles with stiff and flexible segments. Chem Eng J 2023;469:143702. doi:10.1016/j.cej.2023.143702.

[96] Sai T, Ran SY, Guo ZH, Song PA, Fang ZP. Recent advances in fire-retardant carbon-based polymeric nanocomposites through fighting free radicals. SusMat 2022;2(4):411–34. doi:10.1002/sus2.73.

[97] Yang Z, Guo WC, Yang P, Hu JF, Duan GG, Liu XH, et al. Metal-phenolic network green flame retardants. Polymer 2021;221:123627. doi:10.1016/j.polymer.2021.123627.

[98] Zhang L, Wang Q, Jian RK, Wang DY. Bioinspired iron-loaded polydopamine nanospheres as green flame retardants for epoxy resin free radical scavenging and catalytic charring. J Mater Chem A 2020;8(5):2529–38. doi:10.1039/C9TA11021F.

[99] Lu CJ, Bian S, Hu K, Li CC, Zheng KW, Sun QF. Biomass-based epoxy resin derived from resveratrol with high temperature resistance and intrinsic flame retardant properties. Ind Crops Prod 2022;187:115500. doi:10.1016/j.indcrop.2022.115500.

[100] Song X, Deng ZP, You CW, Sun RY, Song F, Wang XL, et al. High-performance and fire-resistant epoxy thermosets derived from plant-derived ferulic acid. Ind Crops Prod 2022;187:115445. doi:10.1016/j.indcrop.2022.115445.

[101] Zhang Y, Zhang XY, Wang P, Liu YD, Wan MT, Zhang K. Phosphorus-free curcumin-derived epoxy resin with exceptional flame retardancy, glass transition temperature and mechanical properties. Polym Degrad Stab 2023;215:110440. doi:10.1016/j.polymdegradstab.2023.110440.

[102] Ma SQ, Webster DC. Degradable thermosets based on labile bonds or linkages: a review. Prog Polym Sci 2018;76:65–110. doi:10.1016/j.progpolymsci.2017.07.008.

[103] Wang BB, Ma SQ, Yan SF, Zhu J. Readily recyclable carbon fiber reinforced composites based on degradable thermosets: a review. Green Chem 2019;21:5781–96. doi:10.1039/C9GC01760G.

[104] Chen XC, Chen SF, Xu ZJ, Zhang JH, Miao MH, Zhang DH. Degradable and recyclable bio-based thermoset epoxy resins. Green Chem 2020;22:4187–98. doi:10.1039/D0GC01250E.

[105] Zhao J, Zhang ZM, Wang CY, Yan XZ. Synergistic dual dynamic bonds in covalent adaptable networks. CCS Chem 2024;6:41–56. doi:10.31635/ccschem.023.202303045.

[106] Montarnal D, Capelot M, Tournilhac F, Leibler L. Silica-like malleable materials from permanent organic networks. Science 2011;334:965–8. doi:10.1126/science.1212648.

[107] Röttger M, Domenech T, van der Weegen R, Nicolaÿ ABR, Leibler L. High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. Science 2017;356:62–5. doi:10.1126/science.aah5281.

[108] Van Lijsebetten F, Holloway JO, Winne JM. Du Prez FE. Internal catalysis for dynamic covalent chemistry applications and polymer science. Chem Soc Rev 2020;49:8425–38. doi:10.1039/D0CS00452A.

[109] Zou WK, Jin BJ, Wu Y, Song HJ, Luo YW, Huang FH, et al. Light-triggered topological programmability in a dynamic covalent polymer network. Sci Adv 2020;6:eaaz2362. doi:10.1126/sciadv.aaz2362.

[110] Scheutz GM, Lessard JJ, Sims MB, Sumerlin BS. Adaptable crosslinks in polymeric materials: resolving the intersection of thermoplastics and thermosets. J Am Chem Soc 2019;141:16181–96. doi:10.1021/jacs.9b07922.

[111] Van Zee NJ, Nicolaÿ R. Vitrimers: permanently crosslinked polymers with dynamic network topology. Prog Polym Sci 2020;104:101233. doi:10.1016/j.progpolymsci.2020.101233.

[112] Yang Y, Xu YS, Ji Y, Wei Y. Functional epoxy vitrimers and composites. Prog Mater Sci 2021;120:100710. doi:10.1016/j.pmatsci.2020.100710.

[113] Li PY, Jiang X, Gu RR, Tian H, Qu DH. Catalyst-free dynamic covalent C=C/C=N metathesis reaction for associative covalent adaptable networks. Angew Chem Int Ed 2024;63:e202406708. doi:10.1002/anie.202406708.

[114] Karatrantos AV, Couture O, Hesse C, Schmidt DF. Molecular simulation of covalent adaptable networks and vitrimers: a review. Polymers 2024;16:1373. doi:10.3390/polym16101373.

[115] Gandini A. The furan/maleimide Diels-Alder reaction: a versatile click-unclick tool in macromolecular synthesis. Prog Polym Sci 2013;38:1–29. doi:10.1016/j.progpolymsci.2012.04.002.

[116] Rulísek L, Sebek P, Havlas Z, Hrabal R, Capek P, Svatos A. An experimental and theoretical study of stereoselectivity of furan-maleic anhydride and furan-maleimide Diels-Alder reactions. J Org Chem 2005;70:6295–302. doi:10.1021/jo050759z.

[117] Zhou JW, Guimard NK, Inglis AJ, Namazian M, Lin CY, Coote ML, et al. Thermally reversible Diels-Alder-based polymerization: an experimental and theoretical assessment. Polym Chem 2012;3:628–39. doi:10.1039/C1PY00356A.

[118] Liu CL, Fang WH, Cheng QQ, Qiu BW, Shangguan YG, Shi JG. Revolutionizing elastomer technology: advances in reversible crosslinking, reprocessing, and self-healing applications. Polym Rev 2024:1–44. doi:10.1080/15583724.2024.2405904.

[119] Jin YH, Lei ZP, Taynton P, Huang SF, Zhang W. Malleable and recyclable thermosets: the next generation of plastics. Matter 2019;1:1456–93. doi:10.1016/j.matt.2019.09.004.

[120] Avshalomov R, Jarach N, Dodiuk H. Breaking the unbreakable bond: towards sustainable adhesives' future. Eur Polym J 2024;209:112920. doi:10.1016/j.eurpolymj.2024.112920.

[121] Gerdroodbar AE, Karimkhani V, Dashtimoghadam E, Salami-Kalajahi M. Vitrimerization as a bridge of chemical and mechanical recycling. J Environ Chem Eng 2024;12:112897. doi:10.1016/j.jece.2024.112897.

[122] Liu T, Zhao BM, Zhang JW. Recent development of repairable, malleable and recyclable thermosetting polymers through dynamic transesterification. Polymer 2020;194:122392. doi:10.1016/j.polymer.2020.122392.

[123] Liguori A, Hakkarainen M. Designed from biobased materials for recycling: imine-based covalent adaptable networks. Macromol Rapid Commun 2022;43:2100816. doi:10.1002/marc.202100816.

[124] Black SP, Sanders JKM, Stefankiewicz AR. Disulfide exchange: exposing supramolecular reactivity through dynamic covalent chemistry. Chem Soc Rev 2014;43:1861–72. doi:10.1039/C3CS60326A.

[125] Zhang Q, Qu DH, Feringa B, Tian H. Disulfide-mediated reversible polymerization toward intrinsically dynamic smart materials. J Am Chem Soc 2022;144:2022–33. doi:10.1021/jacs.1c10359.

[126] Zheng J, Png ZM, Ng SH, Tham GX, Ye EY, Goh SS, et al. Vitrimers: current research trends and their emerging applications. Mater Today 2021;51:586–625. doi:10.1016/j.mattod.2021.07.003.

[127] Yang Y, Zhang S, Zhang XQ, Gao LC, Wei Y, Ji Y. Detecting topology freezing transition temperature of vitrimers by AIE luminogens. Nat Commun 2019;10:3165. doi:10.1038/s41467-019-11144-6.

[128] Krishnan BP, Saalwaechter K, Adjedje VKB, Binder WH. Design, synthesis and characterization of vitrimers with low topology freezing transition temperature. Polymers 2022;14:2456. doi:10.3390/polym14122456.

[129] Mangialetto J, Cuvellier A, Verhelle R, Brancart J, Rahier H, Van Assche G, et al. Diffusion- and mobility-controlled self-healing polymer networks with dynamic covalent bonding. Macromolecules 2019;52:8440–52. doi:10.1021/acs.macromol.9b01453.

[130] Nakamura Y, Tenjimbayashi M, Moriya A, Naito M. Impact of telechelic polymer precursors on the viscoelastic properties of vitrimers. Macromol Chem Phys 2022;223:2100433. doi:10.1002/macp.202100433.

[131] Hubbard AM, Ren YX, Konkolewicz D, Sarvestani A, Picu CR, Kedziora GS, et al. Vitrimer transition temperature identification: coupling various thermomechanical methodologies. ACS Appl Polym Mater 2021;3:1756–66. doi:10.1021/acsapm.0c01290.

[132] Zhang XF, Zhang SK, Liu W, Abbas Y, Wu ZP, Eichen Y, et al. Thermally switchable polymers: from thermo-reversibly self-healing hybrid polymers to irreversibly crosslinked flame-retardant networks. Chem Eng J 2021;411:128467. doi:10.1016/j.cej.2021.128467.

[133] Gu S, Xu SD, Lu JH, Pu XL, Ren QR, Xiao YF, et al. Phosphonate-influenced Diels-Alder chemistry toward multi-path recyclable, fire safe thermoset and its carbon fiber composites. Ecomat 2023;5:e12388. doi:10.1002/eom2.12388.

[134] Gu S, Xiao YF, Tan SH, Liu BW, Guo DM, Wang YZ, et al. Neighboring molecular engineering in Diels-alder chemistry enabling easily recyclable carbon fiber reinforced composites. Angew Chem Int Ed 2023;62:e202312638. doi:10.1002/ange.202312638.

[135] Cuminet F, Caillol S, Dantras É, Leclerc É, Ladmiral V. Neighboring group participation and internal catalysis effects on exchangeable covalent bonds: application to the thriving field of vitrimer chemistry. Macromolecules 2021;54:3927–61. doi:10.1021/acs.macromol.0c02706.

[136] He YF, Cui XY, Liu ZS, Lan FJ, Sun J, Li HF, et al. A new approach to prepare flame retardant epoxy resin with excellent transmittance, mechanical properties, and anti-aging performance by the incorporation of DOPO derivative. Polym Degrad Stab 2023;218:110579. doi:10.1016/j.polymdegradstab.2023110579.

[137] Ren JX, Yang GC, Deng XC, Huang SC, Lu CF. A tryptamine-based DOPO derivative as a flame retardant for epoxy resins. Polym Degrad Stab 2023;218:110595. doi:10.1016/j.polymdegradstab.2023.110595.

[138] Wang SD, Lou SH, Fan PH, Ma L, Liu J, Tang T. A novel aromatic imine-containing DOPO-based reactive flame retardant towards enhanced flame-retardant and mechanical properties of epoxy resin. Polym Degrad Stab 2023;213:110364. doi:10.1016/j.polymdegradstab.2023.110364.

[139] Dello Iacono S, Martone A, Pastore A, Filippone G, Acierno D, Zarrelli M, et al. Thermally activated multiple self-healing Diels-alder epoxy system. Polym Eng Sci 2017;57:674–9. doi:10.1002/pen.24570.

[140] McElhanon JR, Russick EM, Wheeler DR, Loy DA, Aubert JH. Removable foams based on an epoxy resin incorporating reversible Diels-Alder adducts. J Appl Polym Sci 2002;85:1496–502. doi:10.1002/app.10753.

[141] Kuang X, Liu GM, Dong X, Liu XG, Xu JJ, Wang DJ. Facile fabrication of fast recyclable and multiple self-healing epoxy materials through Diels-alder adduct cross-linker. J Polym Sci A Polym Chem 2015;53:2094–103. doi:10.1002/pola.27655.

[142] Bai N, Saito K, Simon GP. Synthesis of a diamine cross-linker containing Diels-Alder adducts to produce self-healing thermosetting epoxy polymer from a widely used epoxy monomer. Polym Chem 2013;4:724–30. doi:10.1039/C2PY20611K.

[143] Kuang X, Liu GM, Dong X, Wang DJ. Triple-shape memory epoxy based on Diels-Alder adduct molecular switch. Polymer 2016;84:1–9. doi:10.1016/j.polymer.2015.12.033.

[144] Falireas PG, Thomassin JM, Debuigne A. Imidazolium-catalyzed dynamic ester cross-links towards reprocessable epoxy vitrimers. Eur Polym J 2021;147:110296. doi:10.1016/j.eurpolymj.2021.110296.

[145] Chen JH, Liu BW, Lu JH, Lu P, Tang YL, Chen L, et al. Catalyst-free dynamic transesterification towards a high-performance and fire-safe epoxy vitrimer and its carbon fiber composite. Green Chem 2022;24:6980–8. doi:10.1039/D2GC01405J.

[146] Ren QR, Gu S, Wang YZ, Chen L. A phosphonate-derived epoxy vitrimer with intrinsic flame retardancy and catalyst-free reprocessability. J Polym Sci 2024;62:3195–205. doi:10.1002/pol.20230211.

[147] Wei F, Zhang JH, Wu C, Luo M, Ye BJ, Zhang HJ, et al. Closed-loop recycling of tough and flame-retardant epoxy resins. Macromolecules 2023;56:5290–305. doi:10.1021/acs.macromol.3c00650.

[148] Huang ZY, Klingler WW, Roncucci D, Polisi C, Rougier V, Lehner S, et al. Enabling simultaneous reprocessability and fire protection via incorporation of phosphine oxide monomer in epoxy vitrimer. J Mater Sci Technol 2024;196:224–36. doi:10.1016/j.jmst.2024.01.062.

[149] Zhang D, Cao WH, Guo ZH, Yan HQ, Fang ZP, Chen P, et al. Structure and properties of a flame retardant ternary vitrimer regulated by cyclic and long-chain dicarboxylic acids. Polym Degrad Stab 2023;207:110234. doi:10.1016/j.polymdegradstab.2022.110234.

[150] Chen YZ, Zeng Y, Wu YC, Chen TT, Qiu RH, Liu WD. Flame-retardant and recyclable soybean oil-based thermosets enabled by the dynamic phosphate ester and tannic acid. ACS Appl Mater Interf 2023;15(4):5963–73. doi:10.1021/acsami.2c21279.

[151] Wang C, Huo SQ, Ye GF, Zhang Q, Cao CF, Lynch M, et al. Strong self-healing close-loop recyclable vitrimers via complementary dynamic covalent/non-covalent bonding. Chem Eng J 2024;500:157418. doi:10.1016/j.cej.2024.157418.

[152] Xu YZ, Dai SL, Bi LW, Jiang JX, Zhang HB, Chen YX. Catalyst-free self-healing bio-based vitrimer for a recyclable, reprocessable, and self-adhered carbon fiber reinforced composite. Chem Eng J 2022;429:132518. doi:10.1016/j.cej.2021.132518.

[153] Ye GF, Huo SQ, Wang C, Zhang Q, Wang H, Song PA, et al. Strong yet tough catalyst-free transesterification vitrimer with excellent fire-retardancy, durability, and closed-loop recyclability. Small 2024;20:2404634. doi:10.1002/smll.202404634.

[154] Yu Z, Ma SQ, Tang ZB, Liu YL, Xu XW, Li Q, et al. Amino acids as latent curing agents and their application in fully bio-based epoxy resins. Green Chem 2021;23:6566–75. doi:10.1039/D1GC02126E.

[155] Li Y, Xiao F, Wong CP. Novel, environmentally friendly crosslinking system of an epoxy using an amino acid: Tryptophan-cured diglycidyl ether of bisphenol a epoxy. J Polym Sci A Polym Chem 2007;45:181–90. doi:10.1002/pola.21742.

[156] Song FX, Liu T, Fan Q, Li DX, Ou RX, Liu ZZ, et al. Sustainable, high-performance, flame-retardant waterborne wood coatings via phytic acid based green curing agent for melamine-urea-formaldehyde resin. Prog Org Coat 2022;162:106597. doi:10.1016/j.porgcoat.2021.106597.

[157] Yu Z, Ma SQ, Liu YL, Su Y, Feng HZ, Li PY, et al. Facile synthesis of bio-based latent curing agent and its high-Tg epoxy network. Eur Polym J 2022;164:110965. doi:10.1016/j.eurpolymj.2021.110965.

[158] Yang WJ, Ding H, Zhou W, Liu TX, Xu PW, Puglia D, et al. Design of inherent fire retarding and degradable bio-based epoxy vitrimer with excellent self-healing and mechanical reprocessability. Compos Sci Technol 2022;230:109776. doi:10.1016/j.compscitech.2022.109776.

[159] Ding XM, Chen L, Xu YJ, Shi XH, Luo X, Song X, et al. Robust epoxy vitrimer with simultaneous ultrahigh impact property, fire safety, and multipath recyclability via rigid-flexible imine networks. ACS Sustain Chem Eng 2023;11:14445–56. doi:10.1021/acssuschemeng.3c03189.

[160] Tian PX, Li YD, Weng YX, Hu Z, Zeng JB. Reprocessable, chemically recyclable, and flame-retardant biobased epoxy vitrimers. Eur Polym J 2023;193:112078. doi:10.1016/j.eurpolymj.2023.112078.

[161] Tian PX, Li YD, Hu Z, Zeng JB. Fire-resistant and high-performance epoxy vitrimers for fully recyclable carbon fiber-reinforced composites. Mater Today Chem 2024;36:101965. doi:10.1016/j.mtchem.2024.101965.

[162] Ding HL, Wang J, Yu P, He HF, Wang HY, Zhang W, et al. Rapidly recyclable, monomer recovery and flame-retardant bio-based polyimine networks. Chem Eng J 2024;481:148024. doi:10.1016/j.cej.2023.148024.

[163] Liu T, Peng JY, Liu J, Hao XL, Guo CG, Ou RX, et al. Fully recyclable, flame-retardant and high-performance carbon fiber composites based on vanillin-terminated cyclophosphazene polyimine thermosets. Compos Part B Eng 2021;224:109188. doi:10.1016/j.compositesb.2021.109188.

[164] Yang XY, Ke YZ, Chen Q, Shen L, Xue JQ, Quirino RL, et al. Efficient transformation of renewable vanillin into reprocessable, acid-degradable and flame retardant polyimide vitrimers. J Clean Prod 2022;333:130043. doi:10.1016/j.jclepro.2021.130043.

[165] Wang S, Ma SQ, Li Q, Yuan WC, Wang BB, Robust ZJ. Fire-safe, monomer-recovery, highly malleable thermosets from renewable bioresources. Macromolecules 2018;51:8001–12. doi:10.1021/acs.macromol.8b01601.

[166] Zhang P, Jia SY, Xie RS, Chen L, Xiong Y. Furan-derived Schiff base covalent adaptable thermosets with recyclability and anti-flammability. Green Chem Eng 2024;5:364–73. doi:10.1016/j.gce.2023.08.005.

[167] Daglar Ö, Eisenreich F, Tomovic Z. Chemical and solvent-based recycling of high-performance epoxy thermoset utilizing imine-containing secondary amine hardener. Adv Funct Mater 2024;34(49):2408299. doi:10.1002/adfm.202408299.

[168] Peng JY, Xie SY, Liu T, Wang DY, Ou RX, Guo CG, et al. High-performance epoxy vitrimer with superior self-healing, shape-memory, flame retardancy, and antibacterial properties based on multifunctional curing agent. Compos Part B Eng 2022;242:110109. doi:10.1016/j.compositesb.2022.110109.

[169] Li PS, Zhang QR, Ma JY, Liao ZY, Zhang JY, Xie HY, et al. Synthesis of bio-based polyimine networks with flame-retardancy, acid-degradablility, and reprocessability. Polymer 2024;302:127101. doi:10.1016/j.polymer.2024.127101.

[170] Wang CC, Xu H, Xie ZT, Zheng J, Wu JR. Extrudable, robust and recyclable bio-based epoxy vitrimer via tailoring the topology of a dual dynamic-covalent-bond network. Polymer 2023;289:126487. doi:10.1016/j.polymer.2023.126487.

[171] Nabipour H, Wang X, Song L, Hu Y. A furan-derived epoxy thermoset with inherent anti-flammability, degradability, and raw material recycling. Mater Today Chem 2023;27:101315. doi:10.1016/j.mtchem.2022.101315.

[172] Cui CH, Wang F, Chen XX, Xu T, Li Z, Chen KX, et al. Covalent adaptable networks with dual dynamic covalent bonds for self-repairing infrared transmitting materials. Adv Funct Mater 2024;34:2315469. doi:10.1002/adfm.202315469.

[173] Ma Y, Zhao Z, Zheng Z, Li J, Li M-H, Hu J. High-performance poly(thioctic acid)-based thermosets featuring upcycling ability for in situ foaming enabled by dual-dynamic networks. Matter 2024;7(11):4046–58. doi:10.1016/j.matt.2024.08.008.

[174] Anguita JV, Smith CTG, Stute T, Funke M, Delkowski M, Silva SRP. Dimensionally and environmentally ultra-stable polymer composites reinforced with carbon fibres. Nat Mater 2020;19(3):317–22. doi:10.1038/s41563-019-0565-3.

[175] Di Trani N, Masini A, Bo T, Paci MM, Batra JS, Reggiani M, et al. Probing physicochemical performances of 3D printed carbon fiber composites during 8-month exposure to space environment. Adv Funct Mater 2024;34:2310243. doi:10.1002/adfm.202310243.

[176] Aamir M, Tolouei-Rad M, Giasin K, Nosrati A. Recent advances in drilling of carbon fiber-reinforced polymers for aerospace applications: a review. Int J Adv Manuf Technol 2019;105:2289–308. doi:10.1007/s00170-019-04348-z.

[177] Allen KA, Kearney LT, Gupta S, Ghossein H, Keum JK, Damron JT, et al. Understanding interfacial crystallization dynamics on carbon fiber reinforced polypropylene composite manufacturing. Compos Part B Eng 2025;291:112027. doi:10.1016/j.compositesb.2024.112027.

[178] Wu YS, Lu HT, Qin FX, Yang S, Xu P, Peng HX. Establishing interphase with "rigid-flexible coupling" crosslinked network by supramolecular structure to improve interfacial properties of high-modulus carbon fiber composites. Compos Part B Eng 2025;291:111968. doi:10.1016/j.compositesb.2024.111968.

[179] Zhang J, Chevali VS, Wang H, Wang CH. Current status of carbon fibre and carbon fibre composites recycling. Compos Part B Eng 2020;193:108053. doi:10.1016/j.compositesb.2020.108053.

[180] Giorgini L, Benelli T, Brancolini G, Mazzocchetti L. Recycling of carbon fiber reinforced composite waste to close their life cycle in a cradle-to-cradle approach. Curr Opin Green Sustainable Chem 2020;26:100368. doi:10.1016/j.cogsc.2020.100368.

[181] Pickering SJ. Recycling technologies for thermoset composite materials - current status. Compos Part A Appl Sci Manuf 2006;37:1206–15. doi:10.1016/j.compositesa.2005.05.030.

[182] Cheul-Kyu L, Yong-Ki K, Phirada P, Jung-Suk K, Kun-Mo L, Chang-Sik J. Assessing environmentally friendly recycling methods for composite bodies of railway rolling stock using life-cycle analysis. Transp Res Part D Transp Environ 2010;15:197–203. doi:10.1016/j.trd.2010.02.001.

[183] Fan XT, Zheng J, Yeo JCC, Wang S, Li K, Muiruri JK, et al. Dynamic covalent bonds enabled carbon fiber reinforced polymers recyclability and material circularity. Angew Chem Int Ed 2024;63:e202408969. doi:10.1002/ange.202408969.

[184] Feng HZ, Xu XW, Wang BB, Su Y, Liu YL, Zhang CZ, et al. Facile preparation, closed-loop recycling of multifunctional carbon fiber reinforced polymer composites. Compos Part B Eng 2023;257:110677. doi:10.1016/j.compositesb.2023.110677.

[185] Fei ME, Chang YC, Hao C, Shao L, Liu WC, Zhao BM, et al. Highly engineerable Schiff base polymer matrix with facile fiber composite manufacturability and hydrothermal recyclability. Compos Part B Eng 2023;248:110366. doi:10.1016/j.compositesb.2022.110366.

[186] Shi XH, Li XL, Li YM, Li Z, Wang DY. Flame-retardant strategy and mechanism of fiber reinforced polymeric composite: a review. Compos Part B Eng 2022;233:109663. doi:10.1016/j.compositesb.2022.109663.

[187] Mukhtar M, Klosterman D, Morgan AB. Preparation, cure, characterization, and mechanical properties of reactive flame-retardant cyanate ester/epoxy resin blends and their carbon fiber reinforced composites. Compos Part B Eng 2024;282:111580. doi:10.1016/j.compositesb.2024.111580.

[188] Zou B, Qian ZY, Zhang ZX, Xing WY, Zhong SS, Li JJ, et al. Quantitative assessment of whether phosphorus-based flame retardants are optimizing or degrading the fire hazard of aircraft carbon fiber/epoxy composites. Compos Part B Eng 2024;279:111413. doi:10.1016/j.compositesb.2024.111413.

[189] Vaughan M, Beaucamp A, Collins MN. Development of high stiffness carbon fibres from lignin. Compos Part B Eng 2025;292:112024. doi:10.1016/j.compositesb.2024.112024.

[190] Yadav R, Zabihi O, Fakhrhoseini S, Nazarloo HA, Kiziltas A, Blanchard P, et al. Lignin derived carbon fiber and nanofiber: manufacturing and applications. Compos Part B Eng 2023;255:110613. doi:10.1016/j.compositesb.2023.110613.

[191] Zamani P, Zabihi O, Ahmadi M, Zamani MR, Zohuriaan-Mehr MJ, Kannangara T, et al. Assessing sustainability and green chem in synthesis of a vanillin-based vitrimer at scale: enabling sustainable manufacturing of recyclable carbon fiber composites. Compos Part A Appl Sci Manuf 2024;179:108016. doi:10.1016/j.compositesa.2024.108016.

[192] Jian H, Liang YQ, Deng C, Xu JX, Liu Y, Shi JY, et al. Research progress on the improvement of flame retardancy, hydrophobicity, and antibacterial properties of wood surfaces. Polymers 2023;15(4):951. doi:10.3390/polym15040951.

[193] Cheng LS, Ren SB, Lu XN. Application of eco-friendly waterborne polyurethane composite coating incorporated with nano cellulose crystalline and silver nano particles on wood antibacterial board. Polymers 2020;12(2):407. doi:10.3390/polym12020407.

[194] Munir MT, Aviat F, Pailhories H, Eveillard M, Irle M, Federighi M, et al. Direct screening method to assess antimicrobial behavior of untreated wood. Eur J Wood Wood Prod 2019;77:319–22. doi:10.1007/s00107-019-01390-2.

[195] Cai JJ, Zhang XR, Wang ZM, Xie JQ, Zhang XK. A bio-based antibacterial epoxy resin coating with outstanding flame retardant and mechanical properties. Prog Org Coat 2024;190:108369. doi:10.1016/j.porgcoat.2024.108369.

[196] Niculescu AG, Tudorache DI, Bocioaga M, Mihaiescu DE, Hadibarata T, Grumezescu AM. An updated overview of silica aerogel-based nanomaterials. Nanomaterials 2024;14:469. doi:10.3390/nano14050469.

[197] Prasad C, Jeong SG, Won JS, Ramanjaneyulu S, Sangaraju S, Kerru N, et al. Review on recent advances in cellulose nanofibril based hybrid aerogels: synthesis, properties and their applications. Int J Biol Macromol 2024;261:129460. doi:10.1016/j.ijbiomac.2024.129460.

[198] Sun H, Yang B, Ji DX, Ma C, Pang RX, Yuan BL, et al. Bioinspired aerogels: ingenious structure, remarkable performance, and versatile applications. J Mater Chem A 2024;12:12358–80. doi:10.1039/D4TA00851K.

[199] Nita LE, Ghilan A, Rusu AG, Neamtu I, Chiriac AP. New trends in bio-based aerogels. Pharmaceutics 2020;12:449. doi:10.3390/pharmaceutics12050449.

[200] Dungani R, Hua LS, Chen LW, Nurani W, Solihat NN, Maulani RR, et al. Potential of lignin and cellulose as renewable materials for the synthesis of flame-retardant aerogel composites. Mater Today Commun 2024;41:110501. doi:10.1016/j.mtcomm.2024.110501.

[201] Wang CL, Eisenreich F, Tomovic Ä. Closed-loop recyclable high-performance polyimine aerogels derived from bio-based resources. Adv Mater 2023;35:2209003. doi:10.1002/adma.202209003.

[202] Yang Y, Wang ZY, He QQ, Li XJ, Lu GX, Jiang LM, et al. 3D printing of nacre-inspired structures with exceptional mechanical and flame-retardant properties. Research 2022;2022:9840574. doi:10.34133/2022/9840574.

[203] Wang R, Fu T, Yang YJ, Song X, Wang XL, Wang YZ. Scientific discovery framework accelerating advanced polymeric materials design. Research 2024;7:0406. doi:10.34133/research.0406.

[204] Chen ZW, Yang BR, Song NN, Chen TT, Zhang QW, Li CX, et al. Machine learning-guided design of organic phosphorus-containing flame retardants to improve the limiting oxygen index of epoxy resins. Chem Eng J 2023;455:140547. doi:10.1016/j.cej.2022.140547.

[205] Jafari P, Zhang RR, Huo SQ, Wang QS, Yong JM, Hong M, et al. Machine learning for expediting next-generation of fire-retardant polymer composites. Compos Commun 2024;45:101806. doi:10.1016/j.coco.2023.101806.

[206] Wu XY, Hartmann P, Berne D, De Bruyn M, Cuminet F, Wang ZW, et al. Closed-loop recyclability of a biomass-derived epoxy-amine thermoset by methanolysis. Science 2024;384:eadj9989. doi:10.1126/science.adj9989.

[207] Cao Y, Wu Y, Huang YM, Xiang HP, Zhang LY. Photo/thermal dual-responsive azobenzene-based photosensitive resin for 4D printing. Chem Eng J 2024;498(15):155140. doi:10.1016/j.cej.2024.155140.

[208] Nguyen LT, Maes S, Du Prez FE. Enabling the reprocessability and debonding of epoxy thermosets using dynamic poly(β-Amino Amide) curing agents. Adv Funct Mater 2024:2419240. doi:10.1002/adfm.202419240.