

Recyclable inherently flame-retardant thermosets: Chemistry, properties and applications

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ABSTRACT

Thermosets are polymeric materials that contain permanent networks and thus are difficult to recycle. They are not reprocessable once cured and often do not degrade under mild conditions. Over the past decades, the use of polymeric materials in fire safety applications has increased, and so is the need for them to be more sustainable. From this standpoint, recently two major challenges in designing next-generation thermosets have attracted much attention in the scientific community: embedded fire safety and reprocessability/recyclability. In this review, a detailed report on research progress in design of fire-safe and thermomechanical reprocessable/recyclable thermosets is presented. Such thermosets are designed not only to enable the reuse and recycling of the polymer material but also recover valuable components (carbon fibers or rare additives) that are encapsulated in the matrix. The flame retardant recyclable thermoset materials are categorized based on the chemistry of the labile bonds (covalent adaptable networks): i.e. (i) esters (carboxylic and phosphate esters), (ii) sulfur-containing linkages, (iii) nitrogen-containing structures, and (iv) other phosphorus-containing structures. In addition, the use of bio-based raw materials in constructing these thermosets is also highlighted. The synthetic route, fire performance, recycling method, degradation mechanism, and progress in various approaches being developed by researchers towards recyclable and fire-safe thermosets are summarized in detail in this review.

1. Introduction

Commercial thermosets are commonly manufactured from liquid comonomers that react irreversibly to form three-dimensional cross-linked solid material. Their manufacturing process typically involves a curing step, which is accelerated by an external stimulus such as heat or UV irradiation. Due to their high mechanical strength, excellent solvent resistance, thermal stability, and good chemical resistance, thermosets have played an increasingly important role in many fields, including electronic encapsulations, fabrications of printed circuit boards, coatings, adhesives, and matrixes for high-performance composite materials [1]. They currently represent around 20% of global fossil based plastic production with an estimated annual production of ~65 million tons [2]. A large variety of thermoset resins of varying chemistries are widely used in industry, including phenolic resins, urea formaldehyde resins,

unsaturated polyesters, and epoxy resins. Globally, epoxy resins account for approximately 70% of the thermoset market, due to their high thermal stability, chemical resistance and flexibility. More than 60% of the global production is used in the coatings industry. Furthermore, epoxies are probably the most versatile family of engineering/structural adhesives because they are compatible with many substrates and can be easily modified to achieve wide range of properties. To reduce the weight of transportation vehicles (planes, trains, automobiles, etc.) and reduce fuel consumption, structural composites and adhesives will be the key market drivers for epoxy resins over the next years. Recovering polymer matrix material and/or reinforcement fibers from the thermoset composite is an emerging issue [3].

Nevertheless, there are two major drawbacks of thermosets: i.e. (i) their inherent flammability, making them unsuitable in fire-safe applications; and (ii) the highly cross-linked networks with intrinsic

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resistance to deformation, rendering them not reprocessable or recyclable [4].

To overcome thermoset's inherent flammability, there are two main solutions: Firstly, the inclusion of inorganic and/or organic additives (i.e. halogen-based flame-retardants) through physical doping [5,6], which leads to leaching problems, bioaccumulation and persistence of flame-retardants (FRs) in the environment [7]. Phosphorous (P)-based FRs, i.e. melamine polyphosphate (MPP), ammonium polyphosphate (APP), diethyl phosphonic metal salts, phosphazenes and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) are suitable greener alternatives, showing low release of harmful gases and smoke during combustion [8]. Secondly, reactive approach of flame-retardants (i.e. phosphates, DOPO and cyclophosphazene derivatives) in polymeric material can be a more effective solution for fire-safe application, which allows FRs covalent linked to the thermoset network [9]. The FR is thus a part of the network, which is beneficial in design of recyclable material. This ensures no deconstructive leaching problem subsequent thermal or chemical treatments.

As mentioned earlier, due to the cross-linked network (C–C or C–N bonds), most thermosets are cured to obtain a desired shape, resulting in a fixed material that cannot be easily reprocessed or recycled by heat or by solvent [10]. These aspects limit their end of life (EoL) disposal options, i.e. only incineration, landfill and some recycling methods are applicable. Depending on the final product, thermoset wastes can be recycled through three technologies: mechanical, thermomechanical, or thermochemical recycling [3]. Mechanical recycling of thermoset leads to lower quality composites, which are typically formed by grinding the thermoset waste into powders and using them as filler in polymer matrices or other applications. On the other side, thermochemical recycling involves the application of solvolysis, or pyrolysis-oxidation processes finalized to recover the valuable fiber or filler from the plastic waste or energy by decomposition of the thermoset matrix (TM) [11, 12]. Harsh conditions and solvents (i.e. dimethylformamide) are used for the dissolution of thermoset. Such as, ammonium chloride as a solvent at 140 °C was exploited for the recovery of copper (Cu) [13].

It is clear that both mechanical and thermochemical approaches are time and energy consuming. In addition, they only allow for a partial recycling of thermoset waste, as the recovery of TM or its monomers is not well studied. The thermoset matrix represents the largest part in an EoL of composite material, thus fully recyclable thermosets and more effective recycling technologies should be developed to achieve circular economy. In addition, current recycling technologies do not consider the presence of doped flame retardants (FRs) fillers or reacted FR moieties in thermosets, which are responsible for the production of toxic species, as they often undergo thermal decomposition or solvolytic degradation together with TM and monomers [14]. Most of flame retardants in plastic wastes are halogen-based compounds, which can easily degrade or release harmful species at high temperatures or extreme pH conditions [15]. Thus, together with a high recovery rate of the polymer matrix, future thermosets should not only allow the recovery of functional flame retardant moieties, polymer matrix and fillers, but also more sustainable in terms of increasing material lifetime and treatment at EoL [15].

Instead of using FR as an additive, thermosets containing covalently incorporated FR are more feasible for recycling. Therefore, the primary emphasis of this review will be on covalently integrated FR thermosets. As currently thermomechanical recycling is considered as the most commercially feasible recycling method, which aims to lengthen the lifetime of a material. Some recent developments in the literature are moving toward this direction [16]. Furthermore, instead of treating conventional FR thermoset waste, another way around could be to design thermosets with inherent reprocessability or recyclability in the very beginning, not only to avoid using solvents or complicated procedure but also guarantee material quality after recycling. In 2010, Leibler et al. pioneered a new generation of materials containing associative covalent networks, coined vitrimers, which were demonstrated

to undergo stepwise topological rearrangements via heat triggered exchange reactions [17]. They are rigid at ambient, however “flow” at elevated temperature, which opens new application possibilities like self-healing material or recyclable material in a wide temperature range [18–20]. Bowman and co-workers introduced another broader term “covalent adaptable networks” to generalize more explicit and comprehensive features of dynamic covalent bond based networks [4], including reversible ester bonds, disulfides exchange, metathesis of dioxaborolanes, –Si–O–Si– exchange, transalkylation, imine metathesis et al. [21–23]. These networks are designed to break and reconnect reversibly under external stimuli, thus rendering the network malleable and reprocessable [24–26].

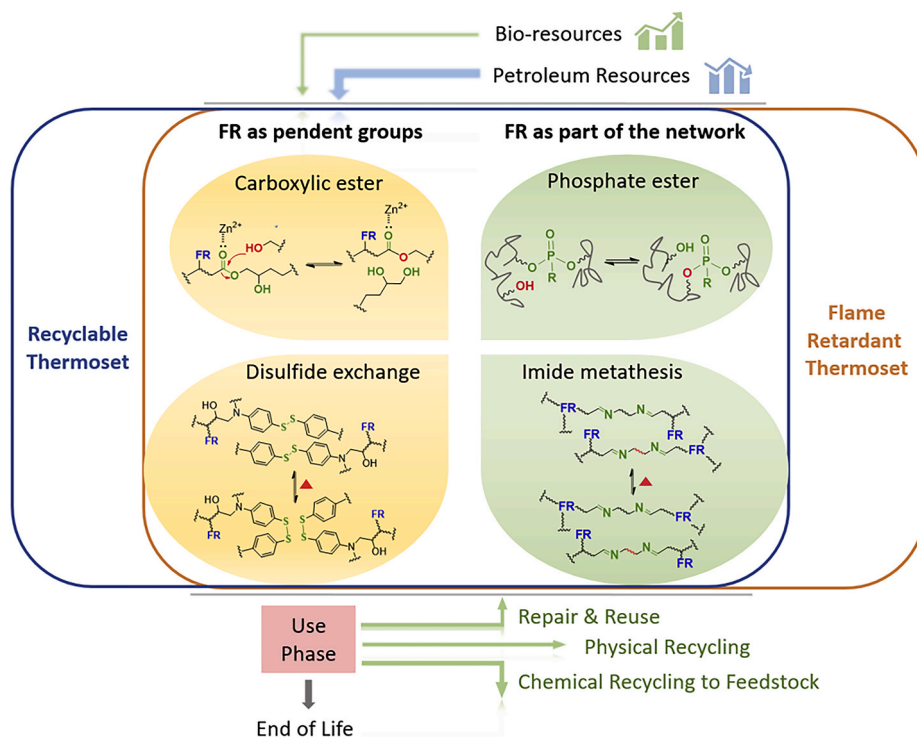
Fire-safe recyclable materials that strike a balance between thermoset rigidity, mechanical characteristics, and thermal/chemical reprocessability can be achieved by combining functional FR units with covalent adaptive networks (CANs) [27,28]. In 2017, Wang et al. reported thermosets from bio-based raw material (i.e. vanillin) which addressed simultaneously the recyclability and flammability issues [29]. The combination of flame retardancy and recyclability of covalently integrated thermoset materials will undoubtedly favor their application range and lifetime prolongation in the direction of circular economy and environmental protection. The various structural design strategies reported in the literature for manufacturing recyclable FR thermosets with CANs are summarized in Scheme 1.

In this review, we classify the reprocessable/recyclable flame-retardant thermosets into four groups based on the reversible adaptable bonds, i.e. carboxylic ester, phosphate ester, disulfide and imine based linkages (Scheme 1). FR functionality will be addressed in each group either as pendant or as networked units. Additionally, the creation of various bio-resource based recyclable flame-retardant thermosets is covered in a separate part to show more sustainable approaches. This review includes a detailed summary of the material structures, synthetic processes, physical properties, fire performance, mechanical qualities, and recycling properties.

1.1. Carboxylic ester-based covalent adaptable networks

Transesterification is a classical associative exchange reaction. It is the process of exchanging alkoxy groups of the ester with another alcohol, through an acid catalyst, which protonates the carbonyl groups and makes the ester an electrophile, or through a base catalyst, which makes the alcohol a nucleophile and result in nucleophilic acyl substitution. It is the most studied mechanism for recycling covalent adaptable networks and can be implemented in the epoxy/acid and epoxy/anhydride thermoset systems which are widely used in industry [30]. To achieve decent self-repairing property and reprocessability, epoxy covalent adaptable networks are often prepared with the epoxy to anhydride ratio fixed at 1/0.5 and an adequate catalyst (i.e., zinc salt) content to catalyze the transesterification. Topology freezing transition temperature (T_v) is used in vitrimer field to indicate the temperature where fast transesterification reactions happens. When an ester based (carboxylic, boric, or phosphate ester) epoxy thermoset experiences temperature above T_v , it starts soften or flow (stress relaxation), leading to thermo-reforming and self-healing and thus enabling recycling [31].

Some ester moieties containing thermosets can flow like viscoelastic liquids at high temperatures. However, at low temperatures, the bond-exchange reactions within the networks are very slow and they behave like classical thermosets. Thermal transition is fundamental to enable the reconstruction of damaged, shape-memory effects, dynamics of supramolecular chemistry, covalent-bond reformation and physical reshuffling in such systems [32]. There are studies focused on varying the catalyst type and concentration to alter the transesterification rates and to vary the activation energy of flow in order to define temperature windows for specific applications [18]. In recent years, covalent adaptable networks with high mechanical properties and shape memory capabilities have been developed, though with low performance in



Scheme 1. Current structural design for covalently integrate recyclable flame-retardant thermosets, including FR as pendant group or part of the network, and the commonly used adaptable bonds aiming at recyclability, together with considerations regarding the material resources and end of life, especially the bio-resources increase.

terms of thermal stability and flammability. These drawbacks are relevant especially for thermosets used in applications requiring high T_g and fire resistance. Thus, new approaches have been explored to realize the desired properties.

DOPO contains a highly reactive P–H bond which allows it to react with various thermoset monomers. It can react with different acrylates containing monomers through phospho-Michael addition [36]. DOPO can also react with the epoxy oxirane ring groups through nucleophilic

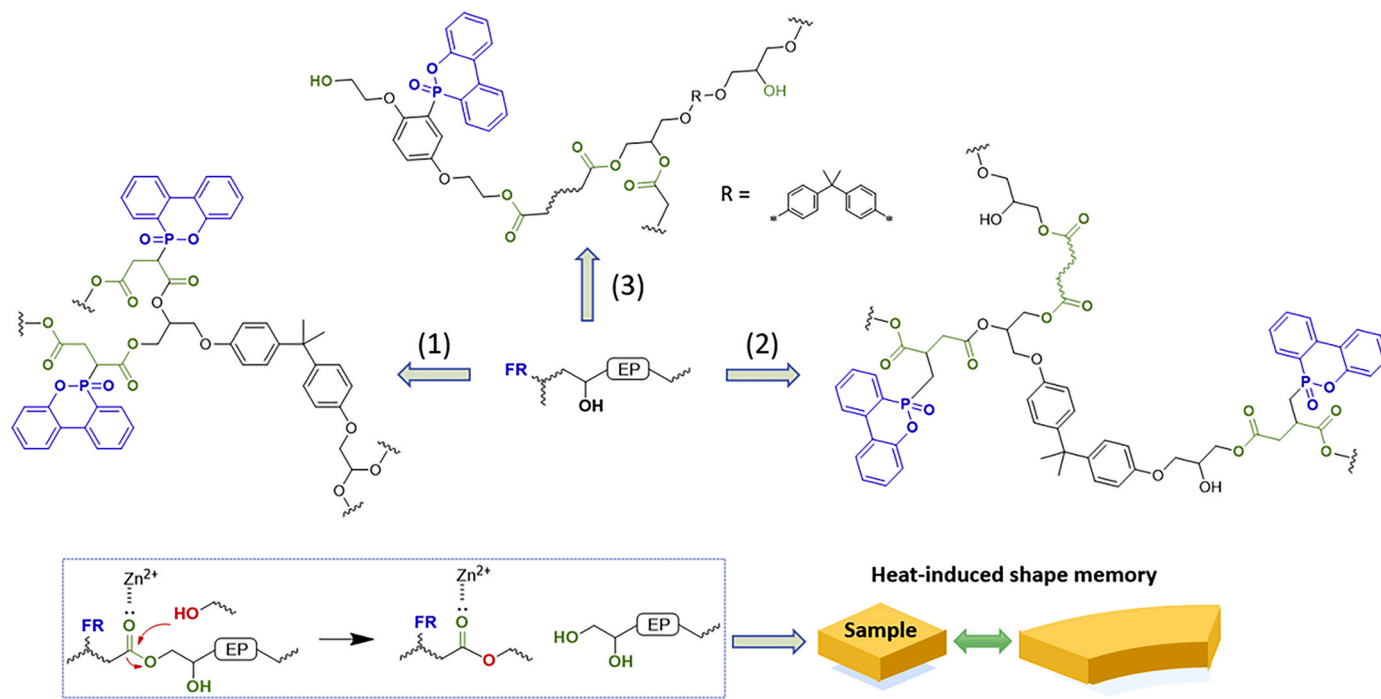


Fig. 1. Structures of (1) multi-reusable thermoset with temperature-triggered shape memory effect [33], (2) catalytic transesterification based recyclable, malleable and intrinsically flame-retardant thermoset [34], and (3) a catalyst free transesterification based recyclable FR thermoset [35], with the recycling mechanism in the dashed box and the resulting shape memory effect.

ring opening reaction, leading to an intrinsically flame retarded resin [37–40]. Phosphorous flame-retardant monomer obtained via the reaction of DOPO with maleic anhydride (MA) (DOPO-MA) was melt-blended with poly(butylene terephthalate) (PBT) to prepare flame-retardant PBT/DOPO-MA composites, where DOPO-MAH reacted with the terminal hydroxyl groups of PBT matrix [36]. Using similar flame-retardant incorporation approach, Feng et al. prepared a transparent shape memory epoxy (TSME) thermoset showing a 100% shape recovery ratio and good fire retardancy, processibility, and mechanical properties [33]. The flame-retardant epoxy thermoset was obtained by curing DGEBA resin with a multifunctional anhydride curing agent (DOPO-MA), catalyzed by zinc acetylacetonate hydrate. This flame-retardant modified epoxy thermoset (Fig. 1 – route 1) could exhibit a shape memory effect, when directly triggered by a high-temperature flame, and it could be recycled and reused as a reinforcing filler for polyesters using a simple mechanical recycling method. The epoxy material did not show improvement in mechanical properties or increase in T_g compared to pristine DGEBA polymer, but it did exhibit about four times higher storage modulus with respect to that of the virgin polymer. The TSME thermoset could be recycled into a new sample through a ball-milling/hot-pressing process. The best-recycled sample could reach a tensile strength as high as 85.4% of the original sample (Table 4).

The T_g value of the unprocessed TSME polymer was 111.3 °C, while after recycling the T_g value dropped to 107.6 °C. The tensile strength of the original epoxy thermoset is about 31.6 MPa at room temperature, which is comparable to the common commercial epoxy resins. The modulus of the epoxy thermoset at the recycling temperature is quite low (9.5 MPa at 150 °C), compared to 1800 MPa at room temperature, thus ball-milling could be utilized to facilitate the physical recycling process. The epoxy thermoset powders can be easily molded into required shapes. In this work, a straightforward prototype of a prospective fire damper manufactured from epoxy thermoset was exhibited. This was accomplished by their shape memory property. The fire damper demonstrated good thermal stability and self-extinguishing capability. During the fire tests, the fire damper did not burn and significantly reduced the conveyance of flame and flue gas through form recovery. The shape recovery occurred as a result of the heat produced by the flame and flue gas.

By introducing sufficient carboxylic ester bonds into the system and using DOPO as pendant group, Chen et al. synthesized another class of flame-retardant epoxy vitrimers (EVs) by curing DGEBA with adipic acid (AA) and [(6-Oxido-6H-dibenzo[c,e] [1,2]oxaphosphorin-6-yl)methyl]butanedioic acid (DDP i.e. DOPO derivative, flame-retardant co-curing agent) in the presence of TBD as a transesterification catalyst (Fig. 1 – route 2) [34]. The best performing flame-retardant epoxy vitrimer (30% DDP/EV) exhibited high T_g (~110.7 °C), good thermal stability and excellent flame retardancy with a UL-94 V0 rating and a high LOI of ~34%, which are also summarized in Table 4. In addition, the peak heat release rate (PHRR) and the total heat release (THR) both showed reduction of 63% and 32%, respectively, compared to pristine DGEBA system. Meanwhile, the flame-retardant vitrimer 30%DDP/EV showed high malleability, which could be reprocessed in 15 min at 200 °C without sacrificing the mechanical properties and flame retardancy of the material. Interestingly, the calculated activation energy E_a for 30% DDP/EV was 80.51 kJ/mol and similar to the result that had been reported for epoxy vitrimers based on transesterification [17]. At the same time, 10%DDP/EV had a higher E_a around 97.68 kJ/mol, indicating that the incorporation of DDP resulted in the decrease of the stress relaxation rate by hindering the transesterification process.

Chen et al. proposed a catalyst free approach for developing transesterification based DOPO embedded FR thermoset (Fig. 1 –route 3) [35]. They employed the commercially available phosphaphenanthrene-based diol named 6-(2,5-bis(2-hydroxyethoxy)phenyl)dibenzo[c,e] [1,2]oxaphosphinine 6-oxide (DHH) to demonstrate the proposed strategy, and to further explore the relationship

between the fire safety and dynamic transesterification of the material. DGEBA, AA, 1,4-Bis(2-hydroxyethoxy) benzene (HQEE) and DHH were combined in different molar ratios to readily form flame-retardant AAD-EP through a one-step reaction. The percentage of DHH gave a very interesting effect on the mechanical property of the material. With less DHH, AAD0.25-EP had the highest tensile strength of 70.5 MPa, while AAD0.5-EP with higher DHH had decreased tensile strength at 67.8 MPa. The phenomenon could be explained by a combination of the cross-linking density and chain rigidity introduced by phosphaphenanthrene structure. When the DHH content was low, the phosphaphenanthrene rigid structure played a major role, and when the DHH content was increased, the reduced cross-link density became dominant; thus, the tensile strength of AAD-EP first increased and then decreased. Both the thermosets and their composites possessed high mechanical properties, good thermal stability ($T_{5\%} > 380$ °C), fire-safety efficacy and notable reprocessability (Table 4). The LOI values improved to 34.5% and 36.0% for AAD0.25-EP and AAD0.5-EP, with respect to 22% for AA-EP. More importantly, due to the dynamic ester-linkages, the epoxy vitrimer could be dissolved in ethylene glycol (EG) as the dihydroxy molecules participated in bond exchange reactions. Furthermore, they fabricated recyclable carbon fiber reinforced polymeric composite, of which the resin matrix could be dissolved via transesterification using diols as solvents, to recover the CFs with nearly 100% yield.

Besides DOPO, other phosphorus containing (i.e. phosphonate) moiety can be also introduced as pendant group to obtain functionalized epoxy resin. Zhang et al. reported such flame retardant ternary vitrimer regulated by cyclic and long-chain dicarboxylic acids, starting from FR functionalized epoxy monomers [41]. By incorporation of pendant FR units in the epoxy/carboxylic ester thermosets as shown in Fig. 1, a new concept of flame-retardant, flame-triggered shape memorable and recyclable material for fire-safe application was demonstrated. The dynamic transesterification of carboxylic esters enables reconfigurable/multiple shape memory behavior and the arbitrary programming of both the temporary and permanent shapes.

1.2. Phosphate ester-based covalent adaptable networks

Phosphate ester is a compound with the general structure $O=P(OR)_3$ and composed of alkyl or aromatic substituents, which can be found in a diverse range of materials, such as DNA, RNA and ATP, as well as synthetic flame retardants, insecticides and herbicides [42,43]. They can be prepared by optional routes, such as esterification of phosphoric acid, oxidation of phosphite esters, and alcoholysis of phosphorus oxychloride. For a few decades, organophosphorus compounds have also been considered as environment-friendly flame retardants for polymers and have attracted increasing interest after the European Union banned the toxic halogenated flame retardants [44]. Similar to carboxylate esters, phosphate esters are able to perform the reversible transesterification reaction with alcohols, which is particularly promising in developing multifunctional materials. Unlike conventional carboxylate esters, there are three dynamic P–O bonds in phosphate ester network. Such systems have a great potential for structural tenability and the following section will introduce three possible methods.

1.2.1. Polyphosphate ester thermosets

The reactions and functionalizations of phosphate esters has been studied in great detail over the last few decades because of their importance in biochemistry [45]. Transesterification itself is a method to functionalize phosphate esters, it normally requires high temperature and catalytic condition with favorable leaving groups. Sijbesma and co-workers utilized transesterification and directly synthesized phosphate triester cross-linked polytetrahydrofuran (pTHF) network (Fig. 2) [21], through a one-step synthetic procedure by heating a mixture of triphenyl phosphate, pTHF ($M_n \sim 650$ g/mol), and NaH. The resulting polyester-based thermosets demonstrated their recyclability at elevated temperatures without the use of an external catalyst. In this work, the

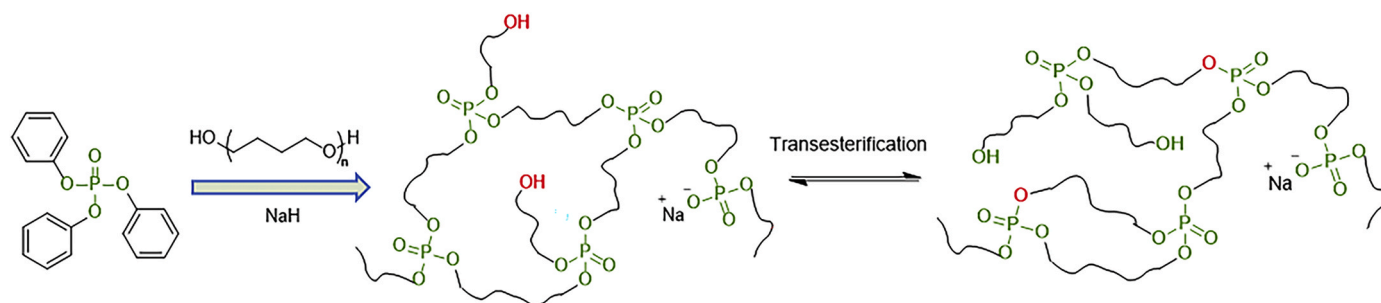


Fig. 2. Synthesis pathway of a polyphosphate ester thermoset and network rearrange mechanism via transesterification [21].

prepared materials were not characterized for their fire performances. The presence of P in the network was identified spectroscopically with ^{31}P NMR (-0.8 ppm– 1.2 ppm). Although the first phosphate triester system had very low T_g around 15 °C, it inspired the preparation of other phosphate-based works. The same group developed another dynamic covalent network based on phosphate triester cross linked OH-end-functionalized polyester covalent adaptable network [46]. The transesterification activation energy of this system was calculated to be around 68 kJ/mol, which is similar to other fast-exchanging dynamic covalent chemistries such as vinylogous urethane transamination (60 kJ/mol), dioxaborolane metathesis (77 kJ/mol), and *trans*-thioetherification (63 kJ/mol).

1.2.2. Phosphate derived cross-linkers

A more common method to introduce phosphorus in covalently integrate thermoset is using phosphate ester based functional molecules as hardener/cross linkers. As discussed earlier, the introduction of phosphate adaptable bonds can induce material reprocessability via network rearrangement. More importantly it also confers intrinsic flame retardancy due to the presence of phosphorus. Combining sustainable characteristics with good flame retardancy and easy recyclability in

epoxy thermosets is very challenging. The incorporation of phosphate groups can be a very efficient approach for the preparation of multi-functional adaptable networks with fire safe property.

Liu et al. pioneered the development of phosphate-based cross linker from bio-resources to obtain fire-safe thermosets [47,48]. They prepared an itaconic acid-based epoxy resin (EIA), which was cross-linked with phytic acid (PA) to form phosphate-based adaptable networks (Fig. 3 – route 1), using PA-cured bisphenol A epoxy as control sample [47]. EIA was synthesized through the reaction between bioresource itaconic acid (IA), tetrabutylammonium bromide (TBAB) and epichlorohydrin (ECH) under reflux conditions. Consequently, the phosphate-based adaptable networks were obtained by uniformly mixing EIA to PA without any additional catalyst. Some of the properties of EIA are summarized in Table 4 [47]. Due to the high P content in the phosphate-based networks, the material exhibited very good flame retardancy compared to PA-cured epoxy, EIA system could achieve UL-94 V0 rating and very high LOI of 31.2 – 33.5% (Table 4).

The phosphate adaptable networks containing 1 mol% of PA (EIA-PA-1) were used to test the recovery effectiveness. The dynamic reaction of phosphate exhibited a faster rate with a bond exchange activation energy of 49 – 90 kJ/mol, which was lower than that of the dynamic

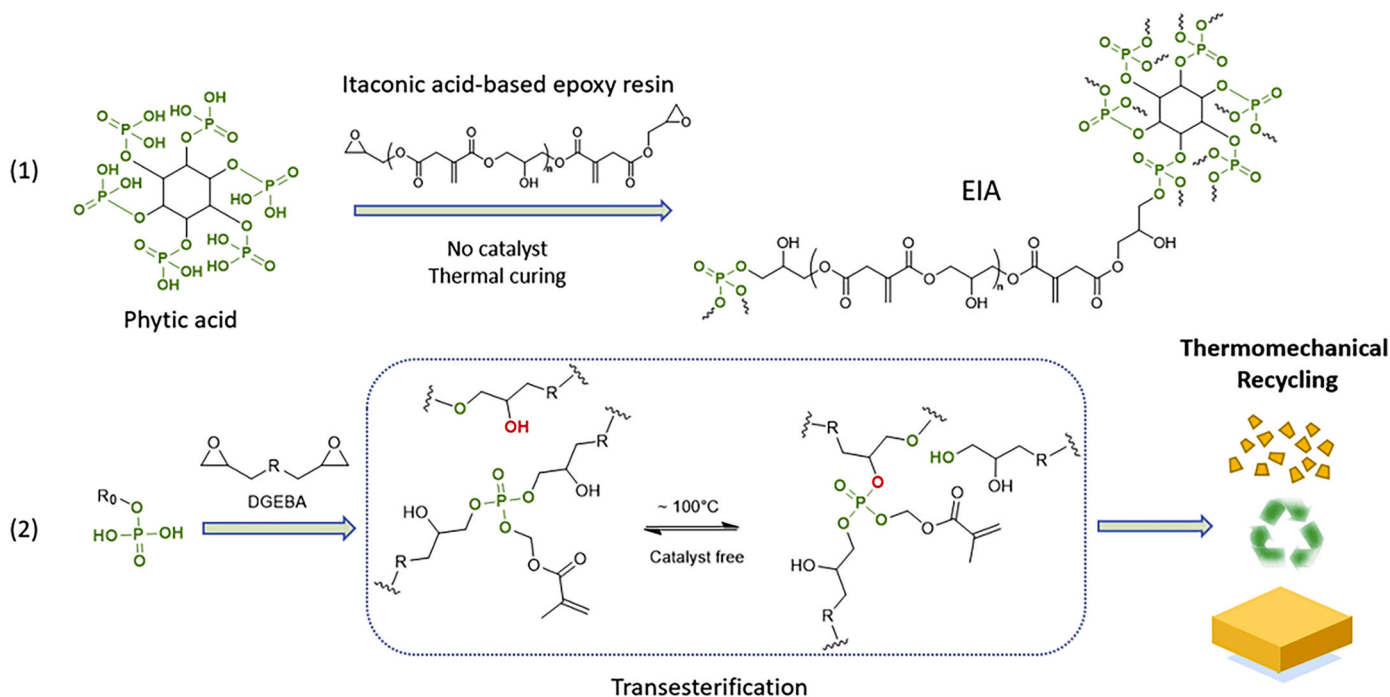


Fig. 3. Phosphate tri/di-ester networked flame-retardant recyclable thermosets: (1) phosphate thermoset of phytic acid reacted with itaconic acid-based epoxy resin (EIA) [47], and (2) β -hydroxy phosphate ester containing robust fire-proof vitrimers [49], with the catalyst-free transesterification mechanism presented in the dashed frame and the resulting thermomechanical recycling feature.

reaction of carboxylate without catalyst reported in the literature [50, 51]. EIA-PA-1 was chopped into small pieces and hot-pressed to recover the original shape at 160 °C under 5 MPa for 1.5 h. Using DMA and FTIR instrumental characterization, it was confirmed that the recycling strategy did not affect the chemical structure and mechanical properties of the material [47]. Furthermore, under mild basic conditions, the presence of phosphate groups in the networks conferred higher degradability. A piece of EIA-PA-1 (0.64 cm³) degraded within 60 min in 1 M NaOH ethanol/water (1:9, v/v) solution at 50 °C. However, effective methods to separate the monomers after the full degradation of the polymer matrix were not addressed.

Similarly, another phosphate diester-based acrylate cross-linker was also developed by Feng et al., and the resulting thermoset could be cured without catalyst, as shown in Fig. 3 - route 2 [49]. This system showed good fire-proof properties and transesterification based recyclability. The vitrimer was obtained by mixing an acetone solution of phosphoric acid 2-hydroxyethyl methacrylate ester (i.e. ~ 25 wt% diester content) with an acetone solution of epoxy monomer (EPON-826). The resulting mixture was dried to evaporate the acetone and cure the system at the same time. The post-curing was performed by a compression molding machine at 120 °C for 1 h. The T_g of the final cured thermoset measured by DMA was around 67 °C. The activation energy for bond exchange was calculated to be 56.2 kJ/mol, which is lower than that of a large majority of reported covalent adaptable networks [49]. The presence of a large amount of hydrogen bonds in the PE-CANs guaranteed a high malleability over 80 °C and crosslinking density around 365.1 mol/m³. The properties of such vitrimer is summarized in Table 4.

The phosphate ester containing vitrimer could be fully recycled due to the rapid exchange reaction between phosphate esters and neighboring β -hydroxyls. Above 250 °C, the phosphate thermoset could decompose to form cellular char, which could effectively offer fire protection acting as oxygen barrier and thermal shield [49]. One of the main drawbacks of phosphate ester-based networks is their poor hydrolytic stability, more specifically the occurrence of swelling and slight dissolution after 72 h of immersion in several polar solvents including water. Additionally, another undesirable feature for their up-scaling in the industry is the solvent-based synthesis method.

The development of UV curable P containing adaptable thermoset is very attractive, when it is also recyclable and re-moldable after light curing. A concern in such systems is the use of catalyst, as the activation of adaptable network rearrangement normally involves the use of appropriate catalysts (e.g. zinc acetylacetonate hydrate or organic base) [30]. Addressing these two points, Feng et al. obtained catalyst-free transesterification induced recyclable thermoset using a UV curable phosphate diester-based acrylate cross-linker [52]. Compared to the control sample made of 1,6-hexanediol dimethacrylate (HAD), bis [2-(methacryloyloxy) ethyl] phosphate (BPA) monomers acted as flame retardants and allowed the formation of reversible adaptable bonds and hydrogen-bonding sites, while acrylate groups represented UV curable units as well as transesterification components. The curing process resulted in an intrinsic flame-retardant and adaptable network with high cross-linking density and good recyclability (i.e. through abundant P-OH and C=O groups), even at temperatures lower than T_g (~152.4 °C). The blank thermoset with only HDA showed high flammability in air after 12 s ignition and burned out completely. In contrast, the after burning flame of the BPA thermoset was much smaller after the same 12 s ignition and extinguished after 15 s, mainly related to a condensed phase flame retardant mechanism (also summarized Table 4). The stress relaxation behavior of BPA revealed a low value of activation energy (42.8 kJ/mol) which makes this material promising for recycling. The T_v value of the BPA thermoset is only 9.1 °C, which was far below the T_g . Some report claimed T_v is the thermoset's upper temperature limit for service and lowest temperature for recycling [53]. As a result, the BPA network showed appealing thermal recyclability, but it has a potential defect for daily use.

Using this thermoset system, the research group investigated the

recyclability and fire-safe properties of carbon-fiber reinforced BPA composites [52]. The phosphate containing monomer (BPA) was modified and used as a cross linker to manufacture composites containing 4 layers of woven carbon fabric with about 57% weight fraction. The presence of hydrogen bonding ligands in the BPA network resulted in a considerably high T_g and strong mechanical performance of the composite. The carbon-fiber reinforced BPA composites showed high tensile strength up to 370 MPa. The composites do not catch fire after 70 s of flame exposure. More interestingly, the valuable carbon fibers could be recovered after washing with hot NaOH aqueous solution, which hydrolyzed and removed the BPA matrix. SEM measurements showed that this recycling treatment did not damage the structure of carbon fibers, which could then be reused to reinforce the BPA material again and obtain regenerated cross-ply composites with comparable mechanical property.

Green synthesis strategy to combining β -hydroxy phosphate ester bonds with waste materials is reported to construct high-performance covalent adaptable networks. He et al. constructed recyclable thermoset using commercially available epoxidized natural rubber (ENR) cross-linked with biomass-derived D-Fructose 1,6-bisphosphoric acid (DF) [54]. Benefiting from the energy dissipation capability of the abundant hydrogen bonds between the phosphate and the free hydroxyl groups under external load, the ED (ENR-DF) sample showed high strength (16.6 MPa) and toughness (56.9 MJ/m³). ED samples exhibited low T_g from 0 to 28 °C, and among them, the ED-30 showed shape memory effect. In particular, ED-30 could be modified into an "arch bridge" shape at 80 °C and fix at 0 °C immediately. Once the temperature rose to 80 °C again, the shape of the sample could be completely recovered. The fire performance was not evaluated, although it has great potential in fire-safe applications.

Transesterification of these ester based recyclable systems require catalyst. Sometimes ionic liquid can be used as transesterification catalyst as it is less likely to be covalently incorporated in the material. Wang et al. developed a catalyst free epoxy based vitrimer system, by introducing a phosphate-based ionic liquid named 1-butyl-3-methylimidazolium diphenyl phosphate ([Bmim]DPOO) as a curing agent with DGEBA resin [55]. This material exhibited good mechanical properties under ambient conditions (Table 4). The curing activation energies for 5% vitrimer, 10% vitrimer, and 15% vitrimer were 124.0, 103.8, and 90.4 kJ/mol, respectively. The relatively high curing energies were attributed to the electrical withdrawal effect and the large steric hindrance of the phenoxy-substituted phosphate groups. The phosphate transesterification activation energy (E_a) was calculated to be 86.4 kJ/mol for the 15% vitrimer. These systems showed good shape memory performance, self-healing properties and flame-retardant properties, which are summarized in Table 4. However, the hypothesized reaction mechanism predicts that the reaction will hypothetically emit methane and benzene during the curing phase, necessitating further optimization for application in industry.

1.2.3. Phosphate functionalized epoxy resin

Instead of introducing phosphate units as the curing reagents, it is also possible to functionalize the epoxies directly to develop the thermosets. It is a different synthetic approach and normally requires more synthetic steps. Wang and coworkers directly synthesized a series of di/tri-phosphate and tri-phosphite networked cycloaliphatic epoxides, cured with phthalic anhydride, and achieved reprocessable fire-resistant thermosets [56–58]. The phosphorus containing epoxies provided good flame retardancy and thermal reprocessability compared to the commercial cycloaliphatic epoxy resin ERL-4221 (3,4-epoxy cyclohexyl methyl-3,4-epoxy cyclohexyl carboxylate), with one example presented in Fig. 4 [56]. The detailed synthesis of phosphate ester containing cycloaliphatic epoxides consisted of two steps: synthesis of olefins via nucleophilic substitution reaction of phosphoryl chloride with cyclohex-3-enyl-1-methanol, and then epoxidations of olefins to give the epoxides. The phosphate functionalized epoxy was cured with

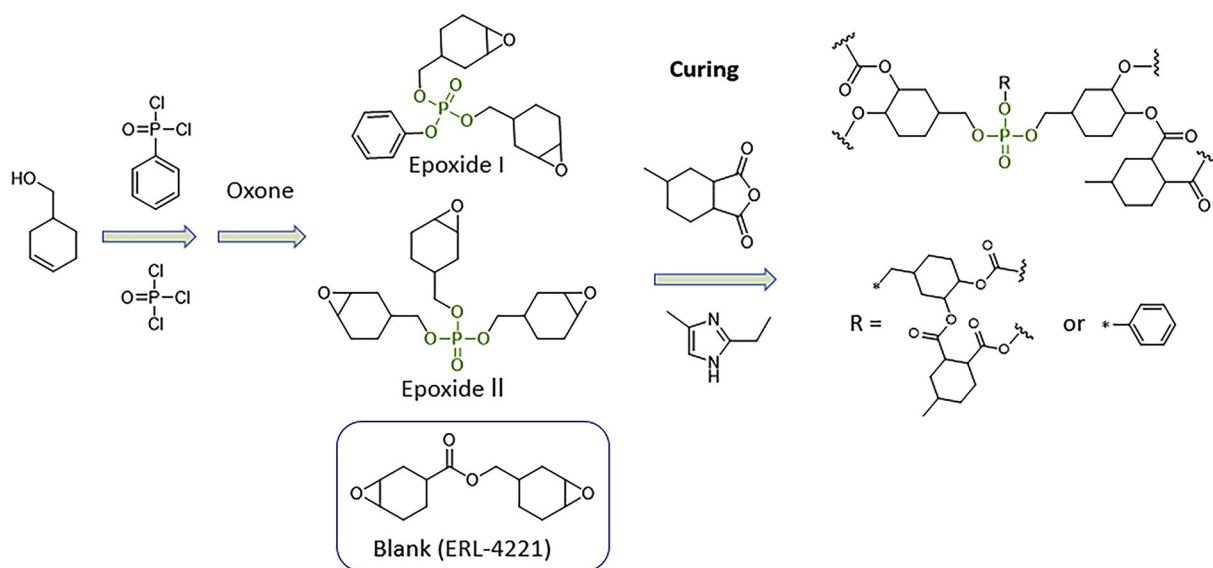


Fig. 4. Synthesis route of phosphate-containing cycloaliphatic epoxy resins cured recyclable FR thermosets [56].

4-methylphthalic anhydride and using 2-ethyl-4-methylimidazole as catalyst, and it resulted in transparent thermosets, which were stable below 220 °C, with very high glass transition temperature at 227 °C (Table 4).

The crosslinking density of trifunctional Epoxide II cured thermoset was much higher by 294% and 64.7% than that of Epoxide I and ERL-4221, respectively. The rigid trifunctional epoxide II cycloaliphatic structure and the dense crosslinking network resulted into significantly high T_g (199 °C from DSC and 227 °C from DMA), while Epoxide I has T_g around 113 °C from DSC and 130 °C from 130 °C. Using Hartree-Fock computational calculation through Gaussian 03W program package, they calculated the optimized geometries and bond lengths of C–O bond in phosphate and primary carbon–ester. The bond length of C–O in phosphate was 1.420 Å while that in primary carbon–ester bond was shorter at 1.415 Å, which explained the bond weakness of phosphate than carbon–ester. The material can rapidly decompose in the temperature range of 200–300 °C, which represents a favorable temperature range for application as encapsulates in microelectronic industry. Their thermal degradation temperature is lower than that of the commercial cycloaliphatic epoxide ERL-4221 cured with the same curing agent. The early thermal degradability of phosphate cycloaliphatic epoxides was attributed to the weak C–O bond in the P–O–C structures. It could be readily tuned by copolymerizing phosphate-containing epoxides with commercial ERL-4221 by simply adjusting their ratios.

Taking advantage of the less stable nature of phosphate and phosphite, a phosphite-type trifunctional cycloaliphatic epoxide with a weaker C–O bond in the P–O–C was designed [58]. Wang and co-workers demonstrated that the combination of excellent reprocessability, non-halogen flame retardancy, acceptable thermal stability, and high mechanical modulus endows the potential for phosphate/phosphite networked cycloaliphatic epoxides towards environment-friendly microelectronic and optoelectronic packaging applications.

As P–O bonds are hydrolytically unstable, in addition to thermo-mechanical recycling, thermochemical recycling using solvent is possible to degrade the FR thermosets. Ma et al. synthesized another phenylphosphonate based epoxy monomer (DGEP) which was cured with DDM to obtain a fully degradable thermoset [59]. In comparison to DGEBA/DDM system, DGEP/DDM showed self-extinguishing capability and could be degraded after 40 min in a sodium hydroxide-methanol solution at 50 °C, due to hydrolysis and alcoholysis of phenylphosphonate structures.

To conclude, among the various systems, phosphorous ester based

recyclable thermosets may provide a multifaceted solution [21,52]. They offer not only excellent fire protection [60], but also have industrial relevance due to readily available starting materials and a straightforward synthesis procedure. In addition, phosphorous ester can also exist in various forms, such as phosphate triester, phosphate diester, and phosphite ester. The development of phosphate ester based thermosets has inspired new types of multifunctional vitrimer materials [49]. Yet, their relative low T_g and poor hydrolytic stability are critical limitations for industrial exploitation. Replacing the phosphate units with phosphonate moieties will introduce P–C bonds in the thermoset network. This will theoretically result in better material stability, as P–C bond is chemically and thermally stable analog to a P–O bond [61].

1.3. Disulfide-based covalent adaptable networks

Disulfide bonds are involved in many biological and chemical processes. In biology, disulfide linkages play an important role in defining the properties of proteins, especially in the folding process [62]. In the last decade, different disulfide synthesis methods have been studied. Thiols can be easily oxidized to disulfides by mild oxidizing reagents like bromine or iodine. Other methods such as reductive coupling of sulfonyl chlorides and reaction with sulfur monochloride has also been investigated [63]. The S–S bond has a relatively low dissociation energy (~240 kJ/mol, compared to the C–C bond ~ 346 kcal/mol), which makes it suitable for building covalent adaptable networks [64]. Some recent studies report that applying the disulfide exchange in polyhydroxyurethane networks result in more rapid reprocessing of material networks, via not only change of the exchange rate but also decrease of the underlying temperature dependency (activation energy) up to 78 kJ/mol [65]. The dynamic exchange of disulfide bond is based on a radical-mediate reaction (Fig. 5) [66].

Covalent adaptable networks based on reversible aromatic disulfide crosslinks were previously investigated for the design of recyclable composite materials [67]. Sustainable approaches using eugenol-based

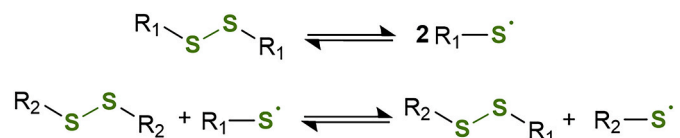


Fig. 5. The disulfide bond exchange reaction through a radical-mediate mechanism [66].

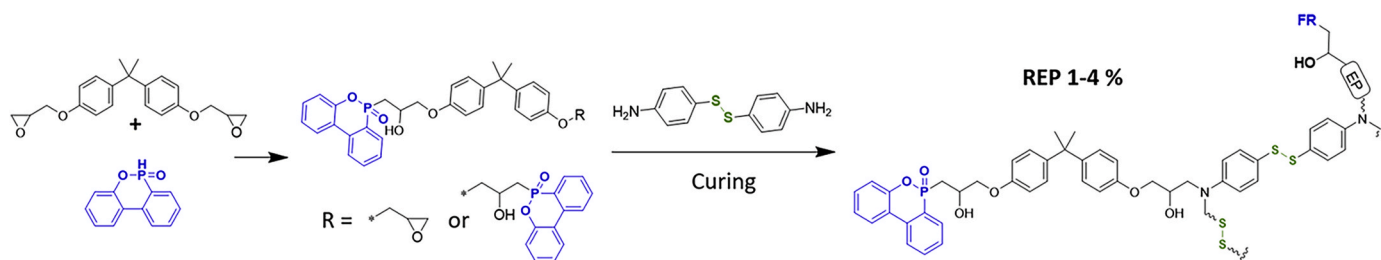


Fig. 6. Synthetic route of recyclable FR thermosets (REP 1–4%) using DOPO modified epoxy resin cured with disulfide bonds containing diamine hardener [69].

epoxy and disulfide containing aromatic amines have also been addressed to achieve recyclable thermosets [68]. Using similar disulfide containing amine hardener, Li et al. improved the flame retardancy of a series of recyclable epoxy thermoset (REP) composites by the pendant functionalization with DOPO, retaining good recyclability and mechanical properties (Fig. 6) [69]. As mentioned earlier, DOPO contains reactive P–H bond, it can directly react with the oxirane ring of epoxy, leading to a FR functionalized resin and later to intrinsically flame retardant material [37–40].

Fire performance investigations showed that with only 3 wt% DOPO in REP composites, the LOI value increased to 27.8% (21.7% for blank thermoset) and helped achieve UL-94 V0 rating. Self-extinguishing behavior and a strong reduction (43.5%) in PHRR were observed for the modified thermoset with 4 wt% DOPO content, while pristine sample based on DGEBA completely burned during UL-94 test (Table 4). The positive effect in the flame retardancy of REP composites was ascribed to the phosphorous-containing flame-retardant, which plays a role in both the condensed phase and gas phase during its decomposition. The decomposition of the phosphorus-based compound promoted the dehydration and the formation of char, which acted as a barrier, inhibiting the release of heat and oxygen. In addition, the release of phosphorous-containing free radicals ($\text{PO}\cdot$ and $\text{HPO}\cdot$) was responsible for a remarkable EHC reduction and a significant flame inhibition, due to the quenching of $\text{H}\cdot$ and $\text{OH}\cdot$ active radicals [9] (Fig. 7).

REP composites containing DOPO showed good transparency and mechanical properties, while the presence of exchangeable disulfide crosslinks improved the recyclability. The dynamic disulfide bonds exchange could be activated by heating above the T_g , which is the driving force of REP thermoset recyclability. The E_a values decreased from 166 kJ/mol for REP-1% to 123 kJ/mol for REP-4%, respectively, which is related to the crosslink density of the networks. Li et al. tested the recyclability of REP samples containing 3 wt% DOPO (REP-3%) through grinding the composites into powders and hot-pressing at 200 °C and

100 bar for 5 min. The reprocessing of the cured resin led to defect free laminates (i.e. highly porous) which still exhibited high transparency and the 90% of the initial tensile strength.

Besides of DOPO, the phosphazene-based compounds also allow for the development of thermosets with enhanced fire behavior, especially due to the synergistic flame-retardant effect exerted by nitrogen- and phosphorous-containing moieties [70]. This class of compounds can significantly improve the fire behavior of dynamic covalent networks, as the phosphorous atoms can terminate oxygen radicals in the gas phase and the nitrogen atoms can be responsible for the formation of a porous char exerting thermal insulation during the combustion [71]. Among the phosphazene-based compounds, cyclophosphazenes are inorganic heterocyclic compounds whose rings are constituted by the repetition of phosphorus and nitrogen (N) atoms. They can be easily functionalized and show high thermal stability, therefore these molecules are receiving particular attention from the scientific community [72].

Zhou et al. synthesized a self-healing and flame-retardant cyclo-triphosphazene-based epoxy thermoset exhibiting both reprocessability and reparability comparable to common thermoplastics [73]. The chemical structure of the thermoset was mainly composed of a cyclo-linear cyclo-triphosphazene-linked bifunctional epoxy resin (CTP-EP). Hexachlorocyclo-triphosphazene was left to react with p-hydroxybenzaldehyde and after some synthetic modification of the resulting compound, benzyl mercaptan and photoinitiator 1173 (2-benzoyl-2-propanol) were reacted under UV light irradiation at room temperature (Fig. 8) [73]. The last synthesis step included an oxidation by 3-chloroperoxybenzoic acid to obtain CTP-EP (87% yield) as a colorless viscous liquid. To avoid a high crosslink density which makes self-healing difficult, the click chemistry was used to prepare a bifunctionalized epoxy resin. CTP-EP was cured by a disulfide-containing aromatic diamine agent, 4,4'-dithiodianiline, at 100 °C for 2 h and post-cured at 160 °C for 2 h to obtain the cross-linked self-healing epoxy polymer (CTP-EP/DTDA).

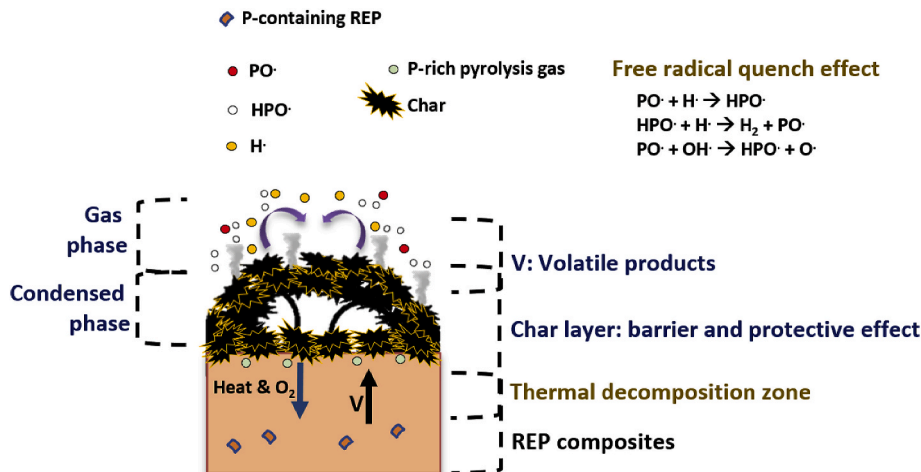


Fig. 7. Simplified combustion mechanism of recyclable epoxy resins containing DOPO additive [69].

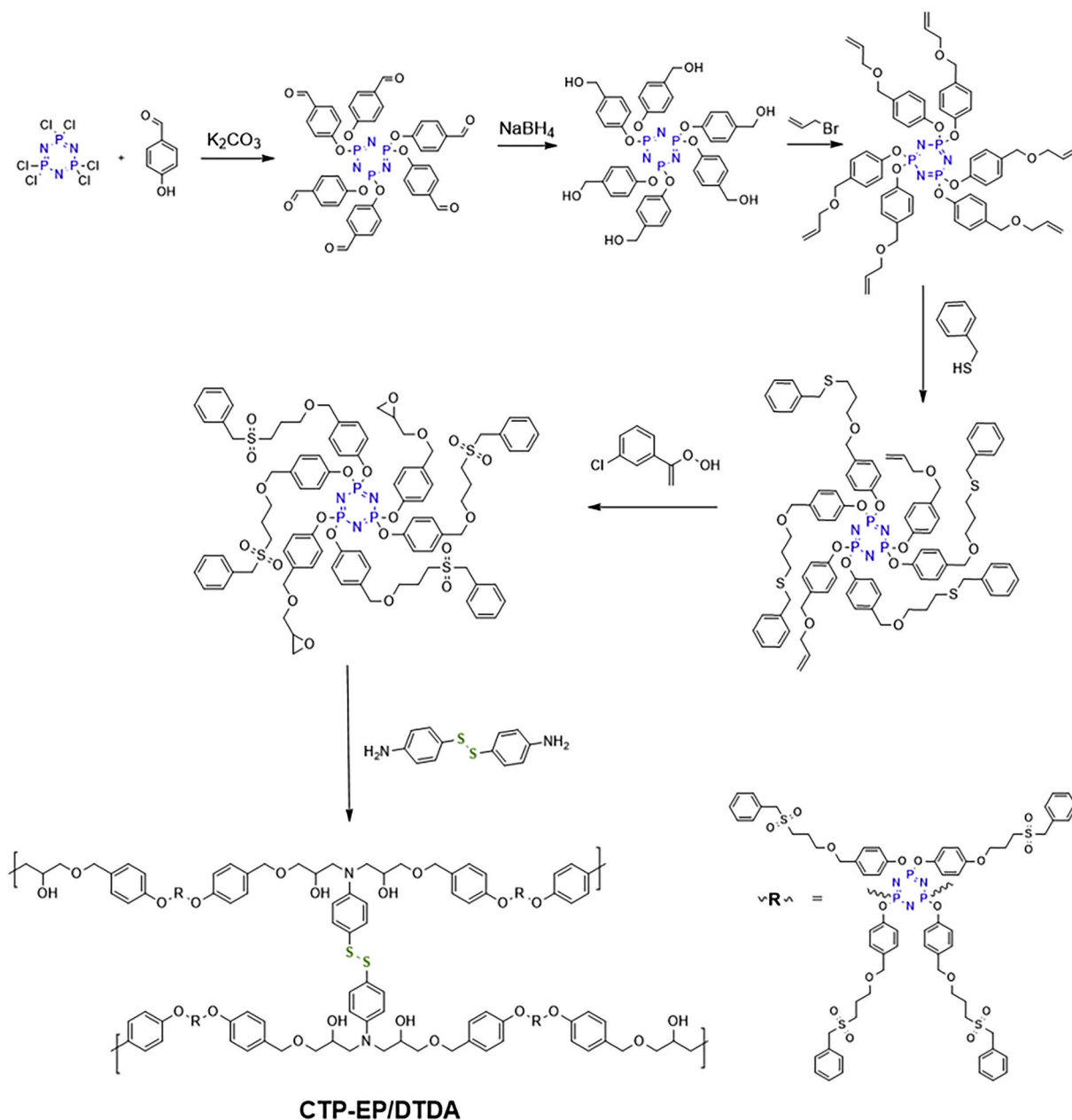


Fig. 8. Synthesis route of the self-healing and flame-retardant cyclotriphosphazene-based epoxy thermoset (CTP-EP/DTDA) starting from hexachlorocyclotriphosphazene and p-hydroxybenzaldehyde, and the curing process through reaction with 4,4'-dithiodianiline (disulfide-containing aromatic diamine agent) [73].

The hardening of the resin occurred through a step-growth polymerization of the epoxy and amino groups [74]. After curing, the CTP-EP/DTDA thermoset showed T_g around 129 °C and no residual exothermic curing peak was observed, indicating that the system was completely cured. CTP-EP/DTDA epoxy thermoset appeared as a typical thermoset at ambient conditions, but it showed a behavior similar to thermoplastic materials, as it could be easily reprocessed at elevated temperatures by hot-pressing (200 °C and 10 MPa for 10 min) (Table 4). Such multi-self-healing performance was attributed to the radical-mediated aromatic disulfide exchange mechanism and the presence of reversible cross-linkages in the polymer matrix. The study of the mechanical performances revealed that the recycled CTP-EP/DTDA samples, after the second and third healing cycles, still retained 93.9 and 89.8% of their original tensile strength, respectively [73]. Therefore, the cyclotriphosphazene-based covalent adaptable network exhibited a notable healing efficiency even after three cycles and thus could be

reshaped and reprocessed as well as common thermoplastics. The incorporation of the cyclotriphosphazene-based structures into the polymer matrix boosted the formation of a phosphorus-rich char showing a highly thermal insulating honeycomb structure. The system exhibited LOI values of around 30.5% and a V0 rating in UL-94 vertical flame spread tests (Table 4).

Such CTP-EP/DTDA epoxy covalent adaptable networks represent promising matrix for light-weight carbon fiber-reinforced materials, as their use not only guarantees outstanding multiple self-healing and flame-retardant properties but also reduces weight and prolongs service life in transportation applications. These multifunctional and recyclable cross-linked polymers may contribute to energy saving and reduce pollution.

Nie et al. developed a bio-based self-repairing flame-retardant polymer exhibiting high dielectric properties by the reaction of eugenol, multi-mercaptoester and disulfide bonds containing amine

(Fig. 9) [75]. The main raw materials are easily sourced, renewable and petroleum-free, and the products exhibit good thermal stability and recyclability. The procedure is mainly based on three steps: i) eugenol (EUG) and multi-mercaptoester (TPTPAE or TMPAPE) were mixed under inert gas atmosphere and reacted in the presence of catalyst to obtain eugenol based polyester monomer; ii) epoxidized eugenol-based polyesters were synthesized by catalytic reaction between eugenol-based polyesters with epichlorohydrin under inert gas condition; iii) epoxidized eugenol-based polyesters and disulfide containing amines were mixed and cured by melt polymerization to obtain bio based self-repairing flame-retardant materials with high dielectric properties. The research group demonstrated also the self-repairing thermoset prepared by this methodology has excellent dielectric and fire retardant properties (Table 4).

Similar to disulfide dynamic covalent bonds, thermosets containing diselenide bonds have also been developed to obtain stimuli response networks. Unlike other thermoset systems discussed earlier, this system utilizes the light induced metathesis principle. As diselenide bonds have very low bond energies (~170 kJ/mol) compared to disulfide bonds (240 kJ/mol), visible light is sufficient to trigger their metathesis. Du et al. synthesized diselenide containing polyurethane (dPTD) and fabricated composites with multi-functionalized graphene oxide (mfGO) via in-situ polymerization [76]. The dPTD-mfGO2 composite containing 2 wt% of mfGO exhibited shape memory and self-healing properties with 3 min of visible-near infrared light irradiation. In small scale fire tests dPTD-mfGO2 composite exhibited a LOI about 24.9% and UL-94 V2 rating without flaming drips. Diselenide based thermoset represents an interesting approach, however the light sensitive nature of the bond might be a hindrance for real world application.

Based on the above mentioned examples, we could conclude that the reprocessing functionality in the disulfide adaptable bonds containing FR thermoset is mainly due to the hardening/cross linker moiety, which has less of an influence on the final thermoset materials. The mechanical performance, stability, and T_g of these systems are comparable to those of conventional epoxy thermosets. However, the potential release of SO_x

gas during combustion of sulfide containing thermoset is a serious problem [77], which is not well addressed by the authors in this section and smoke toxicity is a very important parameter in fire safe applications. Thus, a careful consideration of these aspects and a good balance of properties is needed while designing such materials.

1.4. Imine-based covalent adaptable networks

The phosphorous-based flame-retardants are not the only ones replacing the halogen-based compounds. Azomethines, also known as Schiff bases, are a sub-class of imines and thus they can be secondary ketoamines or secondary aldimines depending on their structure. The Schiff bases can be obtained through the condensation (i.e. dehydration) reaction between primary amines, mainly the aromatic ones, and carbonyl compounds as aldehydes (Fig. 10). The Schiff bases are often polydentate macro-acyclic or macrocyclic ligands containing both nitrogen and oxygen donors, where the donor can also be varied between sulfur, phosphorus, nitrogen, and oxygen [78]. The chemical nature of the donor determines the ligand coordination.

The Schiff bases are generally artificial and exploited to produce many important catalysts, such as Jacobsen's catalyst, which exhibits an outstanding enantioselectivity [79]. Schiff bases formed from condensation reaction of aromatic aldehydes with primary amines are receiving considerable attention because of their enormous versatility in the formation of metal complexes with expanded architectures or in the synthesis of flame retardant polymer-based systems with high recyclability and greener features [80,81]. The use of Schiff bases can lead to the formation of imine-based adaptable networks in the polymer matrix.

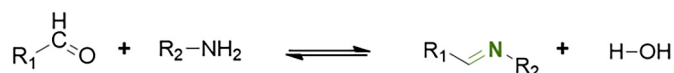


Fig. 10. General scheme for formation of Schiff bases from primary amine and aldehyde.

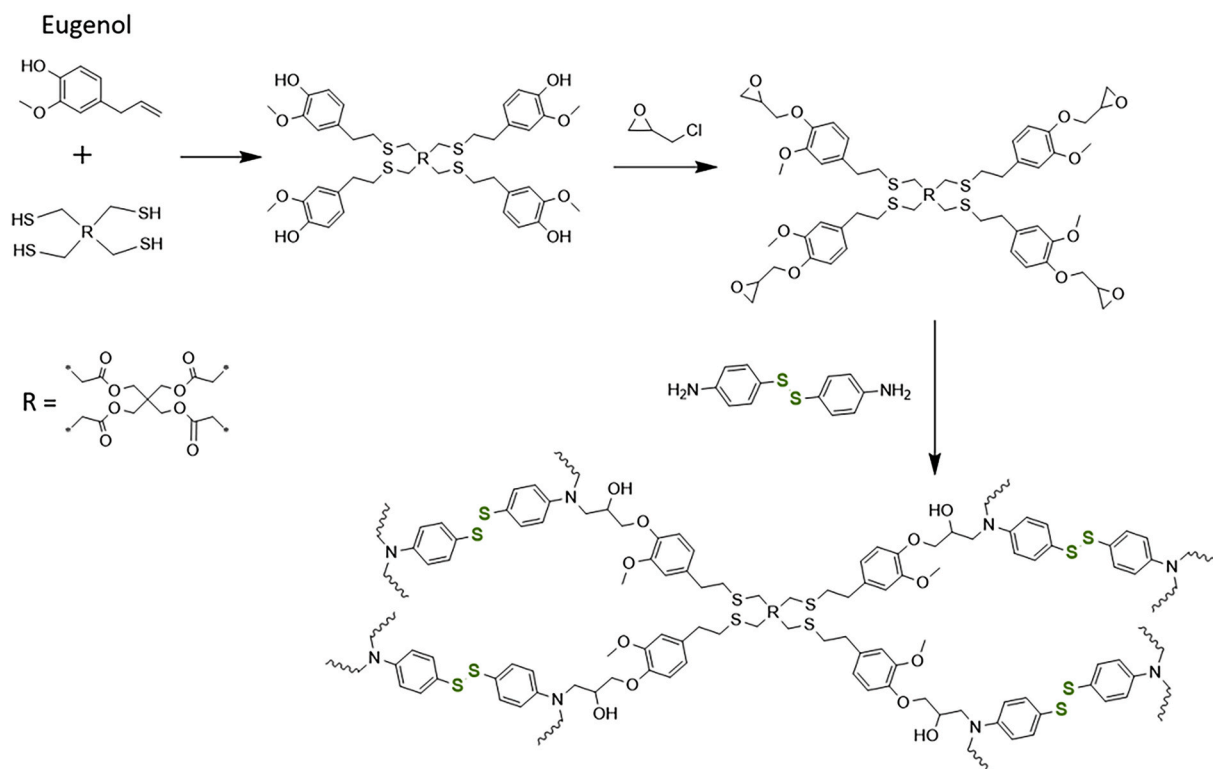


Fig. 9. Synthesis route of a bio-based self-repairing FR thermoset [75].

The reformation of imine covalent adaptable networks occurs through the condensation reaction between amino and aldehyde groups as well as the amino exchange reaction without any catalyst. In particular, the imine bonds can interchange either via dissociative mechanism or associative pathways within the network with an activation energy of 33–129 kJ/mol [82,83]. If sufficient amounts of N is introduced to such network, it will introduce fire resistance, yet sacrificing material stability [84,85]. In general, the thermal stability of most imine adaptable networks limits the performances, and their potential flammability greatly restricts the industrial application. Thus, the preparation of such FR functionalized imine thermosets may allow to obtain both outstanding recyclability and flame retardancy. In this section, several FR compounds attached either as pendent (DOPO) or networked functional groups (e.g., phosphonate, phosphate and cyclophosphazene) are reported.

Imine based covalent adaptable networks offer additional advantages for chemical recycling. The hydrolysis of the imine occurs at mild conditions in the presence of water and acidic solutions, allowing the reformation of the original functionalities through a dissociative mechanism. On the other side, associative pathways are based on exchange reactions (i.e. transimination and imine metathesis) in a water-free environment [86]. While the transimination does not require the presence of a catalyst and generates a new imine and a new primary amine, the metathesis pathway forms two new imines [87]. In this frame, Taynton et al. prepared polyimine networks from triamine mixtures, aldehydes and diamine. A rise in temperature revealed that these networks were characterized by a stress-relaxation behavior and an Arrhenius-like malleability [88]. Also, Chao et al. synthesized a self-healable organogel composed by imine cross-linkers and studied the influence of excess of primary amines and polar organic solvents on the transimination pathway [89]. Due to their nitrogen and unsaturated carbon rich structure, Schiff bases are largely used in electrochemical cells, drug discovery and flame retardancy [90].

Biorenewable and environment-friendly alternatives to bisphenol A epoxy resins have captured growing attention due to their ecological and economic necessity. Vanillin is a lignin-derived industrial scale monoaromatic monomer, mainly containing functional carbonyl, hydroxyl, and phenolic aldehyde groups, and a promising sustainable candidate for highperformance polymers [91]. Due to its chemical structure full of oxygen-containing species, vanillin is also largely used as a synergistic flame-retardant additive or in the synthesis of new phosphorus-based derivatives [92]. Meanwhile, bio-based epoxy resins combining high performance and excellent fire resistance are more difficult to be achieved.

Wang et al. reported the one of the first few thermoset with both good flame retardant and potential recycling properties [29]. Two novel bio-based epoxy monomers EP1 and EP2 were synthesized by a one-pot reaction involving Schiff base formation and phosphorus–hydrogen addition between vanillin, diamines, and diethyl phosphite, followed by reacting with epichlorohydrin. Using DGEBA cured with DDM as blank control, they synthesized bio-based high P containing thermosets, EP1-DDM (6.5% P) and EP2-DDM (7.2% P) (Fig. 11 – route 1). DSC determined T_g s were 183 °C and 214 °C for EP1-DDM and EP2-DDM, respectively, higher than DGEBA-DDM with T_g of 166 °C. The higher T_g of the cross-linked polymers have a close tie with their cross-link density and the rigidity of the chain segment structure. They calculated the average molecular weight between cross-link points (M_c), which were almost doubled comparing to the blank. The thermal stability of the FR thermosets was increased as well. The $T_{5\%}$ for EP1-DDM was at 286 °C, for EP2-DDM at 287 °C, which were much lower comparing with DGEBA-DDM at 356 °C. This could be ascribed to the fact that the O=P–O bond in epoxy resin was more apt to degrade than C–C bond. After curing both thermosets, EP1-DDM and EP2-DDM, showed excellent flame retardancy with UL-94 V0 rating and high LOI of ~32.8%, which was due to the outstanding intumescent and dense char formation ability. Meanwhile, it was found that the cured

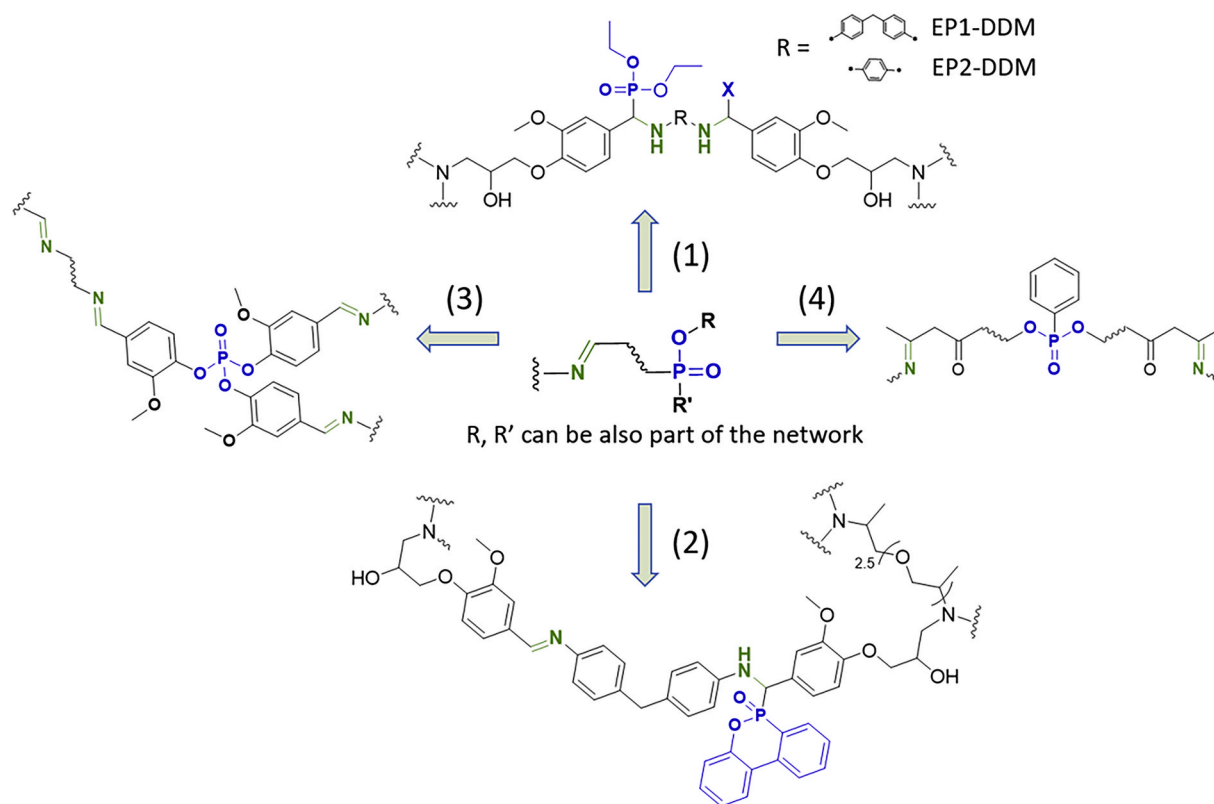


Fig. 11. Simplified structures of: (1) the first recyclable flame retardant thermoset [29], (2) a DOPO containing degradable FR epoxy thermoset [93], (3) another malleable FR thermoset from renewable bioresources [27], and (4) a phosphonate-based FR polyimide thermoset [94].

vanillin-based epoxies had exceedingly high tensile strength of ~ 80.3 MPa, and tensile modulus of ~ 2709 MPa, much higher than the cured DGEBA with tensile strength of 76.4 MPa, and tensile modulus of 1893 MPa.

Yang et al. reported another vanillin-based imine-containing vitrimers with excellent flame retardancy and good reprocessability using DOPO functionalized bio-based epoxy precursor, as shown in Fig. 11 – route 2 [93]. Two vanillin-based epoxy monomers, shorted as VAD-EP and VDP-EP containing both imine bonds, were synthesized via in situ condensation reaction with DDM and following epoxidation by epichlorohydrin. In addition VDP-EP was functionalized via addition reaction between DOPO P–H bond and the Schiff base ($C=N$) double bond. Epoxy vitrimer materials (AxPy-D230) were cured with D230 diamine hardener by adjusting the ratio of VAD-EP and VDP-EP monomers. Sample A8P2-D230 had the mass ratio of VAD-EP and VDP-EP at 8:2, which reached the UL-94 V0 rating and LOI value of 27.0% with only 0.66% of phosphorus content. The excellent fire performance was ascribed to condensed phase and free radical scavenging mechanisms. For sample A7P3-D230, the mass ratio was 7:3, the tensile strength and elastic modulus of the epoxy were 75.5 MPa and 2.5 GPa, respectively, i. e. 48.6% and 18.8% higher than A10P0-D230 sample. The epoxy vitrimer containing Schiff base has tunable tensile strength and toughness, and its T_g reached maximal 71 °C. Based on the good recyclability results, carbon fiber reinforced composites were prepared by using epoxy system A7P3-D230 and CFs. The bio-based epoxy vitrimer based carbon fibers (CFs) reinforced composites could be completely recycled. Interestingly, the recycled CFs maintain unchanged chemical structure, mechanical properties and morphology as the original CFs.

Following a waste-to-wealth approach, Wang et al. synthesized a Schiff base precursor from renewable lignin derivative vanillin [27]. By starting from this vanillin precursor, the produced malleable thermosets showed high performances in terms of flame retardancy, reprocessability, monomer recovery and arbitrary permanent shape changeability (Fig. 11 – route 3) [27]. The precursor (79.4% yield), tris (4-formyl-2-methoxyphenyl) phosphate (TFMP), was obtained through the condensation reaction between vanillin and phosphorus oxychloride. The Schiff base covalent adaptable networks (i.e. TFMP-H, TFMP-P, and TFMP-M) were prepared by curing the precursor with hexamethylenediamine (HMD), 4,4-diaminodicyclohexylmethane (PACM) and 4,4-diaminodiphenylmethane (MDA), respectively. With increase of the hardener rigidity and aromaticity, the T_g of the material increased from 87 °C to 178 °C.

The Schiff-base networked thermosets exhibited rapid relaxation with low bond exchange activation energy around 49–81 kJ/mol, which is a positive asset for their recovery but can also significantly limit their use in high temperature applications. Wang et al. found that the remodeling process of Schiff base adaptable networks could involve the occurrence of some side reactions (oxidation, self-crosslinking of Schiff base, etc.), leading to an undesired increase in brittleness of the materials [27,95]. Here thanks to the high aromatic starting material, their structure allowed the thermosets for high glass transition temperatures of ~ 178 °C and good mechanical performances in terms of tensile strength (~ 69 MPa) and tensile modulus (~ 1925 MPa) (Table 4). Besides, they achieved UL-94 V0 rating and V1 rating, together with a high LOI of $\sim 30\%$. These Schiff base covalent adaptable networks are recyclable thermosets derived from a synthesis procedure involving bio-resources and are aimed to represent a greener alternative to the common high performance thermosetting materials. The Schiff base covalent adaptable networks could be recycled by two methodologies, thermo-mechanically within 2–10 min at 180 °C or chemically release the original monomer TFMP with a recovery rate of $\sim 70\%$. The addition of Schiff base CANs in a mixed solution of 1 M HCl and THF (v:v = 2:8) at 20 °C at different treatment time, depending on the chemistry of diamines, led to the release of the original monomer and diamines. The use of HCl and unsustainable organic solvent (THF) could not be avoided. The chemical recycling of Schiff base CANs in a mixed solution of 1 M

aqueous solution and acetone (v:v = 2:8) resulted in the hydrolytic degradation of phosphate structures to TFMP [27]. The use of THF prevents the deterioration of phosphate-based ester moieties, establishing a more anhydrous and nonpolar chemical environment.

Markwart et al. synthesized additive-free vitrimer composites based on vinylogous polyurethanes containing covalently bounded phosphonates as flame-retardant units and prepared glass-fiber-reinforced composites [94] (Fig. 11 – route 4 and with detail synthetic procedure in Fig. 12). It is reported in the literature that, the mixing of amines and acetoacetyl esters can produce vinylogous urethanes on large scale, where the raw materials can be produced by simple acetoacetylation of various polyol building blocks or materials, giving ready access to useful polyacetacetate monomers and polymers [96]. The phosphonate-based flame-retardant vitrimer (PFV) showed both good recycling and flame-retardant properties comparable to the conventional epoxy resins (with and without flame-retardant additives) and other phosphorus-free vitrimers. The PFV was obtained through the generation of a β -ketoester-containing phosphonate-based monomer (1) as shown in Fig. 12, in 69% yield. It involved a two-step synthesis process: 1, 4-cyclohexanedimethanol was transesterified with *tert*-butyl acetoacetate and coupled with dichlorophenylphosphine oxide, preventing the Knoevenagel condensation as a side reaction by addition of pyridine. The aryl group was incorporated to sterically protect the phosphoester-linkages from transesterification and improve the flame-retardant properties acting as a charring agent. Fig. 12 also shows the synthesis of the vinylogous polyurethane networks by polycondensation with amines (poly-1, the yield was quantitative) and the reference vitrimer without phosphorus (poly-2, the yield was quantitative), together with ^{31}P MAS solid-state NMR of poly-1 and ^{31}P NMR of (1). The recyclability of poly-1 and poly-2 was investigated by dynamic mechanical analysis and the recycled phosphonate-based vitrimer (poly-1) exhibited a storage modulus (G') of 0.36 GPa at 50 °C, while the reference sample (poly-2) exhibited a storage modulus of 2.4 GPa at 50 °C [97], with respect to DGEBA-based epoxy resins showing storage moduli of 4.0–8.5 GPa at -25 °C [98]. Poly-1 and poly-2 exhibited properties similar to the as-prepared samples even after recycling for a second and a third time, which is a highly desirable feature for such type of materials. For typical cross-linked networks, the storage modulus (G') dominated the loss modulus (G'').

Markwart et al. thoroughly investigated the thermal and fire behavior of the phosphonate-based flame-retardant vitrimer through forced combustion and flammability tests [94]. Cone calorimeter measurements performed on poly-1 showed a reduction in THE and PHRR by 27% and 33% respectively, compared to the phosphorus-free vitrimer (poly-2) (Table 4). The combustion of poly-1 resulted in the production of a consistent and intumescent multicellular char, exerting an efficient protective layer effect, which lowered the HRR. The phosphorus in poly-1 acted as an acid source during thermal decomposition process and thus boosted the formation of char. HRC values obtained in PCFC tests indicated a gas phase mechanism via flame inhibition for the phosphonate-based vitrimer poly-1 as the main mode of action during combustion, and was further supported by a reduction (14%) of EHC in the cone calorimetry experiment. In UL-94 vertical tests, poly-1 attained a V2 rating, as the material showed some dripping during the combustion, which was beneficial to remove fuel (the bulk of the material) and heat from the pyrolysis front or the fire source [99]. On the contrary, poly-2 could not achieve any classification, as it burned completely to the clamp and formed burning drips. Poly-1 based composites containing glass fibers showed strength and bending modulus similar to permanently cross-linked epoxy resins reinforced with the same glass fiber, without larger scale delamination of the layers under tension and other limitations.

Carbon fiber-reinforced polymers (CFRPs) are prized for their strength and lightweight. CFRPs are commonly used especially in the applications where high strength-to-weight ratio and stiffness (rigidity) are required, such as in aerospace and automotive sectors [102]. The binding polymer is often a thermoset resin such as epoxy or other

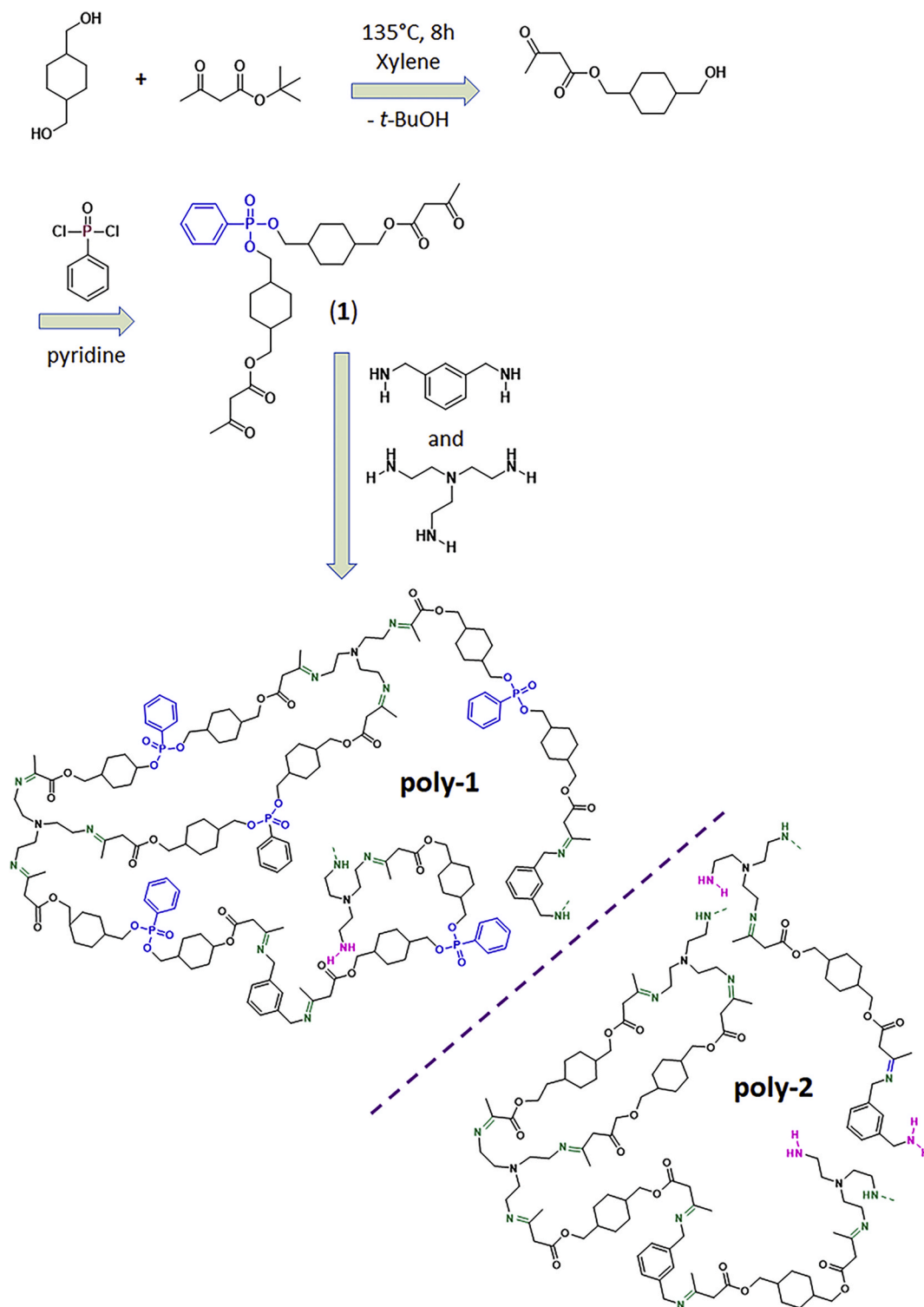


Fig. 12. Detailed synthesis procedure of the β -ketoester-containing phosphonate monomer (1), the formation of the vinyllogous polyurethane network poly-1 and the reference vitrimer poly-2 [94].

thermoplastic polymers (e.g. polyester, vinyl ester, or nylon). However, the increasing consumption of CFRPs is moving the attention of scientific and industrial communities towards a nondestructive recycling of expensive carbon fibers (CFs) and the reduction of fire hazards related to a sustainable and safe utilization of CFs. Liu et al. developed fully recyclable CFRPs with high flame retardancy by incorporating the vanillin-terminated phosphazene monomer, hexasubstituted cyclo-triphosphazene (HVP), into the polyimine binder material (Fig. 13 –

route 1) [100]. The use of vanillin allowed for the sustainable development of CFRPs, as the prepared bio-based flame-retardant HVP was obtained by a commercial bio-based compound derived from lignin [103].

They synthesized the flame-retardant bio-based monomer HVP (90% yield) via nucleophilic substitution reaction of vanillin and hexachlorocyclo-triphosphazene in THF [100]. The cyclophosphazene has six reactive sites which could generate a high crosslinked polymeric

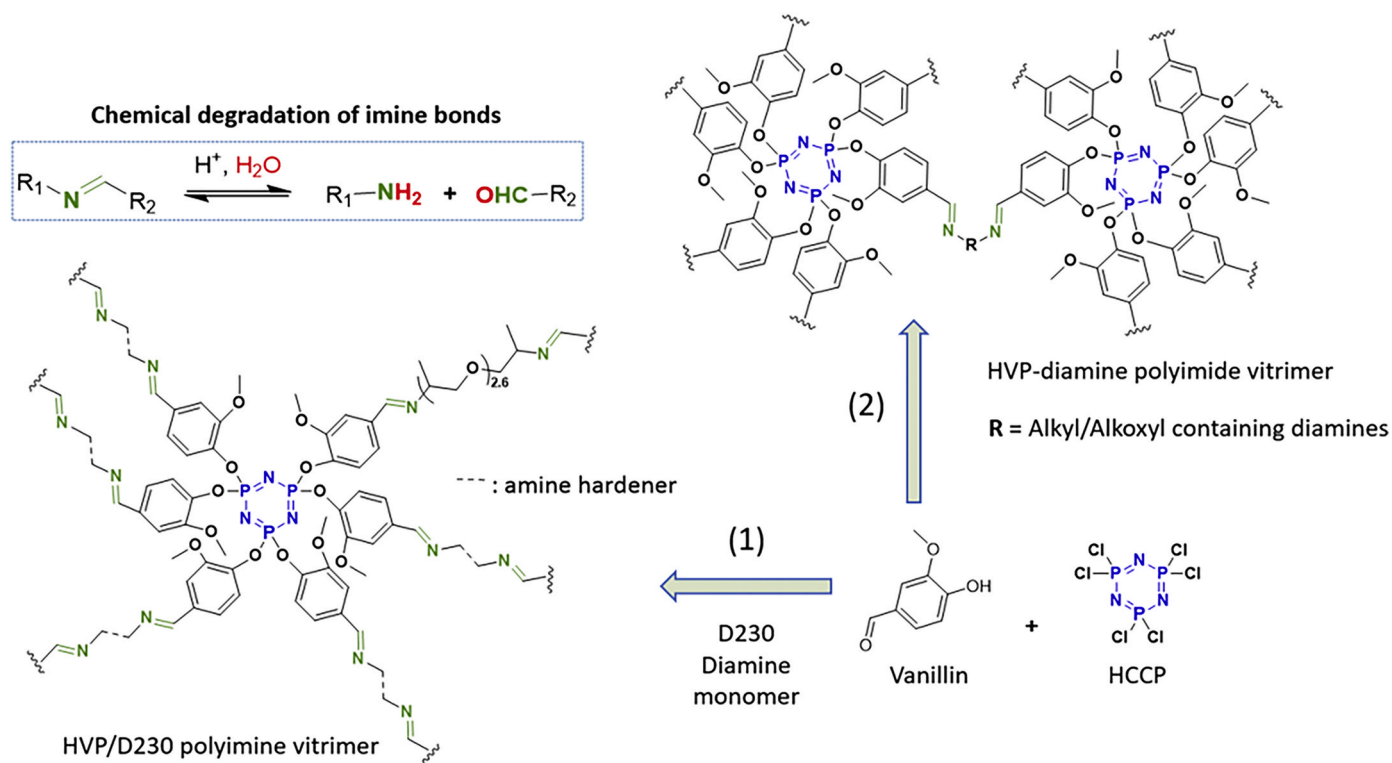


Fig. 13. Structures of (1) hexasubstituted cyclotriphosphazene containing polyimine based FR thermoset [100] and (2) another hexasubstituted cyclotriphosphazene based recyclable FR thermosets with tunable bridging moieties [101], with the chemical degradation of imine bonds illustrated in the dashed box.

network [100,104], high P/N content, good flame-retardant performances and mechanical behavior. The thermosets were obtained by hot-pressing at lower temperature and shorter time. The acid catalyzed degradable of imine bonds (Fig. 13 - dashed box) allowed for an effective nondestructive closed-loop recycling of CFs and HVP monomers (i.e. ~95 wt% of recovery) from the composites under mild conditions (mixture of 1 M aqueous HCl and THF, v:v = 1:2). The regenerated CFRPs could be reprocessed and quickly repaired at elevated temperatures. Besides, the combined use of cyclophosphazene and imine bond led to a hybrid flame-retardant effect both in the gas phase and condensed phase during combustion, endowing the composites flame retardant.

A control sample was prepared by curing diglycidyl ether-based epoxy resin (type E51) with D230 to obtain the E51/D230 sample. The new polyimine HVP/D230 material was prepared by mixing HVP with D230 and then hot-pressed on a plate vulcanizer for 5 min at 120 °C and 18 MPa. E51/D230 system was manufactured with a similar procedure. Both HVP/D230 and E51/D230 reinforced CFRPs were manufactured by incorporation of 65 wt% of CFs, which led to composite HVP/D230-CF and E51/D230-CF, respectively. UL-94 vertical flame spreading test and LOI tests were performed to evaluate the flammability of HVP/D230-CF and E51/D230-CF composites. In particular, the LOI value of HVP/D230-CF and E51/D230-CF were determined to be 34.2% and 21.1%, respectively, and the UL-94 rating of HVP/D230-CF was V0 (Table 4), while no rating was achieved for E51/D230-CF. Compared to E51/D230-CF, the HVP/D230-CF resulted in a shorter burning time, reduced smoke release, lower PHRR and PSPR, which were characterized by cone calorimeter [100]. HVP/D230-CF showed lower THR and SPR than E51/D230-CF, therefore very good flame retardancy and smoke suppression, mainly linked to a gas phase action of HVP in CFRPs. The cyclophosphazene-containing dynamic polyimine thermoset exhibited not only good malleability and recyclability but also comparable mechanical performance to that of commercial counterparts. The HVP/D230 prepreg could be stored for at least 12 months

at room temperature without any subsequent lamination formation, which is fundamental and very convenient in case of storage and transportation [100].

The use of recyclable thermoset polymers in the manufacture of CFRPs may allow to reduce the production of waste in both polymers and carbon fibers. In a context of circular economy, Zamani et al. synthesized a Schiff base monomer (72% yield) through the reaction of vanillin with a phosphonitrilic chloride trimer (PCT) as a phosphorus/nitrogen-rich compound, in presence of K_2CO_3 and THF under reflux for 2 days [105]. The synthesis route converted a bio-derived aromatic material to a vanillin-terminated phosphonitrilic chloride trimer monomer with six aldehyde groups, which could be cured using 4,4-diaminodiphenylmethane (MDA) diamine to obtain a highly cross-linked Schiff base polymer (PVP).

PVP containing Schiff base CFRPs was prepared by following a prepreg approach in which the pre-impregnated carbon fibers are dispersed in the polymer system. After some preliminary steps of mixing between the vanillin-based Schiff base monomer and MDA, the resulting mixture was brushed onto pre-cut dry CF pieces (5 layers) and cured at 70 °C for 2 h. The CFRP was hot-pressed and then cooled down to room temperature to obtain CFRP with a desired thickness [105]. SEM analysis of fracture surface of Schiff base CFRP and pulled out of single filaments under a mechanical load confirmed that the polymer matrix was well penetrated within carbon fibers. Zamani et al. measured the tensile, flexural, and dynamic mechanical properties of Schiff base CFRP and compared its performances to the conventional epoxy resin reinforced with carbon fibers (Epoxy CFRP) (Table 1) [105].

Table 1 shows that the tensile and flexural strengths of Schiff base CFRP were lower than those of a traditional epoxy CFRP, unlike the tensile and flexural modulus as well as T_g which appeared higher. The reparability of the Schiff base CFRP was studied by hot-pressing the sample at 180 °C for 3 min under a 12 MPa pressure and measuring its flexural properties [105]. A mechanically reprocessed Schiff base CFRP could retain ~70 and ~58% of its original flexural strength, even after

Table 1
Results of mechanical and thermomechanical tests of the Schiff base CFRP and epoxy CFRP [105].

Sample	Flexural strength (MPa)	Flexural modulus (GPa)	Tensile strength (MPa)	Young modulus (GPa)	T_g (°C)	Storage modulus at 30 °C (GPa)
Schiff base CFRP (recyclable)	461 (326 and 267) ^a	54.2 (48.2 and 35.3) ^a	455	47.3	129	2.6
Epoxy CFRP (non-recyclable)	622	42.4	606	42.3	123	2.0

^a marked the recycled sample properties.

twice of the repairing process. On the other side, the thermal reformability of the Schiff base CFRP was investigated by reshaping the sample in specific shapes after thermal treatment (180 °C for 15 min) and cooling down the system at room temperature. The Schiff base CFRP could be dissolved in an aqueous solution of THF and HCl 1 M (8:2, v/v) at room temperature without any detrimental effect on the mechanical properties of the reclaimed carbon fibers. These CFs could be reused without any treatment as filler for the fabrication of carbon fiber reinforced polymers. The presence of a high content of phosphorus/nitrogen rings in the chemical structure of Schiff base allowed for a very low flammability and V0 rating in the UL-94 vertical flame spread test. PCFC analysis showed that the Schiff base CFRP exhibited lower PHRR, THR, HRC, and EHC than epoxy CFRP (Table 4). The Schiff base CFRP shows inherent fire-resistant behavior, as opposed to epoxy CFRP which requires the addition of fire retardant additives [105].

Yang et al. synthesized another reactive bio-based flame-retardant with 87.7% yield by nucleophilic aromatic substitution from vanillin and hexachlorocyclotriphosphazene (HCCP) (Fig. 13 – route 2) [101]. Seven different diamines (i.e. ethylenediamine (BDA), 1,3-diaminopropane (PDA), 1,4-diaminobutane (TDA) and 1,6-hexanediamine (HDA), 1,2-Bis(2-aminoethoxy)ethane (BODA) and 1,4-butanediolbis(3-aminopropyl) ether (BBDA) and 4,7,10-trioxo-1,13-tridecanediamine (TTDA)) were used to cure HVP as films and obtain high performance networks with adaptable imine bonds. HVP-diamine networks showed a high tensile strength above 35 MPa and high recyclability, as the HVP monomers could be almost completely (95%) recovered by hydrolysis in an acidic solution. On the contrary, the HVP-diamine networks could not be hydrolyzed with alkaline medium, natural solution of brine, water, and ethanol. The networks cured with BODA (HVP-BODA) exhibited a tensile strength of 57.32 MPa and an elongation at break of 9.73% (Table 4). The reversible imine chemistry of HVP-diamine networks allowed for a high reprocessability under hot-pressing conditions [101]. The tensile properties of samples were not significantly reduced after 3 reprocessing cycles. The type of diamine used strongly influenced the fire behavior and thermal stability of HVP-diamine polyimide networks, for example alkyl containing diamines-based samples had the highest LOI value of around 28% and exhibited V0 rating in the UL-94 test (Table 2). The LOI values and UL-94 classes for the other samples cured with alkoxy-containing diamines are reported in Table 2, which showed that all these formulations were very flame-retardant and exhibited high LOIs (>24%) [106].

The preparation of such HVP-diamine networks represents a new strategy to develop bio-based imine adaptable networks from vanillin as a renewable resource. The advantage of such a waste-to-wealth approach is a good balance between mechanical behavior and flame retardancy. In addition, the acid-degradability and the low environmental impact allow for a greener and more economical process than conventional high performance thermosetting polymers. Another novel bio-based multifunctional amine curing agent (HVPA) was reported by Peng and co-workers, which was obtained from a Schiff base reaction between six-vanillin functionalized cyclophosphazene and N-methyl-ethylenediamine [107]. By the use of HVPA to cure the bio-based epoxy of glycerol diglycidyl ether (GDE), an epoxy vitrimer (HVPA/GDE) was fabricated with not only excellent flame retardancy, good UV resistance and transparency but also fast self-healing, excellent shape memory,

Table 2
Results of LOI and UL-94 vertical burning tests of HVP-diamine polyamide adaptable networks [101].

Sample	LOI (%)	First after-flame time t_1 (s)	Second after-flame time t_2 (s)	Dripping	UL-94 class
HVP-BDA	28.2	<0.5	0	no	V0
HVP-PDA	28.2	<0.5	0	no	V0
HVP-TDA	27.8	<0.5	0	no	V0
HVP-HDA	27.5	2.65	0	no	V0
HVP-BODA	24.7	20.44	–	no	none
HVP-BBDA	25.2	21.56	–	no	none
HVP-TTDA	24.6	18.19	–	no	none

easy reprocessability, mild degradation, and superior bacterial resistance.

As demonstrated above, the use of phosphazene-based compounds, bearing simultaneously phosphorus and nitrogen atoms in covalent adaptable networks as flame-retardants, is attracting great attention. Wu et al. patented a similar procedure for developing novel cyclophosphazene-based polyimine vitrimers [108]. The methodology involves following steps: i) preparation of sodium salt of alcohol/phenol compounds with aldehyde groups (Salt I), and without aldehyde groups (Salt II); ii) reaction of Salt I and Salt II with hexachlorocyclotriphosphazene to obtain CP-3AP (Fig. 14 – route 1); iii) condensation reaction between aldehyde group of CP-3AP and dialdehyde compounds with different amines to obtain polyimine vitrimer; iv) reaction between amino alcohol/phenol with CP-3AP to obtain CP-3OH; v) curing reaction between CP-3OH with epoxy resin or diisocyanate to obtain epoxy resin or polyurethane vitrimers (in total 9 samples with different combinations, Table 3). The vitrimers showed good thermal properties, flame retardancy, tensile strength, and the reprocessed vitrimer kept relatively high mechanical properties, as shown in Table 3.

Using the patented compound CP-3AP, the same group prepared a series of catalyst-free phosphazene-based polyimine vitrimers through condensation reactions between the aldehyde groups of CP-3AP, terephthalaldehyde (TPA), and amine groups of diaminodiphenyl methane (MDA) [70] (Fig. 14 – route 2). Synthesis of CP-3AP was obtained with 94% yield by two-step substitution reactions of HCCP to introduce three *p*-hydroxybenzaldehyde groups and three thermally stable phenol groups, which were both fundamental to construct polyimine vitrimers. The phosphazene-based polyimine vitrimers (CTM-x, where “x” is the average –CHO functionality) exhibited excellent fire performance, solvent resistance and reprocessability. The presence of flame-retardant phosphazene moieties and a high amount of aromatic rings in the polymer structure promoted the charring behavior of vitrimers and enabled them to achieve UL-94 V0 rating, high limiting oxygen index (ranging from 34% to 41.6%) and high overall thermal stability with

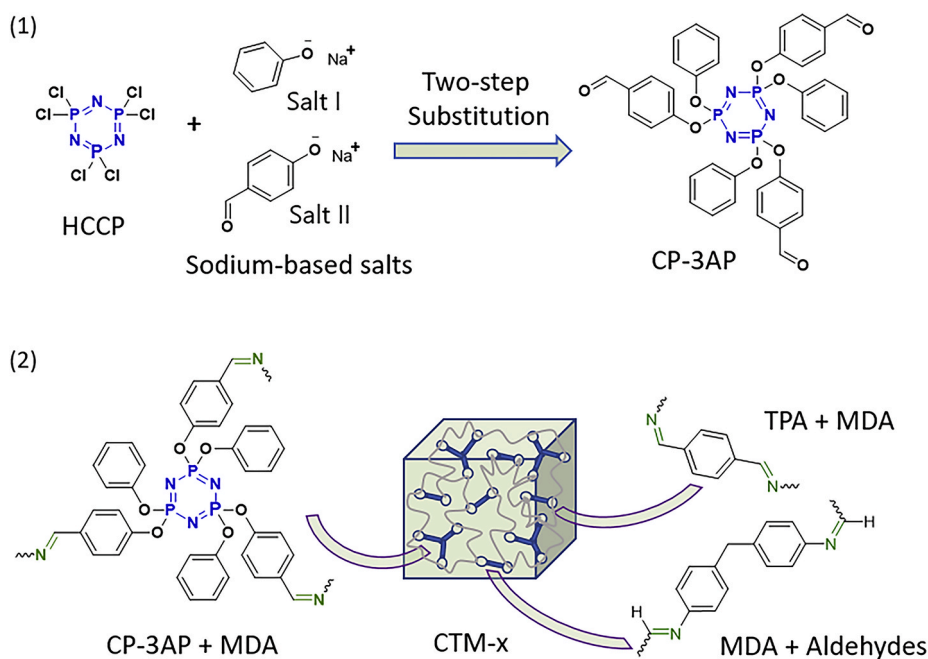


Fig. 14. Simplified synthetic approach: (1) CP-3AP reported in a patent [108], and (2) transamination mechanism of the CTM-x vitrimers between $-\text{CH}=\text{N}-$ bonds and $-\text{NH}_2$ groups; imine metathesis between $-\text{CH}=\text{N}-$ bonds [70].

Table 3
Results of flammability, tensile and thermal tests of polyamide vitrimer [108].

Sample code	LOI (%)	UL-94	Tensile strength (MPa)	Recycled tensile strength (MPa)	T_d ($^{\circ}\text{C}$)	Residue (%)
1	35	V0	67	65	420	70
2	33	V0	63	62	410	67
3	39	V0	77	73	430	75
4	46	V0	66	64	350	62
5	31	V0	53	53	330	56
6	28	V0	67	59	350	52
7	29	V0	34	28	330	48
8	29	V0	69	61	440	54
9	43	V0	71	67	420	76

$T_{5\%}$ (the temperature at which the 5% of weight loss is recorded) of around $455\text{ }^{\circ}\text{C}$ and $\sim 75\%$ of residue at $800\text{ }^{\circ}\text{C}$. The vitrimer CTM-3 showed a T_g of $146\text{ }^{\circ}\text{C}$ and tensile strength of $\sim 56\text{ MPa}$ (Table 4). Zhang et al. evaluated the occurrence of bond exchange mechanisms in the processability by analysis with model compounds and using TOF-mass spectroscopy [70].

The imine adaptable bonds guaranteed a high recycling efficiency; i. e. ensured retention of greater than 90% of mechanical properties, even after three recycling cycles. Also, the CP-3AP component could be almost fully recovered (81%) by acidolysis. In particular, the cross-linking density of the thermoset could be tuned by varying the proportion between CP-3AP and TPA, leading to variable mechanical properties, highly dependent on the chemical composition of CTM-x. When the mole ratio of TPA was higher than CP-3AP, the material started to exhibit poor reprocessability. The research activities involved in the development of more waste-to-wealth approaches for the efficient transformation of renewable resources to functional fillers for application in high performance polymers are thriving [109]. The implementation of such methodologies is responsible for a lower impact on the environment [110]. The above presented Schiff base CFRPs are very promising in the field of carbon fiber composite production, as it is not only fully compatible with the prepregs manufacturing protocols but also easily processable in terms of curing time. Indeed, the scientific

community is spending efforts to develop more sustainable products and CFRPs showing a cradle-to-cradle design (i.e. in a reasonable frame of time the output of biodegradation becomes the production input for the same polymer) [111]. The synthesis of bio-based recyclable thermosets such as the Schiff base CFRP offers a clear example of a closed-loop recycling solution and low energy-consuming process, where both high flame retardancy and sustainability are considered in the fabrication of carbon fiber reinforced polymer composites.

1.5. Bio-based recyclable flame-retardant composites

As intermittently described above, bio-based approaches have been developed in the recent year as alternative solutions to address material sustainability concern. The increasing interest in sustainable products is motivating the development of bio-alternatives to halogen-based flame-retardants from biomass-based raw materials (e.g., PA, chitosan, lignin, cyclodextrins) [112,113]. However, the development of bio-based FR thermosets/composites with satisfying fire performances requires large amounts of FR compounds. Besides, the earth's regenerative capacity can be negatively affected by the extensive use of bio-based compounds, leading to further environmental issues, for example the depletion of natural resources.

To bridge the gap between supply and demand, the scientific community is spending much effort researching sustainable methodologies to find more abundant and efficient sources of phosphorus and other biomass-based flame-retardants. In this context, the phytic acid (PA), which is mainly extracted from plants and soil, represents an environmentally friendly phosphorus-based flame-retardant filler [114]. PA is composed of $\sim 28\text{ wt}\%$ phosphorus and thus can be considered a suitable phosphorous source [115]. PA shows a decomposition temperature of around $200\text{ }^{\circ}\text{C}$ and promotes the dehydration of the carbon source to generate a stable protective layer which acts as an oxygen barrier and thermal shield for the polymer matrix [116]. Patra et al. developed phytic acid-based flame-retardants for cotton and characterized its decomposition process [117]. Liu et al. demonstrated also that phytic acid based adaptable networks could be an promising alternative for the preparation of new bio-based and flame retarded thermosets with high degradability, reprocessability, and malleability [47].

Table 4
Recent recyclable FR covalent adaptable networks – main outcomes.

Matrix	Co-reagent	Dynamic network	Main performances	Ref.
DGEBA	<ul style="list-style-type: none"> • DOPO-MA as a multifunctional curing agent 	Carboxylic ester-linkages	<ul style="list-style-type: none"> • Catalyst: Zinc acetylacetonate hydrate, • $T_g = \sim 111.3$ °C, • 100% shape recovery, • Transparent, • Tensile strength of recycled samples as high as 85.4% of the original one, • Easy recycle by ball-milling/hot-pressing process, • Flame-triggered shape memory effect, • Reuse recycled samples as reinforce filler for PEVA polyester copolymers 	[33]
DGEBA	<ul style="list-style-type: none"> • AA • DDP as co-curing agent (30 wt %) 		<ul style="list-style-type: none"> • Catalyst: TBD, • $T_g = \sim 110.7$ °C, • E_a for 30% DDP/EV at 80.51 kJ/mol, • Reprocessability (15 min at 200 °C), • UL-94 V0 rating, • LOI of $\sim 34\%$, • Decrease of PHRR (63%) and THR (32%). 	[34]
DGEBA	<ul style="list-style-type: none"> • AA • DHH as co-curing agent • HQEE as co-curing agent 		<ul style="list-style-type: none"> • Catalyst free, • $T_g = 65.7$ °C for AAD0.5-EP, 65.5 °C for AAD0.25-EP, and 72.3 °C for blank AA-EP, • AAD0.5-EP exhibited the lowest PHRR and THR values of 451.8 kW/m² and 33.2 MJ/m², respectively, which were 53% and 57% lower than those of AAH0.5-EP, • PHRR are 582.2, 451.8, 960.2, and 900.8 kW/m² for AAD0.25-EP, AAD0.5-EP, AAH0.5-EP, and AA-EP, • THR are 52.6, 33.2, 77.7, and 66.2 MJ/m² for AAD0.25-EP, AAD0.5-EP, AAH0.5-EP, and AA-EP, • UL-94 V0 for AAH0.5-EP and UL-94 V1 AAH0.25-EP, • LOI at 34.5, 36, 23.5, and 22% for AAD0.25-EP, AAD0.5-EP, AAH0.5-EP, and AA-EP, • CFs can be nearly 100% recycled via dissolving the matrix of the CFRP. 	[35]
EIA	<ul style="list-style-type: none"> • Phytic acid (cross-linker), IA, TBAB, ECH 	Phosphate ester-linkages	<ul style="list-style-type: none"> • Catalyst-free, • E_a at 49–90 kJ/mol, • High reprocessability by two methodologies at 160 °C within 1.5 h, • EIA-PA-1: easy reprocessability by reduction into small pieces and hot-pressing at 160 °C under 5 MPa for 1.5 h, unvaried tensile stress-strain curves after reprocessing, • High degradability under mild basic conditions, • UL-94 V0 rating, • LOI of 31.2–33.5%. 	[47]
HDA, BPA (phosphate diester-based acrylate cross-linker)	<ul style="list-style-type: none"> • UV curable 		<ul style="list-style-type: none"> • Catalyst-free, • high $T_g = \sim 152.4$ °C, • low E_a of 42.8 kJ/mol, • $T_v = 9.1$ °C, • Blank thermoset - high flammability and completely burned out, • BPA thermoset - slow flame propagation and flame extinguished after 15 s, • Recycled BPA thermoset with tensile strength 41.2 MPa, • BPA-based CFRPs: high tensile strength up to 370 MPa, flame resistance after 70 s of flame exposure, 100% recovery of carbon fibers with hot NaOH aqueous solution, • Regenerable cross-ply composites with tensile strength over 330 MPa and high thermal recyclability. 	[52]
EPON-826 epoxy	<ul style="list-style-type: none"> • Phosphoric acid 2-hydroxyethyl methacrylate ester (~ 25 wt% diester content) • Acetone solution 		<ul style="list-style-type: none"> • Catalyst-free, • $T_g = 67$ °C, • $T_v = -10$ °C, • E_a at 56.2 kJ/mol, • High malleability over 80 °C and toughness of around 5.44 MJ/m³ at room temperature, • Flame-triggered shape memory effect, • 100% recycling efficiency, • Ignition temperature at 250 °C, • Formation of a cellular layer of charred phosphoric acid, • Easy scale-up to industrial applications, • Swelling and slight dissolving after 72 h of immersion in polar solvents. 	[49]
DGEBA	<ul style="list-style-type: none"> • 1-butyl-3-methylimidazoliumdiphenyl phosphate ([Bmim]DPPPO) (5, 10, and 15%) • DDM 		<ul style="list-style-type: none"> • catalysis-free, • $T_g = 74.6$ °C to 85.2 °C, • $T_v = 91.4$ °C for 15% vitrimer, • E_a at 86.4 kJ/mol for 15% vitrimer, • Tensile strength and modulus for 15% recycled vitrimer at 62.5 MPa and 1433.6 MPa, higher than the original samples (64.7 MPa and 1360.1 MPa), • Shape memory, • Flame-triggered fire alarm, 	[55]

(continued on next page)

Table 4 (continued)

Matrix	Co-reagent	Dynamic network	Main performances	Ref.
Epoxide II (Phosphate cycloaliphatic epoxy resin)	<ul style="list-style-type: none"> 4-methyl phthalic anhydride curing reagent 2-ethyl-4-methylimidazole as catalyst 		<ul style="list-style-type: none"> PHRR decreased by 74.8% (for 15% vitrimer) and 63.6% (for 10% vitrimer) compared to the epoxy resin cured by DDM, LOI of 30.1% for 15% vitrimer and 27.3% for 10% vitrimer. $T_g = 227^\circ\text{C}$ for Epoxide II, $T_g = 130^\circ\text{C}$ for Epoxide I, Rework/removal temperature range of 200–300 °C, Heat-treatment for 4 min at 260 °C, the residue of cured trifunctional epoxide on a glass slide could be easily removed, Formation of condensed phosphorus-containing solids as fire protection layer, LOI of 22.7% for Epoxide II and 23.9% for Epoxide I compared to blank sample ERL-4221 (18.2%). 	[56]
REP resins	<ul style="list-style-type: none"> Reactive DOPO FR additive (3 wt%) Reactive DOPO FR additive (4 wt%) 	Disulfide-linkages	<ul style="list-style-type: none"> Catalyst-free, $T_g = 122^\circ\text{C}$, E_a at 133 kJ/mol, Transparent, Increase of LOI value from 21.7% of net epoxy to 27.8%, UL-94 V0 rating, REP-3%: high recyclability by hot-pressing at 200 °C and 100 bar for 5 min, Highly porous recycled sample still showing high transparency and 90% of the initial tensile strength. $T_g = 105^\circ\text{C}$, E_a at 123 kJ/mol, Transparent, Decrease of PHRR (43.5%), UL-94 V0 rating. 	[69]
CTP-EP	<ul style="list-style-type: none"> HCCP, benzyl mercaptan, 2-benzoyl-2-propanol, 3-chloroperoxybenzoic acid, 4,4'-dithiodianiline (curing agent) 		<ul style="list-style-type: none"> Reaction under UV light irradiation at room temperature, $T_g = 129^\circ\text{C}$, High reprocessability by hot-pressing at 200 °C and 10 MPa for 10 min, Recycled CTP-EP//DTDA: tensile strength retention of 93.9% and 89.8% after the second and third healing cycles, respectively Notable healing efficiency even after three repair cycles, Formation of a P-rich char showing high thermal insulation and honeycomb structure, UL-94 V0 rating in vertical flame spread tests, LOI of 30.5%. 	[73]
EUG, ECH, BMPAEGE, TPTPAE, TMPAPE	<ul style="list-style-type: none"> DADS: 3,3'- DADS, 4,4'- DADS, 2,2'- DADS 		<ul style="list-style-type: none"> Tensile strength of 0.5–1.8 MPa, Elongation at break ranging from 84%–110%, High dielectric properties 11.8–17.2 kHz, 100% repairing efficiency at 8h, PHRR lower than 600 kW/m², THR around 60 MJ/m², LOI ranging from 27% to 29%. 	[75]
TEMP-M, TEMP-P, TEMP-H	<ul style="list-style-type: none"> Curing agents: MDA, PACM, HMD 	Imine-linkages	<ul style="list-style-type: none"> $T_g = \sim 178^\circ\text{C}$, E_a at 49–81 kJ/mol, Tensile strength (~ 69 MPa) and tensile modulus (~ 1925 MPa), TEMP-M, TEMP-P, TEMP-H: recyclable after 2–10 min at 180 °C, Original monomer (TFMP) recovery rate of $\sim 70\%$, TEMP-M, TEMP-P, TEMP-H: UL-94 V0 rating and V1 rating in vertical flame spread tests, LOI of $\sim 30\%$. 	[27]
Vanillin-based epoxy containing Schiff base bonds (VAD-EP and VDP-EP)	<ul style="list-style-type: none"> D230 		<ul style="list-style-type: none"> T_g maximal 71 °C, Tensile strength and elastic modulus of A7P3-D230 75.5 MPa and 2.5 GPa, UL-94 V0 rating for A8P2-D230 with VAD-EP and VDP-EP at 8:2 ratio, LOI value of 27.0% with 0.66% of P content for A8P2-D230, Vitrimer reinforced carbon fibers (CFs) composites could be completely recycled. 	[93]
Poly-1, poly-2 (free-P reference)	<ul style="list-style-type: none"> Polycondensation of monomer with amines 		<ul style="list-style-type: none"> Phosphorous-free vitrimers Recycled poly-1: storage modulus of 0.36 GPa at 50 °C Poly-2: storage modulus of 2.4 GPa at 50 °C, any classification in UL-94 vertical flame spread test DGEBA-based epoxy: storage moduli of 4.0–8.5 GPa at -25°C, Poly-1: decrease of THE (27%), EHC (14%) and PHRR (33%) compared to poly-2, UL-94 V2 rating (with dripping), Poly-1 composites containing glass fibers (GFs): strength and bending moduli similar to permanently cross-linked epoxy resins reinforced with the same GFs, any larger delamination of the layers under tension 	[94]
HVP, E51 epoxy	<ul style="list-style-type: none"> Polyimine binder material D230 diamine monomer 		<ul style="list-style-type: none"> Nondestructive closed-loop recycling of CFs and HVP monomer under mild condition, HVP/D230-CF: LOI of 34.2%, UL-94 V0 rating, compared to E51/D230-CF 21.1% and no rating, Decrease of THR (19.9 NJ/m², 43%) and TSP (2.7 M², 82%) compared to E51/D230-CF, 	[100]

(continued on next page)

Table 4 (continued)

Matrix	Co-reagent	Dynamic network	Main performances	Ref.
HVP	<ul style="list-style-type: none"> • Curing agents: BDA, PDA, TDA, HAD, BODA, BBDA, TTDA 		<ul style="list-style-type: none"> • Prepeg could be stored for 12 months at room temperature without any subsequent lamination formation • Catalyst-free • HVP-diamine vitrimers: high tensile strength above 35 MPa and high recyclability, • HVP-BODA: tensile strength of 57.32 MPa, elongation break of 9.73%, • 95% recovery of HVP monomers by an acidic solution, • high reprocessability under hot-pressing conditions, no decrease of tensile properties after 3 reprocessing cycles, • HVP-diamine (alkyl containing diamine-based samples): LOI of 28%, UL-94 V0 rating, • HVP-diamine (alkoxy containing diamine-based samples): no classification in UL-94 test, • All the formulations: LOI value higher than 24%. 	[101]
PVP	<ul style="list-style-type: none"> • PCT, K₂CO₃, THF, • MDA (curing agent) 		<ul style="list-style-type: none"> • Cradle-to-cradle approach, • T_g = 129 °C, • PVP containing carbon fibers (Schiff base CFRP): pulled out test proved the good penetration of matrix within the carbon fibers, • high flexural and tensile strengths of 461 and 455 MPa, • Decrease of PHRR (120 W/g, 55%) and THR (16 kJ/g, 45%) compared to pure epoxy based CFRP (269 W/g and 29 kJ/g), with much higher residue mass at 34 wt% compared to 3 wt%, • UL-94 V0 rating in vertical flame tests, • High reparability by hot-pressing at 180 °C for 3 min under 12 MPa, • Recycled Schiff base CFRP: retention of ~70 and ~58% of the original flexural strength after two repairing cycles, • 100% recovery of reusable carbon fibers through easy degradation in an aqueous solution of THF and HCl 1 M (8:2, v/v) at room temperature. 	[105]
CP-3AP	<ul style="list-style-type: none"> • MPDA, DDM, BZD, PBZ, EDA, ADH, BZH 		<ul style="list-style-type: none"> • Catalyst-free, • High decomposition temperature ranging from 330 °C to 440 °C, • Tensile strength ranging from 53 MPa to 77 MPa, • Reprocessed vitrimer keeps 95% of tensile strength, • High recycle residue between 54% and 76% UL-94 V0 rating, • High LOI ranging from 31% to 46%. 	[108]
CTM-x	<ul style="list-style-type: none"> • HCCP, CP-3AP, and TPA, • MDA 		<ul style="list-style-type: none"> • Catalyst-free • T_g = 146 °C, • Tensile strength of ~56 MPa, • T_{5%} = 455 °C and 75% of residue at 800 °C, • Recycled sample by hot-pressing with 90% of original mechanical properties (even after 3 recycling cycles), • CP-3AP, 81% recovery by acidolysis, • UL-94 V0 rating, • High LOI ranging from 34% to 41.6%. 	[70]

Wood plastic composites (WPC) are eco-friendly materials prepared by extrusion, injection or molding with wood and plastic as the main components. However, WPCs are highly flammable with the limiting oxygen index ranging from 19.5 to 20.2%. WPCs used in building materials are supposed to show good fire and mechanical performances. Therefore, it is of great importance to develop WPCs with high strength, flame retardancy and durability to meet the requirements in the fields of construction, decoration and electronic devices manufacturing. Pan et al. developed novel recyclable WPCs [118], by introducing imine dynamic covalent bonds through: i) reacting p-benzaldehyde with ethylenediamine at 60–70 °C in ethyl acetate as solvent, with ammonium polyphosphate as flame-retardant additive; ii) drying at 100–110 °C for 8–10h, then grinding to obtain FR solid powder containing imine adaptable bonds; iii) mixing imine containing FR powder, plant fiber and plastic with certain mass ratio, then extruding to obtain flame-retardant reprocessable WPC. The results show that the LOI of imine containing WPC ranges from 26.5% to 31.2% with a content of ammonium polyphosphate less than 20 wt%. Besides, the tensile strength and impact strength are around 26 MPa and 7 MPa, respectively. The viscosity of the WPC is decreased to around 1.5×10^5 Pa s at 170 °C, which allows good material reprocessability at elevated temperature.

Other bio-resource, guaiacol derived from lignin, was chemically modified to 5-aminoguaiacol via nitration and the reduction of nitro-arenes, and then reacted with vanillin to obtain Schiff base bis-epoxy

resin [119]. After curing with DDM, the thermoset showed great mechanical, thermal, reprocessing, antibacterial and flame retardant properties. The glass transition temperature was very high (220 °C) with a char yield more than 40% measure by TGA. The Young's modulus measured at 30 °C was 4489 MPa, which was even higher than those of bisphenol A epoxy resin. Furthermore, the introduction of Schiff base structure endowed the thermoset system with shape memory, degradability and reprocessability at 230 °C under 10 MPa. Natural sugar derivatives are normally excellent charring reagent, which is ideal candidates for designing bio-based fire-safe thermosets.

Following the idea of promoting bio-based sustainable material, Jung et al. demonstrated that tannic acid (TA) can be used as FR hardener for a bio-based epoxy with radical scavenging of the pyrogallol moieties and the charring effect of TA [120]. TA was with the commercially available DGEBA resin through the reaction of epoxy rings reacting with hydroxyl groups in TA (Fig. 15). TA/DGEBA molar ratios were increasing between T-CFRP0.8, 1.0, and 1.2, respectively. DGEBA cured with D230 was chosen as control sample. The most effective flame-retardant TA-DGEBA (TD) thermoset had a limiting oxygen index (LOI) value 46% higher than the control sample. Later, they explored the use of TA-based epoxy thermoset as a polymeric matrix for fabricating and recycling carbon-fiber-reinforced plastic (CFRP) [12]. TA plays a critical role in increasing the adhesion of the interface between the polymeric matrix and the carbon fibers (CFs), ultimately improving the mechanical properties of the CFRP. In addition, its char forming ability

endows the CFRP with superior FR and smoke-suppressing properties. TA-based CFRP can be treated with supercritical deionized water without additives, and the TA-based epoxy thermosets in T-CFRPs could be degraded into carbon spheres and petrochemical derivatives.

As environmental issue becomes more severe, the replacement of fossil resources with bio-resources becomes increasingly important, which will break our dependence of polymeric material on oil or gas. In combination with adopting biomass FR resources, the introduction of recyclable or degradable CANs in thermoset materials may offer an effective way to utilize bio-resources, prolong material lifetime, and thus help to solve current energy and environmental issues.

1.5.1. Summary and perspectives

The combination of multi-functionality such as flame retardancy and recyclability in thermoset materials will greatly extend their application range and prolong their useful lifetime towards safe and sustainable future. However, recycling of materials becomes more challenging as the system becomes more complex. In this framework, the introduction of covalently bonded FR moieties and stimuli-response adaptable bonds replacing some stable C–C/C–N bonds within the thermoset networks can help achieve above-mentioned goals. The covalent adaptable networks will promote thermomechanical recyclability of the thermosets, which is highly desired in terms of recycling.

In this review, we have summarized various types of covalent adaptable networks (e.g. carboxylic/phosphate ester, disulfide and imine based linkages), with covalently functionalized pendant or networked flame-retardant units (DOPO, phosphate, phosphonate, cyclophosphazene, phytic acid, and other bio-derivatives) being adopted by researchers in the development of recyclable thermosets, with general property comparison listed in Table 5. In the literature, key characteristics such as reprocessability, flame-triggered shape memory effect,

fire-safe capability, heat and smoke release reduction were demonstrated for such materials. The flame retardant action in these thermosets was attributed to condensed or gas-phase flame inhibition action, or a combination of both. The reprocessing/recycling mechanism of such FR thermosets can be very complicated and depends on the adaptable bonds and other components present in the network. Coordination chemistry, supramolecular chemistry, and covalent-bond reformation can be involved in the recycling process. In some cases, closed-loop recycling of polymeric material and the recovery of other components such as valuable fibers or fillers could be achieved for fiber reinforced polymer composites. Sustainable approaches such as the use of various biomass as renewable resources for the development of recyclable flame-retardant thermosets is gaining importance. Besides of the good thermomechanical recyclability, in case of adaptable network containing carboxylic/phosphate ester and imine bonds, the monomer/oligomers can be recovered via hydrolysis/solvolytic of the network, indicating thermochemical recycling potential of such complex materials. Yet, thermochemical recycling require further monomer or chemical separation and isolation, which is still problematic at the current stage. More effort is needed in future.

The development of recyclable FR thermosets offers enormous potential for a circular economy. To achieve satisfying thermomechanical recycling yield, a large concentration of adaptable bonds is required; nevertheless, a large number of adaptable bonds may negatively impact the thermal stability, degradation behavior, and mechanical performance of the final material. Prior to their commercial exploitation, however, there are still issues that need to be resolved. These include streamlining the complicated synthesis strategies currently used, expanding the working temperature range (proper T_g), addressing the problems related to the material stability, and achieving a good price/performance balance. In accordance with the intended material use,

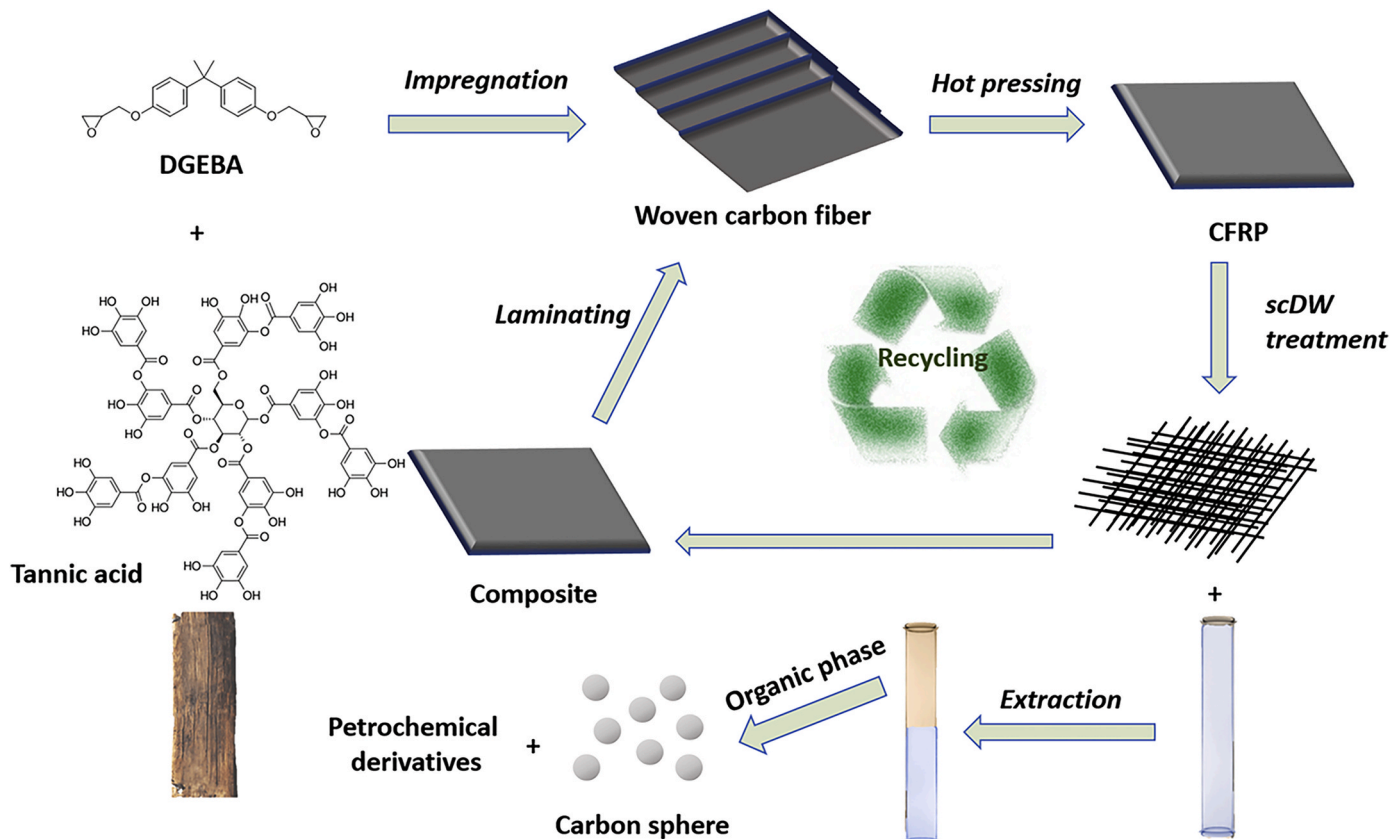


Fig. 15. Process concept developed by Jung and co-workers from fabrication to recycling of T-CFRP composites [12].

Table 5
General summary of FR thermosets with covalent adaptable bonds.

Adaptable bonds	FR units	Complexity of chemistry	Catalysts	E_a	T_g	Mechanical property	Stability	FR property	Thermoset recycling	Composite recycling	Drawback	Ref.
Carboxylic ester	Pendant	↑	Zn salt /organic base	↑	–	↑	↑	↑	Energy intensive ThMe, ThCh	Solvolysis to recover fibers and monomer	Catalyst needed	[33, 35, 36]
Phosphate ester	Networked	↑	Catalyst free	↓	↓	–	↓	↑	Less energy intensive ThMe	Lye wash to recover fibers	Low T_g limited application, Less hydrolytic stable	[47, 49, 56, 58]
Disulfide	Pendant	↓	Catalyst free	↑	↑	–	↑	↑	Energy intensive ThMe	Not well studied	Toxic gas during combustion	[69, 73, 74]
Imine	Pendant /networked	↓	Catalyst-free	↓	↑	↑	↓	↑	Energy intensiv ThMe, ThCh	Solvolysis to recover fibers and chemical mixture	Less hydrolytic stable	[27, 70, 105]

↑: Positively affected or increased; ↓: negatively affected or decreased; –: unaffected.

ThMe: Thermomechanical recycling.

ThCh: Thermochemical recycling.

careful design and balance are therefore necessary.

Author statement

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript. Dr. Wenyu Wu Klingler, Dr. Aurelio Bifulco, and Dr. Sabyasachi Gaan constructed the topic and the main content. All contributed to writing and editing of the manuscript. Carolina Polisi and Zhenyu Huang contributed equally to summarize relevant research articles and patents respectively.

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.

Data availability

Data will be made available on request.

Abbreviations

AA	adipic acid
ADH	anthracene-9, 10-diformaldehyde
BBDA	1,4-butanediolBis(3-aminopropyl) Ether
BDA	ethylenediamine
BMPAEGE	bis (3-mercaptopropionic acid) ethylene glycol ester
BODA	1,2-bis(2-aminoethoxy) ethane
BZD	benzidine
BZH	benzaldehyde
CANs	covalent adaptable networks
CFRPs	carbon fiber reinforced polymer composites
CFRPs	Carbon fiber-reinforced polymers
CFs	carbon fibers
CP-3AP	cyclophosphazene bearing three aldehyde groups
CTM-x	phosphazene based polyimine vitrimers
CTP-EP	cyclotriphosphazene-based epoxy resin
D230	Polyoxypropylene Diamine hardener
DADS	diaminodiphenyl disulfide
DCM	dichloromethane
DDM	4,4'- diaminodiphenylmethane
DDP	[(6-Oxido-6H-dibenz[c,e][1,2]oxaphosphorin-6-yl)methyl] butanedioic acid

DGEBA	diglycidyl ether of bisphenol A
DGEBF	diglycidyl ether of bisphenol F
DMA	dynamic mechanical analysis
DMF	dimethylamide
DOPO	9,10-dihydro-9-oxa-10-phosphaphenanthrene10-oxide
DSC	differential scanning calorimetry
DTDA	4,4'-dithiodianiline
EA	ethanolamine
ECH	epichlorohydrin
EDA	ethylenediamine
EHC	effective heat of combustion
EIA	itaconic acid-based epoxy resin
EP	epoxy resin
EUG	eugenol
EV	epoxy vitrimer
FTIR	fourier-transform infrared spectroscopy
HCCP	hexachlorocyclotriphosphazene
HDA	1,6-hexanediamine
H-FRs	halogen-based flame-retardants
HMD	hexamethylenediamine
HQEE	1,4-Bis(2- hydroxyethoxy) benzene
HRC	heat release capacity
HVP	vanillin-terminated hexasubstituted cyclotriphosphazene monomer
IA	itaconic acid
LOI	limiting oxygen index
MA	maleic anhydride
MDA	diaminodiphenyl methane
MLR	mass loss rate
MPDA	m-phenyldimethylamine
MS	mass spectrometry
NMR	nuclear magnetic resonance
OCCP	octachlorocyclotetraphosphazene
PA	phytic acid
PACM	4,4-diaminodicyclohexylmethane
PBZ	p-benzaldehyde
PCFC	pyrolysis combustion flow calorimetry
PCT	phosphonitrilic chloride trimer
PDA	1,3-diaminopropane
PE-CAN	phosphate esters based covalent adaptable network
PE-CANs	phosphate esters based covalent adaptable network
PEVA	poly(ethylene-co-vinylacetate)
PFV	phosphonate-based flame-retardant vitrimer
phoitiator 1173	2-benzoyl-2-propanol
PHRR	peak heat release rate

pSPR	peak smoke releaser rate
PVP	crosslinked vanillin-terminated phosphonitrilic chloride trimer monomer
R	residual mass
REP	recyclable epoxy resin
SEM	scanning electron microscope
SPR	total smoke release
T	temperature
TBAB	tetrabutylammonium bromide
TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene
TDA	1,4-diaminobutane
TFMP	tris(4-formyl-2-methoxyphenyl) phosphate
T_g	glass transition temperature
TGA	thermal gravimetric analysis
THF	tetrahydrofuran
THR	total heat release
TMPAPE	tetra (3-mercaptopropionic acid) pentaerythritol ester
TOF-mass spectroscopy	time-of-flight mass spectrometry
TPA	terephthalaldehyde
TPTPAE	trimethylolpropane tri (3-mercaptopropionic acid) ester
TSME	transparent shape memory epoxy
TTDA	4,7,10-trioxa-1,13-tridecanediamine
T_v	topology freezing transition temperature

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