Review Article

Recycling of flame retardant polymers: Current technologies and future perspectives

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ABSTRACT

Polymers are indispensable to humans in different applications due to their ease of manufacturing and overall performance. However, after a material lifetime, there is a large amount of polymer-based waste, which greatly contributes to the loss of valuable resources and environmental pollution. Thermoplastics may be readily recycled, but because of their flammability, large amounts of flame retardant (FR) additives are required for many applications. This results in a significant volume of FR polymeric wastes too, particularly halogenated plastics, which are subject to severe recycling regulations. In general, thermoplastics containing FRs are raising concerns, as their effective recycling is strongly influenced by the chemical composition, additive content, and physicochemical characteristics of the waste stream. The recycling of FR thermosets is even more challenging due to their crosslinked and cured nature, which makes them resistant to melting and reprocessing. In many cases, traditional mechanical recycling methods, such as grinding and melting, are not applicable to thermosetting polymers. Current recycling methods do not always consider the recovery of the thermosetting/thermoplastic matrix and the presence of toxic FRs in the polymer network. Sorting and solvent washing treatment are important steps, which are usually performed before recycling the FR polymeric waste to reduce contamination in the following steps.

Considering all the technical difficulties during recycling, the high cost of sorting and solvent washing, and the increasing demand for more sustainable procedures, the scientific community is fostering the transformation toward more feasible and energy-efficient recycling strategies. Also, many directives are imposing strict disposal and sorting rules, limiting the use of FR halogen-based compounds, and promoting the commercialization of more recyclable polymers. This review aims to provide a general overview of currently applied approaches for recycling FR thermoplastics and thermosets, and possible approaches for designing the next generation of FR polymer-based materials. The existing recycling strategies for FR polymers are summarized. Developments in the manufacturing of covalent adaptable networks as an outlook towards circularity in polymers are also addressed in this review.

1. Introduction

Owing to the high flammability and inadequate fire resistance [1], polymers must be modified with FR additives in a variety of applications to prevent the growing number of property losses and fire-related victims [2]. In case of a fire, FRs are designed to extend the flashover time and reduce the combustion of PMs [3], which directly affects the chance of saving lives [4]. A recent study has revealed that the European FRs market is expected to expand at a CAGR of approximately 5.08 % from 2019 to 2024, especially in the electronics and building construction industry [5]. The expanding infrastructure activity in the Asia-Pacific region [6–8], has increased the import of FR products from Europe.

Commercial FRs can be distinguished by their modes of action and chemical composition [9]. The main classes are the halogenated FRs (e.g., PBBs and PBDEs), P-containing FRs (e.g. APP, DOPO, etc.) [10], N-containing FRs [11,12], and inorganic FRs [13,14]. To choose the proper FR for a particular application, both the regulatory requirements and the potential fire scenario need to be seriously considered [15,16]. Nowadays, the development of sustainable PM is essential, and thus a deep understanding of EoL treatment and the environmental impact of FR products is growing in importance [17]. EoL PMs are composed of thermosets or thermoplastics, which need to be effectively recycled for the benefit of future generations. This would also result in the reduction of environmental concerns linked to the discarding of single-use products or EoL treatment. Unfortunately, as shown in Fig. 1, only
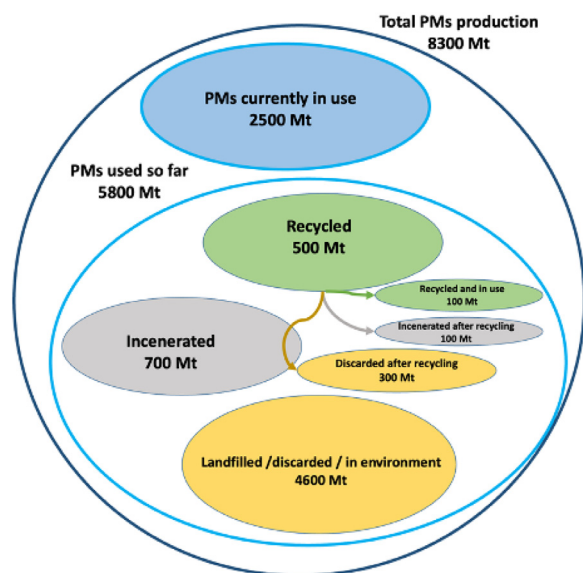
around 6 % of PMs produced from 1950 to 2015 have been recycled, whereas the largest amount of those have been burned or landfilled [18]. It is worth mentioning that looking at similar waste management statistics in Europe in the last five years (Fig. 2), only about 13 % of plastic wastes have been recycled, whereas ~5 % have been mismanaged and the largest amount of those have been unproperly disposed [19]. As confirmed by recent studies, almost all products based on FR PMs underwent the same destiny of pristine counterparts instead of being recycled, leading to soil contamination and greenhouse gas emissions [20]. A large amount of potential reusable FR polymers are lost as waste [21], together with their precious and increasingly demanded additives (e.g. CFs, metals, and rare earth elements) [22]. The depletion of natural resources is also motivating the reuse of solid wastes (e.g., fly ash, eggshell, banana peel powder, red mud, and steel slag) into virgin and recycled FR polymers to enhance the fire safety of products made of such materials [23]. The foreseen transition to recycling FR-containing products has thus motivated the present review.

The recycling of EoL PMs can be performed through several approaches. Primary recycling can be defined as secondhand use, as the wastes are directly reused without any reprocessing. Mechanical (or secondary) recycling, transforms the material into a secondary raw material for the manufacturing of new products [24]. This recycling methodology usually involves several steps, namely separation/sorting, washing, grinding, and reprocessing [24]. Chemical (or tertiary) recycling converts polymers back to their building blocks (oligomers or even individual monomers) by thermal or solvent-assisted depolymerization [25]. The tertiary recycling can also involve advanced thermochemical recycling processes namely pyrolysis, or energy recovery from waste through

Fig. 1. Production to discarding of PMs from 1950 to 2015 [18].
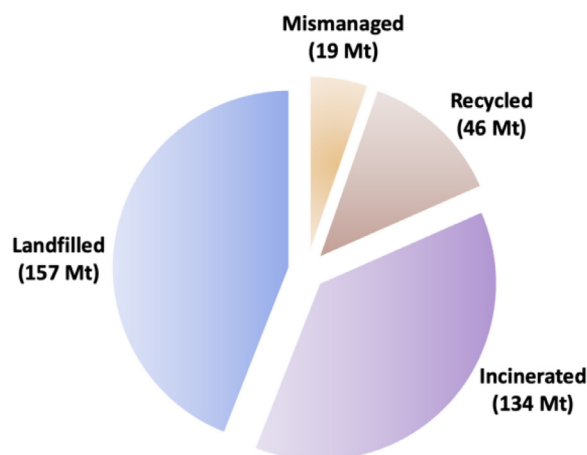
Fig. 2. Projections of EoL plastics by waste management method from 2019 to 2023 [19].
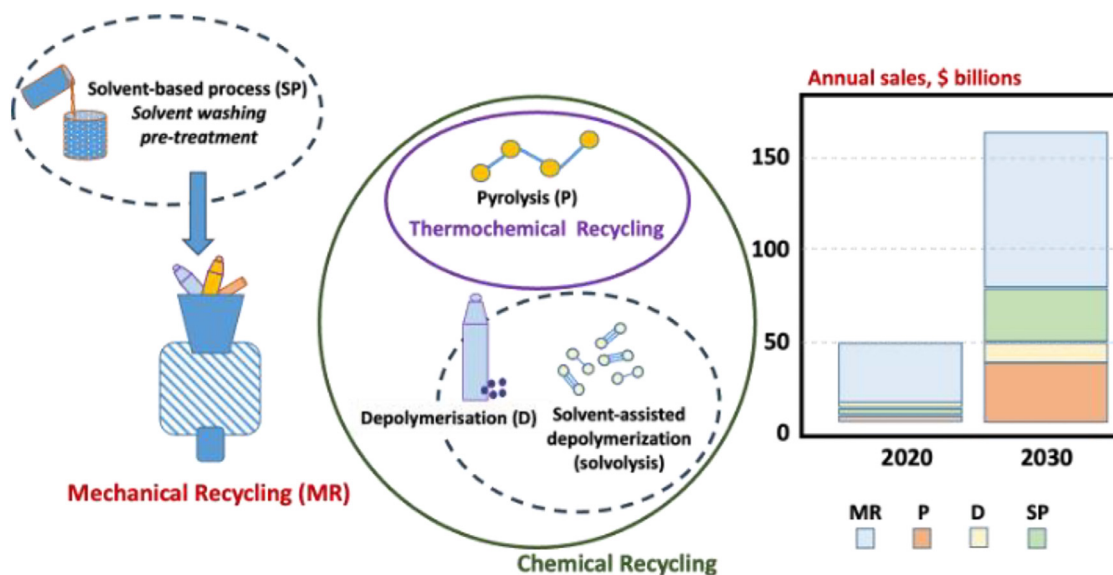
Fig. 3. Main recycling technologies and global revenue from PMs recycling in the coming decade [30].

thermal process [26]. As summarized in Fig. 3, there are two major routes of recycling for EoL PMs: mechanical recycling and chemical recycling (including pyrolysis and solvolysis). The solvent-washing pre-treatment is a solvent-based recycling method [27], involving extraction techniques, such as accelerated solvent extraction, for the efficient removal of additives (e.g., HFRs) from plastics undergoing mechanical recycling. In solvent-assisted chemical recycling, solvolysis (i.e., depolymerization), which is also known as chemolysis, consists of the depolymerization of polymers into their monomers at different operative conditions [28,29]. Thermoplastic wastes are mainly recycled by mechanical and some by thermochemical recycling, whereas only a few classes of thermosets are recycled by solvolysis [7]. The huge amount of EoL PMs and the above-mentioned concerns have spurred the scientific community and the industry to promote the development of more chemical and thermochemical recycling technologies, as evidenced by a significant increase in global revenue from the recycling of PMs in the coming decade (see Fig. 3) [30].

As FRs exert their function only in case of a fire, most EoL PMs still contain intact FRs, which may easily interfere with their recycling and reprocessing, leading to various environmental concerns, such as the toxicity of secondary products and the occurrence of leaching phenomena into the surface and groundwater sources [31,32]. Unlike virgin polymeric wastes [33,34], EoL PMs containing FRs cannot be easily recycled, as the FR may undergo degradation during reprocessing by extrusion, cause the release of toxic gases, or contaminate value-added compounds in thermochemical recycling processes, negatively interfere with solvents used for depolymerization treatments, etc. Since the 1970s, PBDE and PBB have been used as primary FR compounds. Later, these BFRs were replaced by phosphorous-containing and other halogenated FRs [35]. Among PBDEs, pentaBDE and octaBDE (OBDPO or EC 251-087-9) were restricted in 2003, because of their environmental and health concerns, and later also decaBDE followed suit (EC 214-604-9). In 2010, the Stockholm Convention banned tetra-, penta-, hexa- and heptaBDE under the POPs Regulation [35]. As such compounds could still be found in WEEE [36], to foster proper and safe recycling of WEEE, the European Community introduced in 2011 the Restriction of Hazardous Substances Directive to limit the use of PBB and PBDE in EEE [35]. Nevertheless, a recent study has estimated that considering an amount of 220 kilotons of plastic WEEE only around 2 kilotons are effectively recycled [37]. Also, Vahabi

et al. [38] found that FR EoL polymers containing halogenated additives and mineral fillers are more resistant to aging compared to the ones containing P-based species, which are sensitive to hydrolysis. HCs may still degrade during the recycling of the polymer waste, leading to detrimental effects on the reprocessing steps. These aspects require great attention, as BFRs are still very popular in the EEE market, due to their use in the automotive and construction sectors. According to environmental Non-Governmental Organizations, BFRs have also been found in food packaging and children's toys [39]. Fig. 4 shows that the production of WEEE has mostly increased in Europe's last two years.

Therefore, the increasing volume of WEEE in combination with the stricter legislations (safety regulations such as REACH and POPs regulations) has promoted the scientific community to urgently move its attention not only on the replacement of conventional FRs with new formulations but also on the development of recycling processes for which the reprocessing of EoL PMs containing BFRs or other additives is the priority. Given the above, it is not surprising that according to market analysis, the global HFFR market was valued at USD 4.129 billion in 2021 and is projected to increase at a CAGR of 8.50 % by 2028.

Some research groups have recently developed methodologies for the recycling of FR thermoplastics, where the aspects related to sustainability have been seriously considered [40]. Due to its properties, FR PET is widely used in the packaging and fiber industries. However, products based on such material are often not designed for recycling, undergoing polymer degradation and a consequent downgrade during thermomechanical recycling. To address this issue, Bascucci et al. [41] added two PFRs, DOPO-PEPA and AF, to PET by extrusion (Table 1). DOPO-PEPA could enhance lubrification and control melt rheology of PET over long periods, while AF boosted chain extensions and branching in PET, which could counter chain scissions. Morita et al. [42] converted PS and PP mixed plastic spiked with TBBP-A through a thermolysis process into oil by capturing brominated FR compounds using a hydrotalcite (Table 1). In contrast to thermoplastic polymers, thermosetting ones are characterized by permanently linked networks, which make them unable to flow, indeed they first undergo degradation at high temperatures. For this reason, thermosets are usually mostly landfilled or processed by pyrolysis-oxidation (often conducted in fluidized bed reactors or interconnected fluidized bed systems) or solvolysis (e.g., acidolysis) to produce energy from the polymer matrix,

Table 1
Recent recycling strategies of FR polymeric materials – main outcomes.

Type of polymer-based waste	Flame retardant species	Recycling strategy	Recycling efficiency, technical details, and economic aspects	Refs.
PET	DOPO-PEPA and AF	Mechanical reprocessing by multiple extrusion cycles followed by injection molding	• DOPO-PEPA reduces the melt viscosity of PET during extrusion enabling its reprocessing at lower temperatures • After recycling, PET/DOPO-PEPA maintains its most of its tensile properties (e.g., Young's modulus, maximum tensile stress, tensile strain at maximum stress, tensile strain at break, ductility) • After recycling, PET/Aflammit PCO 900 loses its toughness and ductility and becomes brittle	[41]
PS and PP	TBBP-A	Thermolysis	• Hydrotalcite was used to capture FR bromine compounds • Pyrolysis oil was obtained as the product • Pyrolysis in a glass reactor at 400 °C under a nitrogen atmosphere • Product distribution of produced oil (toluene, ethyl benzene, styrene, and 1-methylethyl benzene, were 2-bromohexane, 3–bromo-1-propenyl benzene, 4,5-dibromodecane, 1-bromomethylbenzene, 3-bromophenol, and 4–bromo-2,6-dimethylbenzaniline) • When hydrotalcite is used, the product oil does not contain bromine	[42]
Thermoset fractions of keyboards and printed circuit boards	BFRs and chlorine products	Thermal and catalytic hydrogenation (commercial hydrogenation DHC-8 catalyst and metal-loaded activated carbon)	• Hydrogenation runs were made at 350 °C for a reaction time of 120 min • Pyrolysis oil was obtained as the product (mainly consisting of aromatic hydrocarbons) • Upgraded oils contained a high amount of aromatics (60–89 wt.%) • Almost totally the hazardous toxic compounds, mainly those containing chlorine and bromine, were removed • Product distribution of produced oil from casings, keyboards (60–73 wt.% liquid, 27–35 wt.% gases, and low residue amount of 0–2 wt.%)	[44]
Recyclable FR epoxy resins	Itaconic acid and (1,3,5-hexahydro-s-triazine-1,3,5-triyl) benzyl mercaptan	Upcycling by depolymerization	• Closed-loop chemical recyclable network • Recovery of monomers with a yield of 86 %	[46]
Polyurethane foam	Coating made of anionic polyacrylamide and fibrous nanosepiolite	Solvent-assisted depolymerization	• Closed-loop chemically recyclable coatings • Self-extinguishing behavior and high chemical resistance • Disassembly rate of 96 % • Recovery rate of 97 %	[47]
PA-based glass-fiber-reinforced composite	DBDPE	Mechanical reprocessing with one co-rotating twin screw and three different single screws.	• The stability of DBDPE during the extrusion guaranteed the UL-94 V0 classification of the extruded products and a higher LOI value (> 36) • The maximal decrement percent of mechanical properties (impact strength, tensile strength, and flexural strength) was 5.8 % • Single screw with high depths of the gaps and shorter lengths was the optimal extruder to recycle	[73]
Glass-fiber-reinforced composites made of PBT	Brominated polystyrenics (BPS) and Sb_2O_3	Mechanical reprocessing by injection molding cycles	• After five injection molding cycles, recycled products could achieve a UL-94 V0 classification and a LOI of 32.0 • The increasing of the injection molding cycles causes a significant reduction of the PBT molecular weight, resulting in a lowering of the mechanical properties (notched impact strength, tensile strength, and flexural strength)	[76]
Waste plastics containing chlorine (composed of HDPE, PP, PE, and PVC)	Chlorine compounds	Dechlorination by melt processing and hot water dissolution	• About 98 % of the chlorine was removed as $FeCl_3$ (formed by the reaction between the removed chlorine and iron oxide) • Recycling by melt process with coal tar and converter dust (assumed to contain ferric oxide (Fe_2O_3)) to inhibit the diffusion of the chlorine-containing gas • Reaction conditions of melt process (atmosphere: nitrogen, initial pressure: 1 MPa, reaction temperature: 250 °C) • ~58 wt.% of the iron chloride is captured by the coal tar as a water-insoluble component • The melt process and the hot water process can reduce the chlorine to 5000 ppm or less	[81,82]

Table 1 (*continued*)

Type of polymer-based waste	Flame retardant species	Recycling strategy	Recycling efficiency, technical details, and economic aspects	Refs.
Unidentified plastics in WEEEs	TBBP-A	Solvent washing (extraction) with isopropanol or toluene before pyrolysis	• The temperature was kept at 132 °C for the isopropanol extraction (6 h) while for the toluene extraction (6 h) the temperature was set up at 153 °C for all the investigated fractions • Removal of TBBP-A • Reduction of the bromine content of the WEEE by 36.5 % • Two brominated compounds (2,4,6-tribromophenol and 2,5-dibromobenzo(b)thiophene) were completely removed	[88]
Polystyrene foam, PE, ABS and HIPS	HBCD, other halogenated FRs, and softeners	CreaSolv® Process: dissolution and precipitation techniques (super-heated solvent recycling)	• A demonstration plant based on the CreaSolv® Process is under construction, it will cover all the unit operations (dissolution, purification, polymer drying, and solvent recovery) • Contaminants, additives (such as FRs), hazardous materials, and plasticizers are effectively removed • Mixed plastic waste and laminated materials can be effectively recycled • Recycled plastics have the quality of virgin materials • Closed-loop recycling is possible	[89–94]
Acrylonitrile-butadiene-styrene (ABS) plastic	TBBP-A	Solvent-washing using supercritical isopropanol	• Oil with the content of brominated secondary compounds equal to 60 wt.% was obtained as the product • Debromination efficiency of ∼97.6 % (removed bromine mostly existed in the oil) • For an efficient oil recovery, the temperature should be ≥ 400 °C • The use of KOH in the supercritical isopropanol led to bromine-free oil and enhanced the depolymerization of the plastic • Product distribution of oil (single- and duplicate-ringed aromatic compounds, 42 wt.%, e.g., butyl–benzene and 1,1′-(1,3-propanediyl)bis benzene in a carbon range of C9-C17, and oxygen-containing compounds, 21 wt.%, e.g., phenol, alkyl phenols, and esters)	[95]
EoL LCD TVs mainly composed of plastic PC and ABS	18 wt.% BFRs and 31 wt.% PFRs	Mechanical reprocessing (separating FR plastics in a size reduction-based treatment or in a disassembly-based treatment)	• Closed-loop recycling of co-polymer PC/ABS containing P-based FR was demonstrated at a laboratory-scale • Several technical changes are needed to effectively separate FR plastic through a size reduction-based treatment • Due to the high investment cost, size reduction-based treatment requires high waste volumes to become economically viable • Recycling of PC/ABS plastic containing PFRs in Europe by a disassembly-based treatment is technically feasible and economically viable with existing technologies	[53]
PC/ABS, PC/HIPS, and ABS	Organic phosphate esters, BEO and TBBP-A	Multiple extrusion steps (a maximum of four recycling cycles and accelerated hydrolysis scenario)	• After an accelerated hydrolysis scenario, unlike plastics containing BFRs, none of the halogen-free flame-retarded plastics preserve the original mechanical properties (melt flow rate, mechanical strength, Izod impact) and fire behavior • Before and after the accelerated hydrolysis scenario, ABS samples (30 % and 100 % recyclate) containing brominated FRs could still pass UL-94 5VB tests after recycling • Halogen-free plastic materials showed considerable sensitivity to hydrolysis • None of the halogen-free samples passed the flammability test (UL-94 5VB) after accelerated humidity exposure • After recycling, HFFR PC/ABS and HFFR PC/HIPS failed UL-94 5VB tests • After recycling, ABS/BEO retained its flame retardant and mechanical properties	[118]
PC/ABS, HIPS, and PPO/HIPS	BFRs and P-containing additives	Multiple extrusion steps (i.e., multi-pass 100 % recycle evaluation)	• Only samples containing brominated FRs after recycling could still achieve UL-94 V0 class • HIPS samples containing EBP or EBTBP, and PC/ABS modified by the addition of BPADP showed very good recyclability in terms of Izod impact strength and melt flow rate • Based on preliminary results, PPO/HIPS formulations containing either RDP or BPADP maintained Izod impact strength after recycling	[119]
PA-6/PP blends	APP and different compatibilizers	Multiple extrusion steps	• After four recycling steps, blends showed a slight increase in Young's modulus and a decrease in elongation at break • The degradation of APP during the second extrusion cycle caused the decline in fire performances	[113,114]

Table 1 (*continued*)

Type of polymer-based waste	Flame retardant species	Recycling strategy	Recycling efficiency, technical details, and economic aspects	Refs.
PC/BFR and PC/KSS	BFR, KSS	Multiple extrusion steps (i.e., eight cycles of extrusions) by injection molding	• Recycled PC/KSS retained most of its original mechanical performances (e.g., Young's modulus) • Recycled PC/KSS still showed a V0 rating in the UL-94 test • Recycled PC/KSS and PC/BFR show slightly lower notched Izod impact strength	[116]
PC/ABS resin	BDP	Solvent extraction by DMCHA	• DMCHA was used to extract up to 13.97 % of BDP • PC/ABS resin and DMCHA could also be recovered via precipitation with recycling rates up to 94.63 % and 89.83 %, respectively	[136]
Anhydride-cured epoxies and brominated plastics from EoL WEEE items	BFRs	Thermochemical recycling (thermogravimetry and mass spectrometry analysis)	• Debromination of aromatic structures, release of hardener, glycidyl groups, and bromine-based compounds • For epoxy ester resins, pyrolysis of the ester bond, reforming the reactive epoxides and phthalic anhydride, occurs presumably from 386 °C either on brominated or not brominated systems • Debromination of tribromobisphenol A units and formation of brominated aliphatic take place at 500 °C, also favoring the occurrence of charring reactions • Scission of the isopropyl bridge of bisphenol A occurs at 500 °C in brominated systems and at higher temperatures in not-brominated ones • HBr production at about 600 °C in brominated systems	[164]
Plastics	TBBP-A	Pyrolysis	• Co-pyrolysis in the presence of Fe_2O_3 to form iron bromides and iron oxybromides from the release of HBr • ~90 % conversion rate of the bromine content in TBBP-A into iron bromide	[165]
Brominated epoxy resins	BFRs	Solvent washing	• DMF was used for the dissolution of BER followed by roasting with NH_4Cl • 97 % separation of BER • 93 % of copper-based species recovery from EoL waste of printed circuit boards	[175]
PUs and PIRs	TCPP	Pyrolysis	• Pyrolysis of high-resilient ether PU and semirigid PU at 600 °C were very similar and led to the following main products: ethylene and propylene (combined yield of ~13 wt.%), ~16 wt.% of various oxygenates, and 4–6 wt.% organic nitrogen compounds • PIRs were more difficult to decompose and volatilize than the PUs, resulting in ~20 wt.% higher residue yields • Pyrolysis of TCPP-containing PIR released Cl-containing pyrolysis vapours, for example, allyl chlorides • Pyrolysis of PIR at 300 °C allowed to recover diethylene glycol (2 wt.%) and benzoic acid derivate (6 wt.%), and oxygenated volatiles	[183]
PET textiles	–	Glycolysis	• Waste PET textiles were glycolytically degraded by ethylene glycol and chemically recycled into FR rigid PUFs • LOI of PUFs was around 23.27–25.38 %	[191]
PWBs	BFRs	Pyrolysis	• Powdered inorganic compounds (e.g., $CaCO_3$, CaO, and ZSM-5) were used to reduce the amounts of HBr and brominated oils released during the pyrolysis • ~18 g of Br-free pyrolysis oil per 100 g of PWB-based waste • ~36 g of uncondensed gas (i.e., rich in H_2, H_2O, CH_4, and CO_2), useful in syn gas production, per 100 g of PWB-based waste • Pyrolysis residue rich in Al_2O_3, CaO, C, SiO_2, $CaBr_2$, $ZnBr_2$ useful in the construction sector	[207]
EoL PWBs and waste cables (PVC)	–	Combined pyrolysis and decoupling gasification process	• The pyrolysis oil yield of 20 % (from EoL PWBs) and 27.3 % (from waste cables) • Pyrolysis char yield of 48 % (from EoL PWBs) and 42 % (from waste cables) • Major composition of synthesis gas product (10.91 vol.% (H_2), 23.4 vol.% (CO), and 5.68 vol.% (CH_4)) • 83.8–89.8 % regained by ultrasonication from the char • Reduction of about 36.1–41.7 % in LPG consumption, saving the cost of e-waste recycling up to 25.7–28.7 % with respect to traditional pyrolysis	[208]

Table 1 (*continued*)

Type of polymer-based waste	Flame retardant species	Recycling strategy	Recycling efficiency, technical details, and economic aspects	Refs.
Brominated epoxy resins contained in PWB-based wastes	BFRs	Solvent washing by subcritical acetic acid	• Acetic acid was used at 200 °C to convert BERs to bisphenol A and phenol at 2.6 MPa in about 1 h • At temperatures higher than 240 °C, bromine-free oil phase products could be obtained • At temperatures higher than 240 °C, some BPA degraded to phenol and p-isopropyl phenol • The analysis of costs for the whole process indicated that acetic acid is the main responsible for a large proportion of the total cost • The economic feasibility of the process may be improved by regaining acetic acid via extractive distillation	[209]
HVP/D230, HVP/CF(65 wt.%)-D230 laminate composite	HVP is a monomer derived from vanillin	Thermomechanical recycling and chemical recycling	• HVP/D230 exhibited a Tg of around 98.4 °C and UL-94 V0 class • HVP/D230 degraded and completely dissolved in the mixed solution of 1 M HCl aqueous solution and THF (v/v = 2/8) within 2 h at 25 °C, and nearly 100 wt.% of the HVP was retrieved • HVP/D230 could be reshaped and repaired by hot pressing at 120 °C and 18 MPa for 5 min, while HVP/D230-CF laminates were hot pressed at 120 °C and 18 MPa for 15 min • Recycled and repaired HVP/D230 did not show any decrease in terms of tensile properties (tensile modulus, tensile strength and elongation break) • 1-ply HVP/D230-CF exhibited a tensile strength of 184.4 ± 7.5 MPa, Young's modulus of 18.7 ± 1.1 GPa, and an elongation at break of 1.75 % ± 0.26 % • 12-ply HVP/D230-CF could be degraded at room temperature in the mixed solution of 1 M HCl/THF solution (v/v = 2/8) within 12 h, leading to a total retrieval of CFs and HVP monomer • HVP/D230-CF recovered more than 90 % and 75 % of its flexural strength and modulus, respectively • HVP/D230-CF exhibited less initial flexural creep than E51/D230-CF after 10 min force loading at 60 and 90 °C • Unlike E51/D230-CF, the strain recovery ratio of HVP/D230-CF decreased with the temperature increasing • HVP/D230-CF showed good creep resistance to maintain its dimension, as the creep of HVP/D230-CF was comparable with the one of E51/D230-CF after 50 min recovery	[231]
Polyimine vitrimer	Modified HCCP was used as the starting raw material	Thermomechanical recycling and chemical recycling	• The vitrimer showed a tensile strength of ∼56 MPa, high Tg of about 146 °C, UL-94 V0 class, and high LOI of ∼40 % • After one recycling step, recycled samples kept their tensile strength close to the values of the original samples • After three recycling steps, 90 % recycling efficiency in terms of mechanical properties (tensile strength and elongation break) • Monomers could be recovered by hydrolysis reaction (1 M HCl and THF (v:v = 2:8), within 60 min at 25 °C) • Polyimine vitrimers could be reprocessed by hot pressing small fragments under 15 MPa at 180 °C for 30 min	[232]
Vinylogous polyurethane vitrimers and their laminates with glass fibers	Phosphonate-based vitrimers using dichlorophenylphosphine oxide	Thermomechanical recycling	• After one recycling step, the phosphonate-based vitrimer (poly-1) exhibited a storage modulus of 0.36 GPa at 50 °C, while no P-containing vinylogous polyurethane (poly-2) had a storage modulus of 2.4 GPa at 50 °C (where DGEBA-based epoxy resins sowed storage moduli of 4.0–8.5 GPa at −25 °C) • After two or three recycling cycles, poly-1 kept similar properties as the original sample and unaltered Tg of 70 °C • In UL-94 vertical tests, poly-2 could not be classified, while poly-1 attained a V2 rating • Similarly to permanently cross-linked epoxy resins reinforced with the same glass fibers and processed via vacuum infusion, GFRCs based on poly-1 gave a bending strength of 387 ± 16 MPa and a bending modulus of 20.7 ± 0.7 GPa • GFRCs based on poly-1 showed a fiber failure under tension at the bottom sides and without larger-scale delamination of the layers	[238]

Table 1 (*continued*)

Type of polymer-based waste	Flame retardant species	Recycling strategy	Recycling efficiency, technical details, and economic aspects	Refs.
PE-CANs	HEMAP	Thermomechanical recycling and chemical recycling	• Due to their crosslinked nature, PE-CANs exhibited a rubbery plateau in the storage modulus curve above Tg (∼67 °C) • The activation energy was calculated to be 56.2 kJ mol^{-1} • PE-CANs could be reduced into small pieces and then reshaped by hot pressing at 110 °C for 1 h • PE-CANs could be dissolved in ethanol at 80 °C for 4 h, without using a catalyst, and repolymerized by simply evaporating the solvent and hot pressing • In agreement with stress-relaxation tests, the creep-recovery result of the PE-CANs confirmed their temperature-dependent dynamic crosslinked nature • The activation of the topology rearrangements at 105 °C causes an evident deformation increase (∼3.5 %) and high residual strain (∼3.0 %) • Due to the thermally stimulated associative phosphate esters exchange reactions, PE-CANs show faster strain creep at higher temperatures than 75 °C • The viscosity of the PE-CANs follows an Arrhenius law over a broad range of temperatures • The production of char-forming intermediates above 250 °C confers inherent fire safety characteristics to PE-CANs • The flame-triggered shape memory ability of PE-CANs is mainly due to their dynamic β–hydroxy phosphate ester chemistry	[247]
Epoxy vitrimer based on networked phosphonate esters containing both P–C and P–O bonds	TDPSD, i.e., bis H-phosphite monomer	Thermomechanical recycling	• Phosphonated thermosets exhibited high Tg (94–140 °C) and good thermal stability • Cryo-grinded epoxy vitrimer containing 6 wt.% P could be recycled by hot pressing at varied temperatures (i.e., 150 or 160 °C) under a pressure of 6 MPa for 5 min • Compared to the pristine resin, phosphonated thermosets with 2.5 wt.% P showed reduced pHRR (up to 75 %) during combustion, UL-94 V0 class, and less smoke toxicity • After scratching, a concentration of 6 wt.% P in phosphonated thermosets was necessary for damage reparability and recyclability • Recycling of phosphonated thermosets with 6 wt.% P could be repeated up to three times without any detrimental impact on the overall properties, with only a slight decrease in the flexural strength (15 %) and in thermal stability after the third cycle of reprocessing • Compared to the pristine resin, flax fiber reinforced thermoset composites containing 6 wt.% P and based on networked phosphonate esters exhibited improved flexural strength (∼6 times) from 8.7 to 55.9 MPa for a fiber volume fraction of about 40 %	[249]

small molecular weight compounds, or recover potential reinforcing fillers (e.g., carbon fibers, glass fibers) (Fig. 5) [43]. Table 1 reports main characteristics and outcomes of some recent recycling approaches of FR polymeric materials.

Interestingly, Vasile et al. [44] upgraded thermoset fractions of keyboards and printed circuit boards to liquid products by thermal and catalytic hydrogenation, also removing toxic BFRs during the process (Table 1). To reduce the production of thermosetting wastes and related sustainable concerns, PMs able to undergo closed-loop recycling are being developed, as the item can be used and then converted back to raw materials or turned into a new product indefinitely, without any detrimental impact on its properties during the recycling process [45]. In this context, recently, Wei et al. [46] prepared recyclable FR epoxy resins starting from itaconic acid-derived hyperbranched epoxy resin and (1,3,5-hexahydro-s-triazine-1,3,5-triyl) benzyl mercaptan. The structure of such materials enabled a closed-loop chemical recyclable network, which could be degraded to recover monomers with a yield of 86 %. The hyperbranched topological structure also conferred a notable improvement in terms of toughness and strength of the FR thermosets and the capability to be recycled multiple times without loss of performance, while the incorporation of itaconic

acid allowed the enhancement of flame retardant features [46]. Zhang et al. [47] synthesized a polymer-based coating showing very good closed-loop recyclability and self-extinguishing behavior. The coating, made of anionic polyacrylamide and fibrous nanosepiolite, could be deposited on the surface of flexible polyurethane foam via flocculation assembly to form a particular micromorphology. The research group demonstrated that the coating could resist high humidity, thermal aging (105 °C for 3 h), water, and chemical attack, keeping excellent flame retardant performances. In response to a pH stimulation, the recyclable coating could disassemble and recover with rates of 96 % and 97 %, respectively [47].

In the field of the chemical recycling of EoL PMs, the upcycling of polymeric wastes represents a new approach, involving the depolymerization of the waste into fuels, chemicals, or molecular intermediates and the subsequent reconstruction of these intermediates into valuable and functional chemicals by mild operative conditions [48,49]. The upcycling of permanently crosslinked thermosets aims to recover and reuse a fraction or a partial volume of the polymer matrix and their downstream materials. Türel and Tomović [50] synthesized two liquid monomers based on vanillin to prepare double-dynamic imine-acetal-containing thermosets in solvent-free conditions. Similar to commercial and tra-
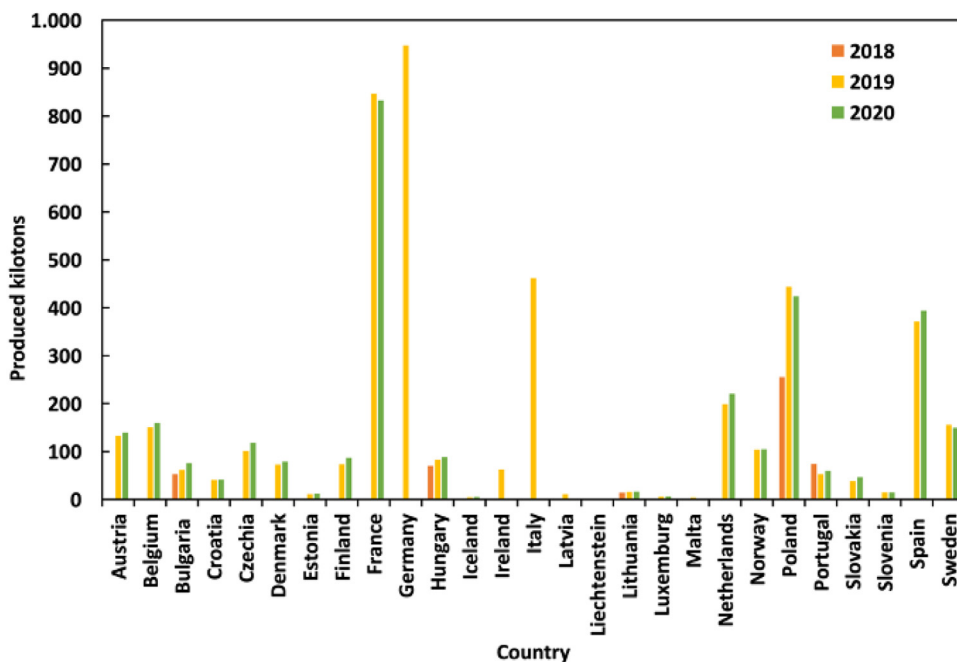
Fig. 4. Waste electrical and electronic equipment, the total collected from 2018 onwards (data from Eurostat 2022).
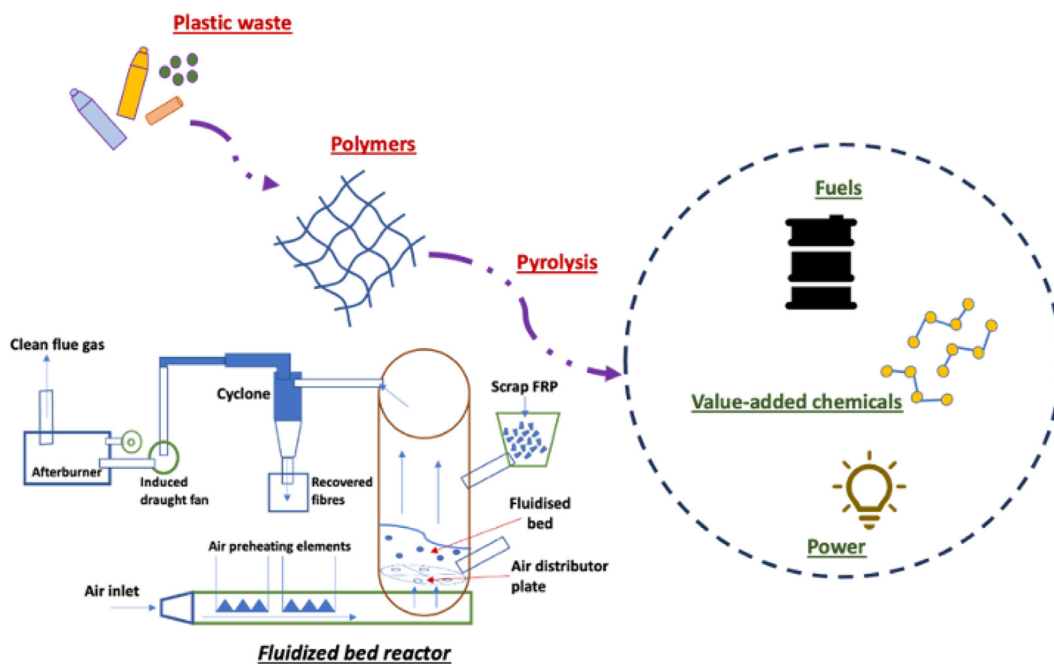
Fig. 5. Advanced thermochemical recycling processes, namely pyrolysis, lead to the production of intermediate chemicals including monomers, fuels, and other value-added products. In fluidized bed combustion, the fibers and other resistant fillers are recovered by separation in a cyclone. The recovered fibers may undergo a full oxidation process in a secondary combustion chamber, where the heat energy can be taken out from the exhaust gases [43].

ditional epoxy systems, these double-dynamic thermosets exhibit tensile strength values in the range of 50–70 MPa, but they could be fully depolymerized into vanillin to give original epoxy monomers and a mixture of polyols suitable for upcycling into high-performance polyurethane [50]. In the literature, the upcycling of FR EoL PMs is still missing, but few studies about that have been reported in the next sections of this review.

As an alternative to permanent crosslinked systems, research efforts on reprocessable FR thermosets have resulted in the development of CANs, which are materials that are easily recycled and reshaped in the absence of extreme operative conditions. CANs

can be produced from renewable and natural resources, such as vanillin. Wang et al. [51] employed vanillin as a precursor to prepare self-extinguishing thermoset composites composed of Schiff base CANs, for which the recovery of the monomer was possible at mild conditions by treatment with an acidic aqueous solution [51]. Reprocessable advanced thermosetting materials may significantly reduce the production of FR thermoset plastic waste, the depletion of precious chemical species, and environmental pollution.

Two foremost concerns of recycling processes, sustainability and effectiveness are strongly affected by the presence of still-functional FRs in EoL PMs. As reported in Fig. 6 [52], the PINFA
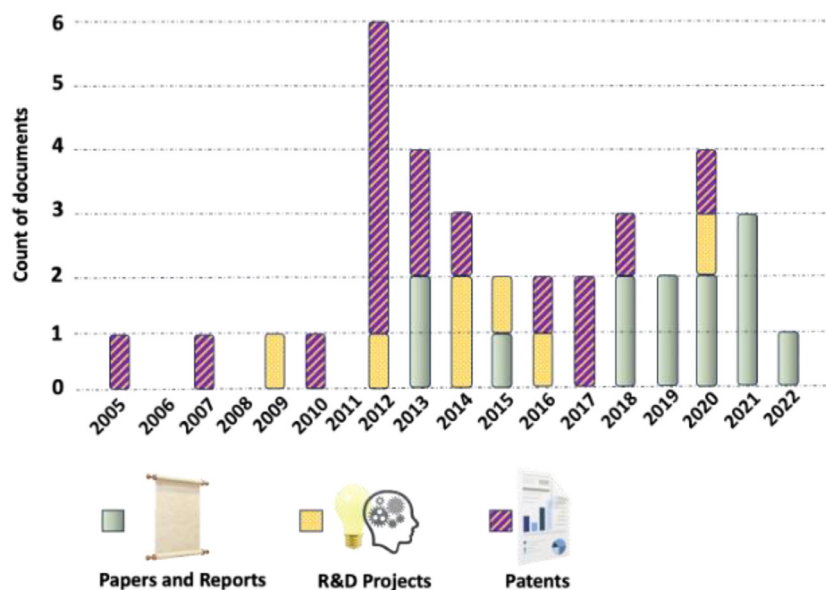
Fig. 6. Count of most interesting documents in the field of PIN FRs and recycling selected by the PINFA. Figure adapted from [52].

found out that the publication rate of papers and reports in the field of PIN FRs and recycling has increased in the last five years, with respect to patents and R&D projects. However, in order to find a solution for all the technical issues that concern the recycling of flame retardant PMs, this positive trend needs to be continuously promoted and encouraged.

Recently, Peeters et al. [53] summarized the main outcomes of some plastic recycling projects, focusing on the miscibility of different plastics, the recyclability of FR plastic housings, and the economic feasibility of closed-loop recycling processes on an industrial scale. On the other side, the review published by Charitopoulou et al. [25] mainly deals with the thermochemical recycling of brominated FR plastics from WEEE, providing several insights on the characteristics (i.e., operative conditions, product distribution, technical aspects) and advantages of catalytic pyrolysis processes compared to the conventional pyrolysis. Finally, Delva et al. [24] published a review discussing the influence of flame retardants in the mechanical recycling of plastic waste also listing several upgrading strategies for common polymeric waste streams.

The objective of this review is to highlight the main drawbacks and achievements related to current recycling methodologies of different classes (thermoplastics, thermosets, and covalent adaptable network systems) of flame-retardant polymeric materials. Also, this review aims to provide a good starting point for future goals, giving an overview of insights into the development of novel recycling methodologies for FR polymeric materials. Considering the most recent standards and statistical reports, the following sections aim to present a comprehensive perspective of the recent progress, challenges, and opportunities related to the recyclability and reprocessing approaches of several FR polymer matrices and their composite products. For simplicity, in this review, the different recycling strategies are broadly classified based on the different chemistry of thermoplastics, thermosets, and CANs. Further, the recycling approaches of plastics containing HFRs and HFFRs, and a few of the most investigated thermosets and CANs are categorized into subgroups.

2. Recycling of halogenated flame retarded thermoplastics

Thermoplastics have a wide range of applications, from packaging, electrical, textiles, and construction to automotive. HDPE, LDPE, PP, and PET are mostly used for packaging and are characterized by a short lifetime. Conversely, PVC, ABS, and PS are largely employed in the electronics and automotive sectors [54]. According to Plastics Europe [55], global plastics production in 2021 reached 390.7 Mt, and fossil-based thermoplastics account for 83.1 % of the production. Since many thermoplastics are highly flammable, many applications require the usage of FRs to deal with high fire risk and fulfill specific requirements. While halogenated molecules are not traditionally a part of plastics, which are generally dominated by hydrocarbons [56], the use of halogen atoms either in small molecule additives or in the backbone of the polymer matrix cannot be ignored. Today, there are many plastics and composites that use HCs and components offering enhanced FR properties to the materials.

Fig. 7 displays some of the most common halogenated FRs. Unfortunately, such HCs find a way to act as endocrine disruptors [59,60], unlike the more inert halogenated PMs like PVC. Moreover, during the life cycle of halogenated FRs, chlorinated or brominated furans/dioxins are produced, leading to toxicity in close human proximity [61]. This is the primary reason for phasing out or even banning such compounds from everyday use by international organizations and governments [62]. The European Commission in October 2019 as part of their Ecodesign Directive (2009/125/EC) approved an eco-design requirement prohibiting the use of HFRs in electronic display stands and enclosures within the European Union. Starting from January 2024, Washington State "Safer Chemicals" regulation will ban all organohalogen FRs from plastic enclosures of most EEEs employed for both indoor and outdoor uses [63].

Direct incineration should be reduced for the disposal of halogenated PMs or plastics containing HCs, as it would lead to an increase of volatile organic species like chloro– or bromo–carbons in the atmosphere [64], which either form corrosive acids and deplete the ozone layer [65]. Also, while most halogenated FRs degrade upon incineration, there exist exemptions like PBDDs and PBDFs which persist in highly toxic flue gases [66]. Therefore, tertiary recycling involving pyrolysis has to be done in a controlled environment trapping any residual halogenated by-products. Under such constraints, there have been a few reports wherein PMs and composites containing halogenated FRs have been effectively recycled. The following sections summarize and elucidate a few such studies.
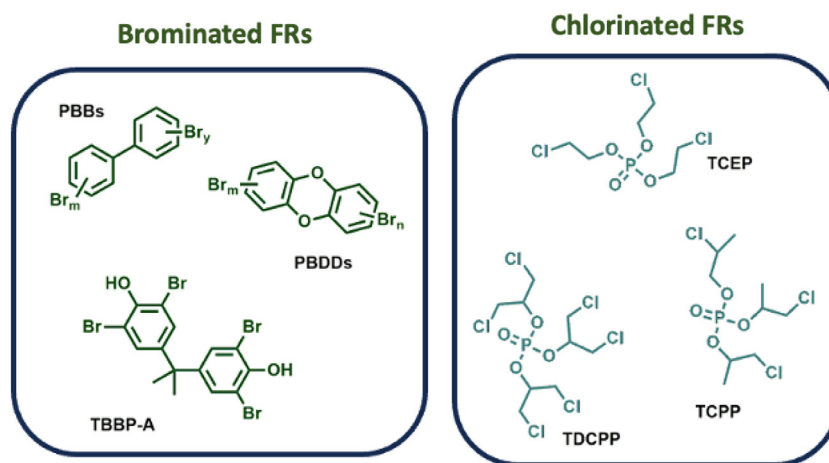
Fig. 7. Chemical Structures of commonly used HFR additives. (Left Box) Brominated FRs: PBDDs, PBBs, TBBP-A [57]; (Right Box) Chlorinated FRs: TDCPP, TCEP, TCPP are phosphate derivatives with 1,3 dicholoropropyl, 2- chloroethyl or 1-chloro-2-propyl groups [58].

2.1. Mechanical recycling of halogenated flame retarded thermoplastics

Mechanical recycling usually involves reprocessing of waste by extrusion, mechanochemical routes, melting, or moulding. Unfortunately, such processes do not dehalogenate the waste, therefore, the HCs are still present in the PMs. For inert halogenated PMs like thermoplastic PVC, this is not a problem and is considered an ideal method to achieve maximum economic utility with minimal environmental impact [67]. Indeed, PVC can be successfully recycled with a slight detrimental impact on the mechanical strength after reprocessing [68]. Since the use of some HCs is restricted, it is now mandatory to isolate them from waste like WEEE and composites before mechanical recycling [24,69]. To face this issue, high-resolution near-infrared devices can be used to screen plastics containing halogenated FRs before their mechanical reprocessing [70]. After the separation of the halogenated FR containing plastic-based fragments, the rest will go to further separation and recycling processes.

Polyamides can be natural (e.g., wool, silk) or artificial polymers. Artificial polyamides (e.g., nylons) can be made through step-growth polymerization and are commonly flame retarded to be used in carpets, kitchen utensils, automotive industry, etc. [71]. Based on a recent market analysis, 35 % of PA consumption is due to the transportation manufacturing industry [71,72]. Zhang et al. [73] studied the recycling of a PA-based glass-fiber-reinforced composite containing DBDPE. Due to its high decomposition temperature, DBDPE did not undergo degradation during several reprocessing steps of the PA-based composite, which could still show self-extinguishing behavior after mechanical recycling (Table 1) [73]. The recycling of FR PA-based glass-fiber-reinforced composite by a single screw extruder with the lowest shear force led to a decrease of only 5.8 % in mechanical properties. Polyesters are polymers composed of repeating units containing ester functional groups. Polyesters can be obtained as thermoplastic or thermoset, depending on their chemical structure. The most representative polyester is a commodity plastic named PET, for which in 2000 circa 30 million tons were fabricated worldwide [74]. PBT is another important thermoplastic engineering polymer, widely used as an insulator and plug connector in the electrical and electronics industries [74]. With respect to PET, PBT shows slightly lower rigidity and strength, but higher impact resistance. Generally speaking, the presence of ester groups, sensitive to hydrolytic degradation, negatively influences the intrinsic viscosity and final prop-

erties of recycled polyesters [74]. To overcome such limitations, solid-state polycondensation offers a valuable solution for the efficient recycling of FR polyesters, as it allows the production of polyesters with less sensitivity to hydrolysis [75]. Shuidong et al. [76] demonstrated the recycling of glass-fiber-reinforced composites made of PBT and BPS. Similarly to the case of DBDPE in PA-based glass-fiber-reinforced composite, DBDPE exhibits a decomposition temperature higher than the reprocessing operative conditions of PBT/BPS-based composites, enabling these latter to provide a V0 rating and good fire performances after recycling (Table 1). Also, the research group found that the rheological and mechanical properties of the recycled glass-fiber-reinforced composites appeared strongly influenced by the intrinsic viscosity of PBT, the average length of the glass fiber, the percentage of glass fiber length, and the carboxyl content of the polymer matrix. After five recycling cycles of PBT-based composites by injection molding, a significant reduction of the shear viscosity, impact strength, tensile and flexural strength was observed.

2.2. Chemical recycling of halogenated flame retarded thermoplastics

Chemical recycling converts plastic wastes into lower molecular weight products. This conversion requires the breaking of covalent chemical bonds, which occurs through quite endothermic and energy-intensive reactions. Based on the primary chemical process involved, this recycling technique can be further classified as gasification, thermolysis, photolysis, solvent washing, etc. In Europe, the removal of plastics containing BFRs from the waste streams is already performed, taking TBC as a reference sorting parameter (Fig. 8).

Plastics showing a TBC higher than 2000 mg/kg undergo recycling, in specific plants for WEEE plastics, and partial incineration. Plastics exhibiting a TBC lower than 2000 mg/kg are considered bromine-free, making them reusable for the manufacturing of recycled products that meet REACH and POPs regulations (European Electronics Recyclers Association 2018) [24]. To perform such selection based on TBC, recyclers can take WEEE Standards as a reference, ensuring that plastics being used again do not contain legacy BFRs [77]. Still today, only the TBC of BFR plastics is monitored in industry, whereas no recycling methodologies, involving sorting processes based on chemical composition, are employed for other FRs. In a recent report, BSEF has estimated that WEEE plastics contain approximately 3.5 % of BFR-containing plastics, including 3.2 % of non-restricted BFRs and 0.2 % of PBDE-containing
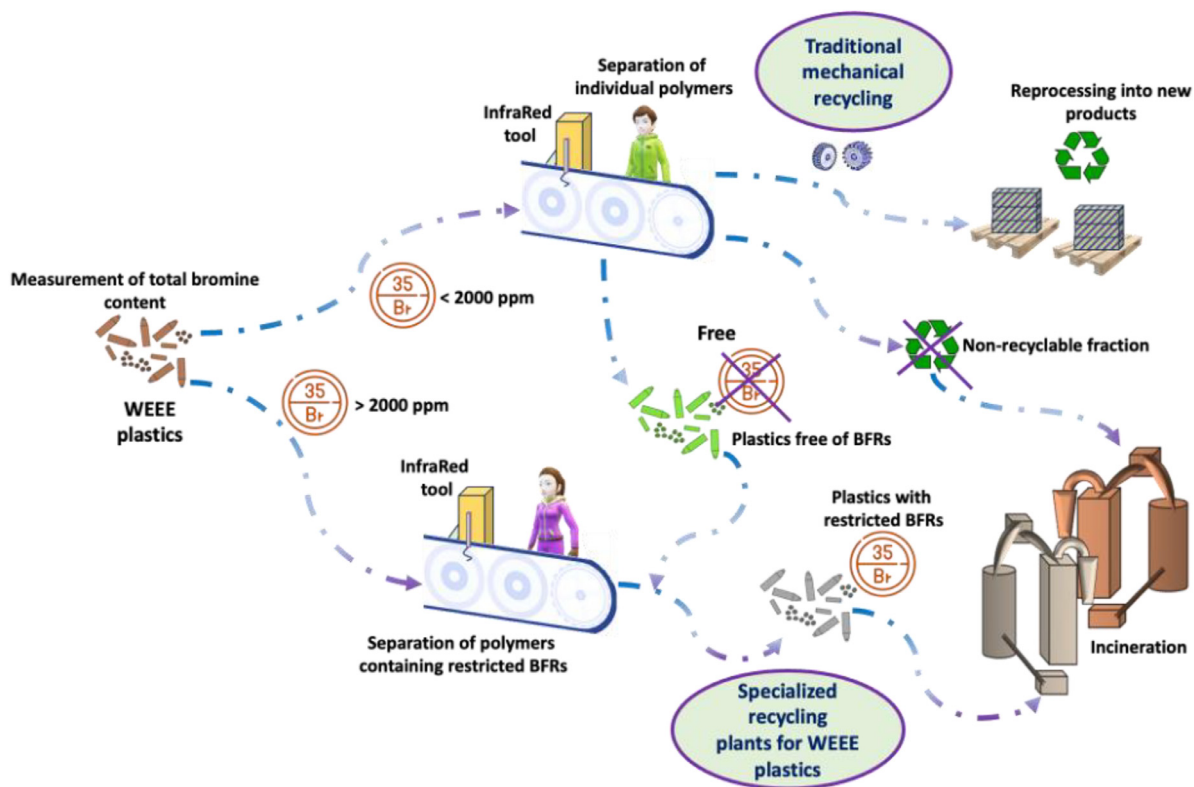
Fig. 8. Waste management of WEEE plastics containing brominated flame retardants (BFRs). Figure adapted from [24].

plastics [78]. In particular, screens and small pieces of equipment contain about 7–8 % brominated plastics, whereas cooling appliances and large pieces of equipment contain lower amounts [78]. However, around half of the plastic waste from WEEE does not undergo proper sorting in Europe, based on a recent study conducted by Sofies, which is an international B-Corp-certified sustainability firm [79]. Most of the plastic waste from WEEE is exported outside the European Union, where it is often burnt without measures to control toxic emissions. According to Sofies, the presence of toxic chemicals in daily products may be reduced, by banning the export of WEEE plastics to third countries, as the sorting process would be effectively carried out [79]. These observations have also been confirmed by BSEF in September 2023 [78]. Considering the 2.6 million tonnes of WEEE plastics produced in 2021 in Europe, only about 54 % of them were collected by officially established WEEE channels (Fig. 9). As regards the collected amount, ∼0.4 million tonnes (i.e., 15 % of the total) undergo proper recycling in specialized WEEE plastic companies in Europe [78]. Unfortunately, around 46 % of all WEEE plastics are not officially collected, which contributes to the illegal exportation of mixed waste outside Europe. On the other side, ∼68 % of all WEEE plastics have an unknown fate, probably due to inappropriate disposal or insecure recycling procedures (Fig. 9) [78].

An early industrial setup was experimented in Japan in 2003 by Yamawaki [80], which successfully gasified WEEE, and obtained usable raw materials without significant amounts of brominated toxic dioxins as by-products. More specifically, the processes developed by Yamawaki involved the treatment at high temperatures (over 1200 °C) of the waste plastics and the subsequent cooling of the produced gases under 200 °C to use them for electric power generation. Actually, this fast change of temperature along the process is responsible for the suppression of brominated and chlorinated dioxins to very low levels. Kakuta et al. [81] in 2008 de-

signed a combination of melt processing and hot water dissolution to dechlorinate plastics containing chlorine like PVC (Table 1). About 98 % of the chlorine from plastics was effectively removed as $FeCl_3$ [82]. Interestingly, the photolytic degradation of BFRs does not seem very effective as compared to thermal pyrolysis. Ling et al. [83] showed that UV radiation and natural sunlight can fragment BFRs into hazardous organobromides. Later on, Khaled et al. [84] proved that brominated volatile photoproducts are released by photo-transformation of PS films containing BFRs, therefore, wastes of such films could be a source of hazardous contaminants when exposed to sunlight.

Brominated FRs have been largely employed in the manufacturing of flame retardant ABS and HIPS, therefore WEEE based on such polymers are often found and need accurate dehalogenation during their recycling. The restrictions on BFRs are imposing an additional step to remove harmful substances from processing WEEE components (Fig. 8) [36]. Beigbeder et al. [70] investigated the optimization of the NIR sorting method in the screening of WEEE, proving that this technology could only detect the presence of FRs, especially brominated ones, without distinguishing between specific classes of these functional additives. BSEF is a Brussels-based trade association representing the international bromine industry. BSEF published a report on the recycling of WEEE in September 2023, where is reported that the BFR levels in WEEE plastics significantly vary across categories [78]. For example, in the period from 2010 to 2022, BFR levels in screens have gradually decreased, while in small and large pieces of equipment have remained relatively unvaried [78]. Interestingly, in recent samples of WEEE plastics, PBDEs represent only a small declining proportion of the TBC. This positive effect comes from the regulatory restrictions, which have decreased the average share of PBDEs in the TBC from above 20 % in 2015–2016 to below 10 % in 2021–2022 [78]. As part of the circular economy action plan 2020, BSEF and its member compa-
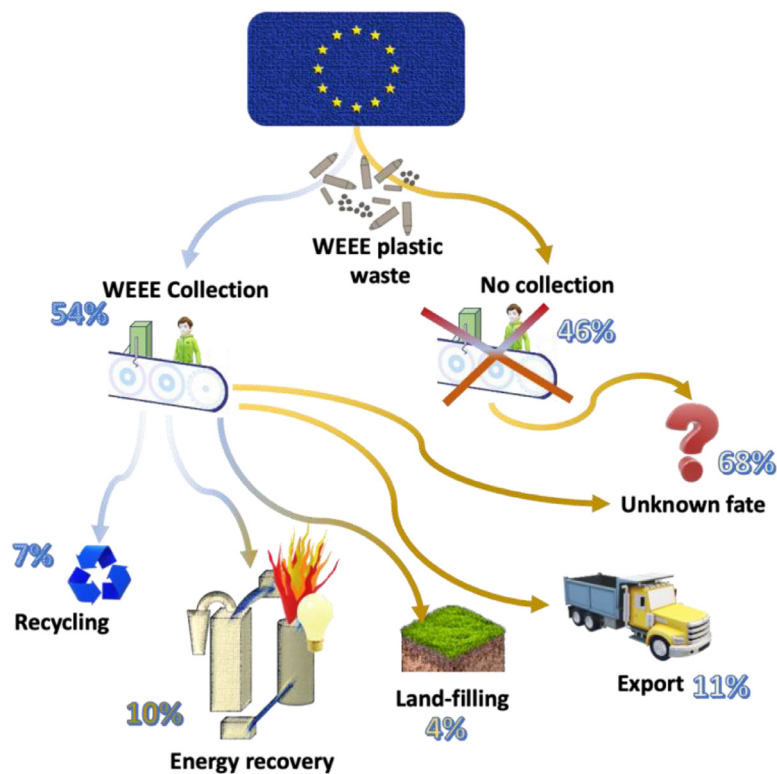
Fig. 9. The fate of WEEE plastic waste in Europe. Figure adapted from [78].
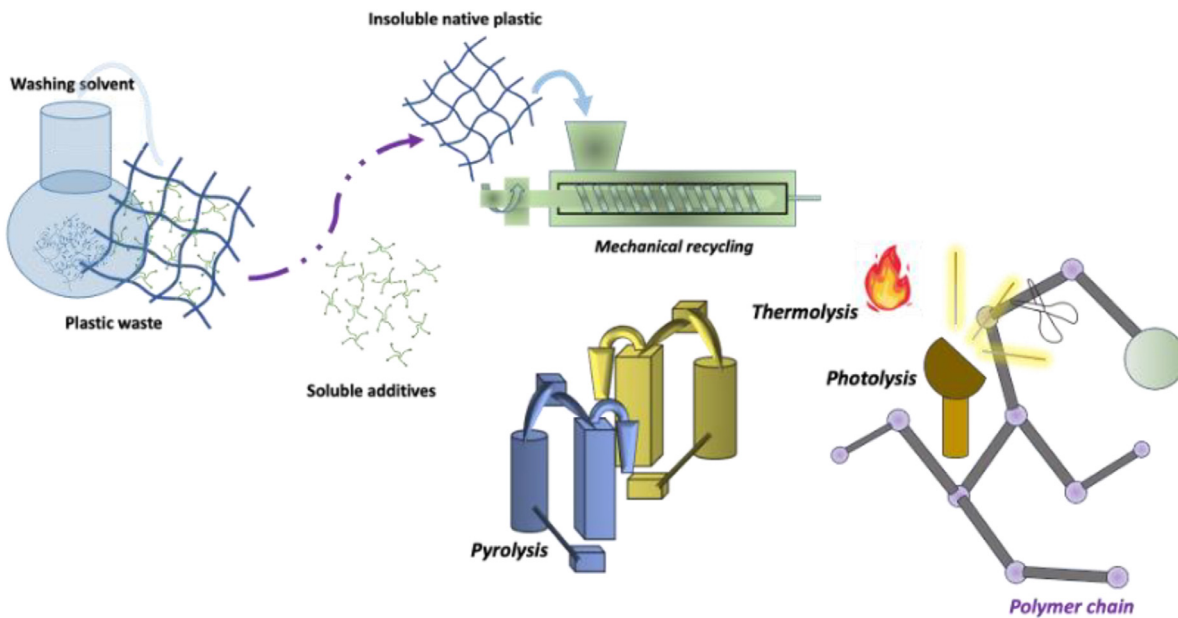
Fig. 10. Solvent-washing treatments separate halogen-based additives from the native thermoplastics, before being reprocessed by mechanical recycling or another sort of reprocessing unit.

nies have started several projects to improve the recycling of EoL plastics containing BFRs [85]. To give an example, BSEF along with the NAFRA and its member companies are supporting a methodology to sort and separate legacy BFRs from non-restricted BFRs by employing novel block-chain technology [85,86].

The pre-treatment of PMs with solvents may be a strategy to avoid the problems related to brominated or chlorinated by-products during the pyrolysis process or other recycling methods

(Fig. 10) [87]. Solvent washing is quite effective in selectively removing the halogenated additives from plastics, as the polymer matrix is usually insoluble in commercial solvents, while additives dissolve well (Fig. 10). For example, in 2019, Evangelopoulos et al. demonstrated that solvent-washing WEEEs with isopropanol or toluene before pyrolysis leads to the removal of TBBP-A and reduces the bromine content of the WEEE by 36.5 % (Table 1) [88]. The research group found that the content of several bromi-

nated organic compounds in WEEEs could be reduced and especially 2,4,6-tribromophenol and 2,5-dibromobenzo(b)thiophene reached complete removal. Finally, the thermal decomposition behavior of WEEEs and the solvent-treated ones was investigated, showing that the reduction of TBBP-A causes anticipation of the starting decomposition temperature. The commercial viability of the solvent-washing method led to the trademarking of the CreaSolv® Process by Fraunhofer IVV in Germany (Table 1) [89,90].

This method is a combination of dissolution and precipitation techniques able to selectively wash away legacy halogenated additives or softeners, while also recovering a large fraction of PE and PS (i.e., the polymer matrix), which are industrially relevant [91]. CreaSolv® Process is part of the EU LIFE co-funded Polystyrene Loop Project finalized to remove the HBCD from post-consumer construction polystyrene foam waste while recovering the bromine [92,93]. A demonstration plant, based on the CreaSolv® Process, of 3000 tons per year is under construction with an estimated cost of over 10 M€. CreaSolv® technology involves physical process steps and thus the polymer matrix of the plastic waste only has a change of its physical state and no chemical reactions occur, leaving intact the polymer chains in the material. Other processes are being scaled-up that involve the super-heated solvent recycling of ABS and HIPS in the PLAST2bCLEANED project and in the CLOSEWEEE project (both founded by the European Union) [94].

In 2012, Wang et al. [95] used supercritical isopropanol at 400 °C as a washing agent for BFR-containing waste computer housing plastic to obtain an oil (i.e., a mixture of aromatics and oxygen-containing compounds) with a content of brominated by-products equal to 60 wt.% and achieve a debromination efficiency of around 97.6 % (Table 1). Also, subcritical water at 350 °C allowed the removal of 90 % of bromine from the waste material. The addition of KOH into the supercritical isopropanol led to a Br-free oil as a product, which could be separated to recover precious phenols and other chemicals.

One of the drawbacks of using supercritical fluids like water, acetone, or alcohol for recycling is the extensive loss of organic components such as CO_2 and H_2O [96].

CPE is a low-cost variation of polyethylene, where chlorine is substituted for some of the hydrogen atoms till achieving a chlorine content of 44 % [97]. Due to its rubbery texture, CPE is often added to PVC in order to increase its weather resistance or cause the softening of PVC-based foils. CPE can undergo a crosslinking reaction with peroxides to produce elastomers used in rubber and cable industries. CPE can be employed as a functional additive to lower the flammability of other polyolefins. However, this variation of PE has been recently added to the Living Building Institute's Red List, which has prohibited its use and commercialization [98,99]. Li et al. [97] studied the possible reuse of CPE, in combination with antimony trioxide, to improve the fire behavior and mechanical performances of recycled PVC/propylene butadiene styrene blends.

Antimony has been recently included in the list of critical raw materials for the European Union and the United States [100,101]. Antimony can be frequently found in plastic wastes, for example (i) a residual FR synergist with brominated compounds; (ii) a decolorizing agent in lead-acid batteries; (iii) a still functional additive in EoL PVC; (iv) a catalytic residue used in the fabrication of PET [102]. To date, no suitable technologies exist for the complete recovery of Sb from plastic wastes [103]. Consequently, traces of Sb can be detected in products derived from the recycling of such materials, and in particular those recycled from waste electronic items. Some major issues related to the incineration of flame retardant plastic wastes containing Sb are not only the trapping of this latter from the flue gases but also its leaching from the bottom ash, which makes very complicated the regain of this metalloid [102,103]. Future research efforts should be devoted to the

development of recycling methodologies considering an effective removal of Sb along the reprocessing of waste plastics or the reuse of EoL PMs containing antimony-based species as flame retardants for recycled plastics.

We can conclude that to recycle WEEE properly, there is an urgent need to dehalogenate them effectively. Chemical recycling is the favored method to achieve this goal, as mechanical recycling only focuses on re-extruding or re-melting the plastics. Solvent washing steps are useful to isolate halogenated additives from the native plastics, which can then be subjected to mechanical recycling or other reprocessing technologies. Still, the only way to eventually degrade the HCs is by thermal energy, using pyrolysis (thermochemical recycling), friction, or gasification.

3. Recycling of halogen-free flame retarded thermoplastics

Considering the health risks and the environmental issues linked to using HCs as FRs for plastics, the global consumption of HFFRs, including organophosphorus, N-based, and other chemicals, has increased up to 70 % until 2019 [104].

P-containing and/or N-containing organic compounds are frequently used as HF alternatives, mainly used in EEE, building construction, transportation, and furniture. A few HFFRs are shown in Fig. 11. However, plastic waste containing HFFRs is challenging to recycle due to the heterogeneous composition and the different physico-chemical properties (e.g., thermal stability) of the polymer matrix and the FR. These aspects represent a limit in the effective recycling of HFFR thermoplastics [105], which the scientific community needs to overcome [106–108]. There are several methods of managing possible contaminants (i.e., halogen-based species) present in HFFR thermoplastics, such as density separation in recycling plants to eliminate brominated FR plastics from the waste stream [109]. Despite efforts to address brominated additives, it has been found that the recovered thermoplastics from WEEE waste are often contaminated by brominated residuals that are usually more resistant to aging than P compounds. Beigbeder et al. [70] applied sorting procedures of brominated plastic wastes by near-infrared to different plastics and featured that the trace of impurities had a negative impact on the fire behavior of recycled thermoplastics. As mentioned earlier, before implementing a recycling approach, it is crucial to identify and separate the components of WEEE by several techniques [110,111,69]. Peeters et al. [53] investigated the technical and economic feasibility of a specific waste stream composed of EoL LCD TVs in two scenarios: (1) manual disassembly and (2) size-reduction process. The EoL LCD was mainly composed of plastics (i.e., PC and ABS) with a content of 18 wt.% BFRs and 31 wt.% PFRs respectively. They set up some laboratory-scale experiments to demonstrate that the closed-loop recycling of PC/ABS-containing PFRs is feasible (Table 1) [53].

3.1. Mechanical recycling of halogen-free flame retarded thermoplastics

Mechanical recycling of HFFR thermoplastics is the preferred waste management strategy due to its low costs and environmental sustainability. Also, it often preserves most of the properties (e.g., mechanical performance, fire behavior) of the material. Many HFFR thermoplastics are extremely sensitive to hydrolysis and thermal degradation. For example, thermoplastics containing PFRs undergo degradation due to phosphoric acid generated by the hydrolysis of FRs. Therefore, the concentration of the FRs may decrease during their service life and recycling process [112].

To understand the influence of FRs on the mechanical recycling of thermoplastics, repeated extrusion cycles are commonly used to study the mechanical recycling of HFFR plastic wastes
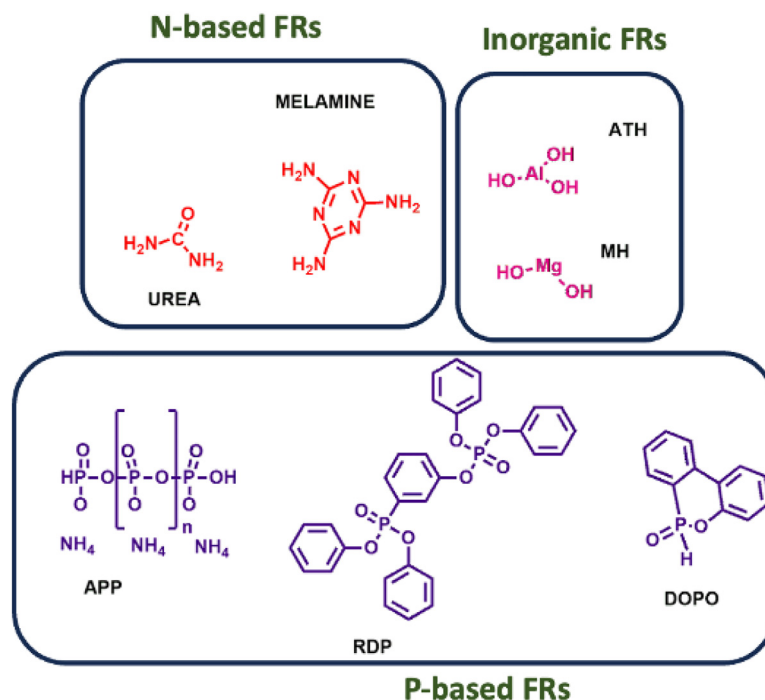
Fig. 11. P-based FRs: RDP, DOPO, and APP are resorcinol bis(diphenylphosphate), 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, ammonium polyphosphate, respectively. N-based FRs: melamine and urea are often used in combination with P-based FRs. Inorganic FRs: ATH is aluminum hydroxide and MH is magnesium hydroxide, both metal hydroxides need a high dose to achieve fire performance.

[41,53,109,113–117]. Imai et al. [118] studied the recyclability of various plastics from WEEE containing BFRs (e.g., BEO and TBBP-A) and HFFRs using multiple extrusion steps (Table 1). Unlike brominated ABS, after the first extrusion recycling step, PC/ABS and PC/HIPS containing organic phosphate esters showed lower mechanical performances and failed the UL-94 5VB tests. With respect to the Izod test, ABS/BEO retained its properties but the majority of plastic materials did not preserve a stable mechanical strength after recycling. Moreover, in order to study the effect of the humidity from the air on the recyclability of both HFFR thermoplastic systems, the research group hydrolyzed (up to ∼100 %) PC/ABS and PC/HIPS samples before their extrusion. None of the recycled HF thermoplastics could pass the UL-94 5VB flammability tests, due to the negative effects of hydrolysis. However, such materials exhibited a significant increase in melt flow rate [118]. On the contrary, virgin and hydrolyzed ABS samples containing brominated FRs could pass the UL-94 tests. It appears clear that the mechanical recycling of HF thermoplastic waste and the quality of the recycled materials are strongly influenced by the chemical composition, water content, and physico-chemical properties of the plastic waste stream [115]. Dawson and Landry [119] studied the effect of different BFRs and P-containing additives on the recyclability (i.e., multi-pass 100 % recycle evaluation) of PC/ABS, HIPS, and PPO/HIPS. After reprocessing, only BFRs could still guarantee the UL-94 V0 rating of recycled materials (Table 1) [119]. Particularly, HIPS samples containing EBP or EBTBP showed very good recyclability in terms of Izod impact strength and melt flow rate, together with PC/ABS modified by the addition of BPADP [119]. Based on preliminary results, PPO/HIPS formulations containing either RDP or BPADP maintained Izod impact strength very well after their recycling.

The recent introduction of eco-labels and restrictive legislations are fostering the replacement of HFRs with PFRs to be used as additives by the original equipment manufacturers during the fabrication of EEE [120]. As a result of this different approach, several PFRs, for example, RDP and BDP, are increasingly found in WEEE, especially in waste streams composed of PC/ABS and HIPS/PPE [120].

PP is a thermoplastic polymer used in a wide variety of applications, especially in the packaging industry, owing to its high chemical resistance. It can be obtained via chain-growth polymerization from the monomer propylene. Concerning its overall performance, PP is a highly flammable no-charring polymer, therefore it requires the addition of flame retardants to pass fire safety requirements [121]. Due to its poor fire resistance, the U.S.-based National Fire Protection Association has assigned a fire hazard classification of four to PP [122]. Almeras et al. [113,114] studied the mechanical performance and flame retardancy of recycled APP/PA-6/PP blends incorporated with different compatibilizers (Table 1). After four extrusion cycles, the recycled blends showed a slight increase in Young's modulus and a decrease in elongation at break. As indicated by ^{31}P NMR results of reprocessed materials, degradation of APP generated orthophosphate and pyrophosphate during the second extrusion, which explained the significant decline in the fire performance [113]. Also, accelerated aging can be used to investigate the effectiveness of a recycling process toward a specific plastic waste stream, as recycling can be considered a form of aging to some extent, particularly when anti-aging agents are consumed. Turku and Kärki [123] studied the effects of accelerated aging of PP-based WPC containing different commercial inorganic FRs (i.e., aluminum trihydrate, zinc borate, melamine, graphite, and titanium dioxide). The tensile strength and modulus declined during aging in all the investigated composites, as the presence of water caused cracks on the composite surfaces. To follow a waste-to-wealth approach and reduce tool wear constraints, Zaman et al. [124] demonstrated the possibility of replacing glass fibers with waste newspaper fibers in the manufacturing of flame-retardant PP-based composites. The research group compounded MH, together with zinc borate and ATH, into the polypropylene filled with 50 wt.% of secondary fibers. Final PP-based composites

showed a significant increase in LOI and a decrease in horizontal burning rate compared to the fiber-reinforced material without HFFRs. The inclusion of HFFRs slightly reduced the mechanical performances of PP-based composites [124]. EoL vehicles represent one of the big issues of our society, as effective recycling of their components is still a challenge. To avoid the formation of huge amounts of stocked waste materials, the transformation of such wastes into second-life products by closed-loop recycling strategies would be highly desirable. From this perspective, Bodzay et al. [125] upgraded recycled PP waste separated from automotive shredder residue to a multi-layered flame retardant composite by the addition of glass fibers as reinforcing agents, an intumescent system, and recycled polyurethane as a charring agent. The recycled layered composite showed tensile and flexural properties similar to the reference PP, therefore it is still useful for several engineering applications [125].

Statler et al. [116] investigated the flammability and mechanical properties of recycled HFFR PC containing KSS, compared with commercial PC/bromine samples. After eight cycles of extrusion, PC/KSS retained most of its original mechanical performances (e.g., Young's modulus) and still showed a V0 rating in the UL-94 test as well as PC/Br samples (Table 1) [116]. Sony Semiconductor Solutions Corporation developed SORPLAS (Sustainable Oriented Recycled Plastic) which is a FR polycarbonate with a high recycled content [126,127]. SORPLAS is formed from PC, recovered by the treatment of water bottles or optical discs, and blended together with a sealed flame retardant, PSS-K, and other additives. Based on Sony, a loading lower than 1 wt.% of PSS-K into recycled PC is enough to guarantee V0 (1.5 mm) flammability class, where usually higher concentrations of common phosphate ester- or bromine-based flame retardants are necessary [126,127].

PPS is a high-temperature engineering thermoplastic composed of aromatic rings linked by sulfides. Due to its chemical structure, PPS exhibits high thermal and chemical stability, making this polymer suitable for being applied as filter fabric for coal boilers in fossil fuel power plants, film capacitors, gaskets, etc. [128,129]. The large use of PPS results in the production of a huge amount of waste. EoL fiber filter bags made of PPS are usually submitted to mechanical treatment for the production of waste PPS powder. Wang et al. [128] investigated the use of such powders as flame retardants for epoxy resin, proving that PPS powders could improve thermal stability and reduce the heat release of final composites. Later on, Wang et al. [129] found a strategy to exploit waste PPS staple fibers in the preparation of flame-retardant fiber-reinforced PLA composites showing enhanced crystallinity and thermal behavior compared to pure PLA material. In a view of sustainability, Dong et al. [130] also used soybean protein, naturally rich in nitrogen, dosed with phosphite to obtain self-extinguishing PLA composites showing reduced flammable gas emission and low environmental impact.

As demonstrated above, PFRs are shown to have multiple effects on the processing and recycling of thermoplastics. For instance, DOPO-PEPA is shown to reduce the melt viscosity of PET during extrusion [131,132] enabling its reprocessing at lower temperatures. As previously mentioned, recently, Bascucci et al. showed that PET/DOPO-PEPA also maintains its mechanical performance and tensile properties (e.g., Young's modulus, maximum tensile stress, tensile strain at maximum stress, tensile strain at break) after three extrusion cycles and an injection molding step [41]. However, PET containing Aflammit PCO 900, a commercial organophosphate compound, completely loses its properties (i.e., loss of toughness and ductility) after such recycling attempts [41]. Such behavior was ascribed to differences between the chemical reactions initiated by these PFRs in PET at elevated temperatures.

As regards mechanical recycling, the control and the complete understanding of the effects related to the shift to PFR thermoplastics on the environment and the recyclability still require additional further research.

3.2. Chemical recycling of halogen-free flame retarded thermoplastics

The optimal recycling method for a specific plastic waste stream significantly depends on the composition of the polymer matrix and its FRs. Tertiary recycling (i.e., depolymerization, pyrolysis, gasification, and dissolution) represents a viable alternative to deal with mixed waste streams composed of HFFR thermoplastics, which are difficult to recycle by mechanical processes. In Europe, 7.2 billion euros are planned to be invested in chemical recycling plants by 2030, and the production of recycled plastics is expected to increase to 3.4 Mt [133].

Mechanical recycling does not involve the separation of additives and plastics from waste streams of heterogeneous compositions, which downgrades the properties of the recycled plastics. To deal with this issue, chemical recycling strategies have been gaining increasing attention, including solvolysis and other depolymerization processes [134,135]. Wang et al. [136] used DMCHA to extract up to 13.97 % of BDP from commercially available plastics, namely PC/ABS resin. PC/ABS and DMCHA could also be recovered via precipitation with recycling rates up to 94.63 % and 89.83 %, respectively (Table 1). Recently, Zadeh et al. [137] demonstrated the possibility of enhancing the flame retardancy of polymer blends made of PP, LDPE, and HDPE using magnesium hydroxide and recycled date palm fiber waste. This sustainable approach strongly reduced the manufacturing costs and allowed to keep good mechanical properties for the final products [137]. Also, Feng et al. [138] opened new perspectives on the flame retardation of HDPE, highlighting the possibility to obtain high-performing polyethylene with sustainable features. The research group used MH and phytic acid, a bioderived compound found in plants, to prepare HDPE showing UL-94 V2 flammability class and very low total smoke production as well as peak heat release rate, compared to neat polymer [138].

Currently, mechanical recycling is the predominant technique employed in HF thermoplastic waste management. The presence of contaminants can degrade the quality of the recycled plastic. Proper cleaning and sorting processes are crucial. As the requirements of recycling quality and scope have been increasing, more efforts are being made in chemical and thermochemical recycling techniques.

4. Recycling of flame retarded thermosets: moving from permanent to dynamic covalent approaches

The unique properties of thermosets have resulted in their extensive usage in various applications, resulting in the production of a huge amount of waste. Once cured, thermosets cannot be remelted or easily reshaped [139]. EoL thermoset materials are considered extremely tough to recycle, even more so the ones containing valuable components (e.g., metal, glass, and carbon fibers) or FRs [15]. Thermosets are also used to prepare fiber-reinforced composites applied as components in lightweight materials [140]. As a result of the high thermal and chemical stability of thermosets, the recycling of such materials is challenging. Currently, thermosets represent around 20 % of global fossil-based PMs, with an average annual production of ∼65 million tons [7,8]. The most common methods to dispose of thermoset wastes are landfills, sea dumping, and incineration [141,142]. According to the Environmental Protection Agency's, such approaches are leading to environmental pollution both within and outside Europe [143].

The European Union's Waste Framework directive has indicated the direct re-use of high-performance EoL thermosets and their components in lower-quality applications (e.g., housing equipment)
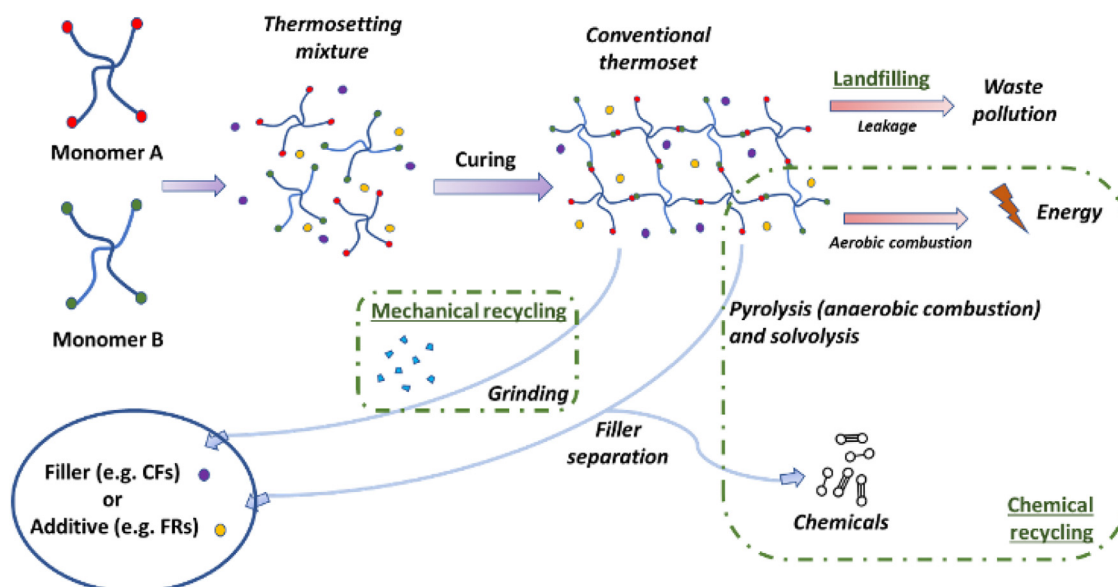
Scheme 1. Main recycling routes and reprocessing methodologies of conventional thermoset composites [144,146].

as the most advantageous method of recycling [144,145]. This waste-to-wealth approach reduces costs and reprocessing steps, though thermoset wastes are not always adaptable for a specific need owing to geometry reasons [146,147]. Direct re-use (primary recycling) may also be a valuable way to solve the problems inherent in recycling thermoset wastes containing FRs, as FRs will continue functioning in the recycled product. However, the limitations of this re-use approach do not allow for considering it as an effective solution in addressing the recycling of thermoset waste. Scheme 1 summarizes the overall recycling routes applied for the waste treatment of conventional thermosetting composites [148]. Thermoset wastes can also undergo mechanical or chemical recycling, depending on the desired final product or other specific needs. Mechanical recycling mainly involves the grinding of the thermoset waste to obtain ground thermoset powders, which are typically re-applied as fillers, without any chemical modification or evaluation, for the preparation of lower-quality composites or cement (Scheme 1) [7,144]. Chemical recycling consists of solvent-assisted depolymerization or pyrolysis-oxidation processes (thermochemical recycling) finalized to regain the precious filler from the composite or recover energy by degradation of the thermoset matrix (Scheme 1) [149,150]. Both approaches do not allow the regain of the thermoset matrix, but only fibers or fillers.

In addition, current technologies adopted in mechanical or chemical recycling do not consider the presence of FRs in the thermoset wastes. Such FRs often undergo the same destiny as the polymer matrix, therefore they are completely burned or re-used as functional additives in the ground thermoset. The largest amount of FRs are HCs, which may release toxic gases and secondary pollutants during the mechanical and chemical recycling of the thermoset waste [24,144]. This lack of consideration causes negative consequences on both the economy and the environment. Recent European restrictions are constantly moving the scientific community toward the development of saving-energy lightweight thermosets-based composites and the implementation of recycling technologies to reduce waste after EoL [151]. The development of "vitrimer" thermosets based on CANs may offer a promising alternative for easier recyclable and reprocessable systems [152,153]. Growing industrial interest in CAN crosslinked systems is demonstrated by recently published reviews and some instances of recyclable thermosets that are about to hit the market [154–157].

4.1. Mechanical recycling of conventional flame retarded thermosets

Mechanical recycling transforms scrap thermoset wastes with different shapes into sized flakes of around 50–100 nm by grinding and cutting steps in a crushing or speed-cutting mill. Indeed, this process is performed for both thermoplastic and thermoset wastes, even containing fillers or FR additives in the polymer matrix [24,149]. Unlike thermoplastic flakes, thermoset ones must undergo additional grinding in high-speed mills to obtain finer products showing sizes in the micrometer range [148]. As recently reported in the literature [158,159], in order to be competitive in the market, especially in terms of costs and energy-demand, the ground products may be properly tailored before being re-used by upcycling as reinforcing fillers for the preparation of polymeric composites showing good overall performances.

4.2. Thermal/Chemical recycling of conventional flame retarded thermosets

Thermal recycling of thermoset wastes mainly consists of two different processes: anaerobic and aerobic combustion [160]. Anaerobic combustion is also named pyrolysis, as it involves the degradation under the inert atmosphere of the organic matrix. In almost all of these waste treatment processes, fillers and additives are not separated by the matrix, therefore they may decompose releasing secondary products and eventual toxic species [161]. The most applied aerobic thermal treatment is incineration, which is not finalized to obtain a recycled product, but it uses oxygen as the main combustive agent to produce recovered energy [43,162]. During the pyrolysis or anaerobic combustion of EoL thermosets, the thermoset matrix breaks down into lower molecular weight organic compounds, which represent value-added chemicals of different types depending on the original material (Scheme 1) [163]. Luda et al. [164] studied the evolved gases from the pyrolysis recycling of sealants and putties, which are both used in integrated circuits and represent two of the main components forming EoL WEEE items. These materials are made of brominated anhydride-cured epoxies, and the study found that their thermochemical recycling resulted in the debromination of aromatic structures, the release of hardener, glycidyl groups, and bromine-based compounds (Table 1) [164]. All these species

negatively impact the environment and human health [60]. Later, Altarawneh et al. [165] also showed that plastic containing TBBP-A could be co-pyrolyzed in the presence of Fe_2O_3 to form lower toxic iron bromides and iron oxybromides from the release of HBr (Table 1), leading to ~90 % conversion rate of the bromine content in TBBP-A into iron bromide. EoL wind turbine blades (WTBs) have been increasing in the last years and thus the demand for effective recycling methodologies of them is growing [166]. Pyrolysis is the most promising technology for the recycling of WTBs, as it allows to regain glass fibers and depolymerize the waste into combustible oil. Xu et al. [166] pyrolyzed the epoxy resin fraction of end-of-life WTBs under different atmospheres and studied the mechanical properties of recovered fibers. The research group obtained good yields (up to 14.98 wt.%) of pyrolysis oil, together with some phenolic products, and 78.80 wt.% of glass fibers showing a slight decrease (5.97 %) of tensile strength. However, the presence of eventual FRs in the polymer matrix was not considered during the recycling process. It appears evident that in order to promote the spreading of pyrolysis technology in the recycling of EoL thermoset wastes containing FRs (e.g., HCs), it is urgent to foster the development of greener strategies enabling the dehalogenation of streams and the reduction of both pollutant emission and the energy demand during the process [167]. Chemical recycling includes glycolysis, solvolysis, and hydrolysis. Some thermosets (e.g., unsaturated polyesters) can be broken down by reacting with glycols or solvents to recover chemicals [168]. Solvolysis represents a method based on the principle that the polymer matrix in a thermoset composite waste can be converted to chemicals (Scheme 1) [169]. These chemicals can undergo further processes to obtain several types of polymers [170]. Nevertheless, the recycled matrix and fibers are often partially damaged and, thus, for downgraded use or not reusable [171–173]. Recycling by solvolysis presents several advantages with respect to thermochemical strategies. More in detail, recycling by solvolysis does not result in the formation of char, which negatively affects the quality of the fiber surface. Moreover, thermal recycling processes usually require higher temperatures and pressurized reactors, while the solvolysis is often performed using environmentally friendly alcohols and supercritical water, where this aspect lowers the costs related to the processing [174]. Nevertheless, the majority of solvolysis methods need to be conducted at temperatures above 200 °C and extreme pH conditions, where the largest number of FRs decompose, releasing hazardous compounds and toxic species into the environment [24,174]. This means that future research efforts will have to focus on the development of low energy-consuming methods, where not only the polymer matrix but also other organic components, for example, FRs or other FR moieties, can be easily regained from the selected solvent.

Some recent works are moving in this direction. With a view of sustainability, Panda et al. [175] developed a recycling strategy enabling the separation (97 %) of BER and the recovery (93 %) of Cu as copper-based species from EoL waste of printed circuit boards (Table 1). The possibility of regaining Cu is highly desirable to reduce the depletion of natural resources. Dimethylformamide was used for the dissolution of BER and its removal prevented the formation of toxic PBDDs and dibenzofurans during the recovery of Cu [175]. Kim et al. [176] fabricated a recyclable flame-retardant carbon-fiber-reinforced EC using plant-originated TA. TA acted as a reinforcing filler, char-former, and smoke-suppressing agent in the final composites. TA-based ECs could be chemically recycled through oxidative degradation treatment with supercritical water, releasing high yields (up to ~99 %) of reusable CFs [176].

The next sections will summarize some recycling strategies for the most common thermosets and recent progress concerning the recycling methods of thermosets with inherent recyclability, allowing the overcoming of several limitations and drawbacks linked to the waste treatment of conventional FR EoL thermosets.

4.2.1. Unsaturated polyester resin

Unsaturated polyesters are composed of cross-linked alcohols and unsaturated dibasic acids. The high chemical resistance and mechanical properties of such polymers make them suitable to be used as matrices in composite materials [177]. UPR and its GFRCs are widely employed in the manufacturing of wind turbines and in the aviation sector. UPR-based end-of-life components and unused prepreg are raising several environmental issues because of their extensive use [168,178]. Therefore, it is vital to develop efficient recycling procedures for UPR-based products. However, UPR and its composites have a permanent three-dimensional polymer network, which makes their recycling quite difficult. Currently, mechanical, thermal, and chemical techniques are available for recycling [179]. Chemical methods are the most effective, although they still require strong corrosive solvents (such as nitric acid) and high temperatures to break the chemical bonds of UPR. Using 80 % hydrazine hydrate and NaOH, Wang et al. [168] broke down ester bonds in UPR by hydrolysis. This moderate hydrolysis-oxidation synergistic catalytic method was carried out at 100 °C and performed via the Fenton reaction to achieve 98.28 % degradation of the resin in UPR-based composites. The research team was able to recover carbon fibers that were similar to virgin carbon fibers in terms of morphology, chemical composition, and tensile strength (i.e., 3.05 GPa for recycled CFs, which was closed to the one, 3.33 GPa, of virgin CFs) [168]. Yao et al. [180] modified the dimethacrylate monomer to make it able to self-polymerize and give an intrinsically recyclable UPR-based material. By adding the resulting resin into an aqueous solution of hydrazine hydrate for 3.5 h at 90 °C, the resin could be selectively cleaved apart and degraded. The research group demonstrated that the degradation products, which were characterized by benzene and carboxyl/carboxylate groups, could be easily separated, and then employed as flocculants or functional species [180].

Due to the high flammability of virgin goods, most of the UPR-based wastes contain FR additives, hence more research efforts need to be devoted to the development of methods involving the recycling of flame-retardant UPRs and related composites.

4.2.2. Polyurethane

PUs are frequently employed in a variety of industrial applications because of their robustness and inexpensive processing. They are used in the production of bedding, electronic components, insulation materials, WTBs, and other commodities [181,182]. However, these materials are challenging to recycle because of the chemical features of PUs, which give them exceptionally lightweight and chemical stability properties (Table 1) [183,184]. Around 30 % of the waste made from PUs is recycled or landfilled, while the other 40 % is transformed into energy using thermochemical processes [185]. Mechanical, chemical, and thermochemical methods (e.g., microwave-assisted pyrolysis) are used for PU recycling [186,187]. The most efficient and promising method is chemical recycling, which involves the breaking down of the PU backbone to recover raw materials that can be recycled into new PU-based goods [185].

Pyrolysis and gasification are mostly exploited to convert PU waste into syngas or added-value monomers, respectively [186]. Glycolysis, aminolysis, alcoholysis, and hydrolysis are frequently employed approaches to perform the chemical recycling of PUs. Because PUs exhibit high flammability, items made from these materials are typically flame retarded with a variety of functional chemicals; TCPP is one of the most commonly used additives [188]. Concerning PU foams contained in covered flooring or in uncovered

recreational products, starting from January 2025, all organohalogen FRs as well as five PFRs (i.e., ethylhexyl diphenyl phosphate, isopropylated triphenyl phosphate, tributyl phosphate, triorthocresyl phosphate, and triphenyl phosphate) will be banned according to the Washington State "Safer Chemicals" regulation [63].

Rigid urethane foams are usually mechanically mixed with flame retardants based on phosphorus, nitrogen, and sulfur to enhance their fire behavior. Also, chemical interactions between the hydroxyl groups in urethane foams and polyols that include chlorine and/or phosphorus can improve the fire resistance of these foams [182]. Due to the presence of Cl-based FRs in the polymer matrix, huge amounts of chlorine compounds are very often released during the pyrolysis at 500–700 °C of PU waste from household appliances [189]. To produce useful chemicals (i.e., semi-volatile organic compounds) by chemical recycling [183], Eschenbacher et al. [183] performed the thermochemical conversion of PUs and PIRs, with and without TCPP flame retardant, via pyrolysis. It is important to mention that a considerable amount of Cl-containing compounds, such as allyl chlorides, was released during the pyrolysis of PIRs containing TCPP (Table 1). The pyrolysis of high-resilient ether PU and semirigid PU at 600 °C were very similar and led to ethylene and propylene (combined yield of ∼13 wt.%), 4 wt.% - 6 wt.% organic nitrogen compounds, and ∼16 wt.% of various oxygenates. The pyrolysis of PIRs resulted in ∼20 wt.% higher residue yields and could be performed at 300 °C allowing for the recovery of diethylene glycol (2 wt.%) and benzoic acid derivate (6 wt.%), and oxygenated volatiles [183]. An interesting approach developed by Zhang et al. [190] utilizes a by-product of PET alcoholysis as a chain extender for the production of flame-retardant waterborne polyurethane showing both good fire behavior and final bonding strength. Also, Li et al. [191] demonstrated the effective chemical recycling of waste PET textiles by glycolysis to obtain flame-retardant rigid PUF, where its improved flame retardancy (LOI value was found to be around 23.27 % - 25.38 %) was ascribed to the presence of aromatic moieties in the depolymerized products compared to regular PUF (Table 1). Based on such results, Hoang et al. [192] proposed a methodology to extract unsaturated polyester resin material from waste PET and combine it with several P-based species to enhance the flame retardancy of rigid PUF.

4.2.3. Printed wiring boards

The amount of electronic waste (e-waste) is increasing around the world and its effective recycling needs to be focused on the recovery of precious metals, such as copper, silver, and gold [193]. Around 30 % of plastics contained in e-waste are landfilled or incinerated [194]. In our daily lives, electronic devices are used more and more, and practically every electronic item consists of a PWB. Due to the widespread use of these products, specific fire safety regulations must be fulfilled for the fire resistance of PWBs. Most of the high-performing polymers that can be found in e-waste are represented by PC, PA, HIPS, ABS, PP, and epoxy resins. These latter are often contaminated with BFRs and heavy metals (e.g., Hg and Pb). To attain UL-94 V0 (i.e., self-extinguishing), FR systems need to be incorporated into PWBs or FR reactive species (e.g., dihydrooxaphosphaphenantrene, poly(1,3-phenylene methylphosphonate), phosphonate oligomers) are required to flame retard the polymer matrix [195]. Yu et al. [196] screened a large amount of housing plastic and PWBs deriving from appliances collected from different e-waste recyclers in China. The research group identified various BFRs, including PBDEs and TBBPA, and evaluated the potential migration of these halogenated compounds from the e-waste components into their recycled products (e.g., LCD monitors). Most of the e-waste samples contained high levels of PBDEs and TBBPA, indicating the need for an urgent consideration of their presence in EoL home appliances [196].

When submitted to thermal degradation, these BFRs contained in the e-waste PMs release hazardous pollutants, such as HBr and PBDE [194]. The discarded e-waste PMs can cause the leaching of toxic species into the groundwater. In the literature, several reviews are reported dealing with the current methods employed to remove the toxins from the e-waste PMs before their recycling, and the recovery strategies used to perform the hydrolysis, solvolysis, pyrolysis, or incineration of electronic EoL materials [194,197,198].

As above mentioned, a wide variety of polymers can be used for the production of PWBs, however, epoxy resins are usually the most employed for the manufacturing of these electronic items [195]. Along with issues related to the flame retardancy of PWBs, some recent European directives are restricting lead (Pb) content in PWB materials. PWB base components containing Pb have been banned under the European Directive on Restriction of certain Hazardous Substances in E&E (RoHS, 2002/95/EC, and RoHS 2, 2011/65/EU), unless their use is expressly permitted [195]. Very high process temperatures are required to provide lead-free soldering materials useful for the fabrication of PWB base products, thus the polymer matrix, one of the key components, should exhibit excellent thermal stability. Due to a glass transition temperature higher than 165 °C, epoxy-novolac resins are frequently chosen to produce halogen-free PWB base materials [199,200]. Unlike PWB materials made of DGEBA, the ones obtained starting from epoxy-novolac resins exhibit greater thermal stability, therefore their effective flame retardation can be achieved even using more sustainable P- or N-based additives, rather than halogen-containing FRs. The use of epoxy-novolac resins is promoting the release on the market of numerous NEMA classes of halogen-free flame retardant laminate materials for the manufacturing of PWBs [201,202]. The growing demand for more environmentally friendly products is fostering the development of easier recyclable PWBs containing HFFRs, showing flame retardant performances comparable to brominated laminates [203]. The majority of FR PWBs are now smelted, which means that ∼1 ton of plastics produces 450 kg of coke and BFRs, which are usually transformed into bromide salts [204,205]. When PWB base goods are mechanically recycled, the resin can be separated and chemically reprocessed to obtain polyols under specific operating conditions [204,205].

The two main technologies used for the recycling of PWBs are leaching and pyrolysis [194]. Unfortunately, when PWBs are pyrolyzed, a lot of contaminants, including brominated pyrolysis oils and hydrogen bromide, are released [206]. Luyima et al. [207] discovered a strategy to reduce the amount of HBr and brominated oils released during the pyrolysis of PWBs. By using powdered inorganic compounds (e.g., $CaCO_3$, CaO, and ZSM-5), the research group could trap HBr and the other brominated species, reducing the amount of total evolved bromine up to 90 % (Table 1) [207]. To give an example, some of the PWB-based waste was reduced in particles, with a size greater than 315 μm, and mixed (PWB/CaO ratio = 5) with CaO or $CaCO_3$. This mixture was pyrolyzed at 900 °C for 2 h and the subsequent gaseous products condensed to Br-free pyrolysis oil (∼18 g per 100 g of PWB-based waste) rich in phenols, benzenes, alkanes, etc. This oil can be used, after treatment, as fuel in other industries like blast furnaces in steel making. Khaobang et al. developed a new concept for e-waste recycling and metal recovery. The decoupling gasification of EoL PWBs and waste cables led to syngas product (i.e., the pyrolysis oil yield of 20 % and 27.3 %, respectively), pyrolysis char (i.e., the yield of about 48 and 42 wt.%, respectively), and exhaust gas, used for the fuel reduction in the pyrolysis burner [208]. The synthesis gas product, rich in the single-ring compound, showed a major composition of 10.91 vol.% (H_2), 23.4 vol.% (CO), and 5.68 vol.% (CH_4). Au, Ag, and Cu could be regained, as 83.8–89.8 % of the precious metal total content, by ultrasonication from the char produced during the pyrolysis of e-

waste materials [208]. Thanks to this combined pyrolysis and de-coupling gasification process, the research group demonstrated a reduction of about 36.1–41.7 % in LPG (liquefied petroleum gas) consumption, which could save the cost of e-waste recycling up to 25.7–28.7 % with respect to traditional pyrolysis [208]. Brominated epoxy resins exhibit high thermal and chemical stabilities, making their degradation under mild conditions very complicated. Xing et al. [209] used subcritical acetic acid to decompose BERs contained in PWB-based wastes. The acetic acid could swell into BERs at 200 °C and convert them to bisphenol A and phenol in about 1 h at 2.6 MPa (Table 1). At temperatures higher than 240 °C, the research group could obtain bromine-free oil phase products, while most of the bromine was transformed into HBr and some BPA degraded to phenol and p-isopropyl phenol [209]. Based on the costs of raw materials (i.e., water and acetic acid), output products (Cu and glass fibers), and electric energy, the research group indicated that acetic acid is responsible for a large proportion of the total cost, therefore the recovery via extractive distillation of this latter could significantly improve the economic feasibility of the EoL PWBs [209].

5. Recyclable and reprocessable CANs containing FR thermosets

5.1. Recycling strategies of FR thermosets based on CANs

Unlike conventional thermosets with a permanent crosslinked network, which strongly limits the EoL disposal options, "vitrimers" are a new class of materials composed of associative covalent adaptable networks [210]. The scientific community and relevant industry are paying growing attention to vitrimers and more generally to materials based on CANs [211], as they are rigid at ambient temperature, but they can "flow" at elevated temperature, owing to topological rearrangements [212], starting from heat triggered exchange reactions. These chemical features make vitrimers able to be reshaped, repaired, and recycled in a wide range of temperatures and conditions, even if they contain FRs or other fillers. Vitrimers are malleable and exhibit the thermal ductility and reproducibility of thermoplastics, albeit with high thermostability, chemical resistance, and mechanical properties like thermosets [213,214]. Thermoset materials based on CANs can include reversible disulfide exchanges, ester bonds, –Si–O–Si– exchange, metathesis of dioxaborolanes, and transalkylation [215]. When the FR specie is covalently bonded or used as an additive in such vitrimer materials, ideally at the end of their life, these inherently FR thermosets can be physically/chemically recycled, reshaped, or repaired under external stimuli (e.g., heat, pH, and UV radiation), without any negative impact on the environment or waste production [216]. Inherently recyclable flame retardant vitrimers can be obtained starting from bio/petroleum-derived raw materials [210], and the FR moiety can be introduced as part of the polymer network or as a pendent group (Fig. 12). In the next section, the recycling methods of thermosets based on CANs are discussed, with a special focus on the two main technologies for the recovery of both polymer networks and fillers [216]. However, some of the authors have published a previous review dealing with the design strategies and chemistry of recently developed recyclable FR thermosets [156]. In particular, in this previous work, the authors have described flame retardant features, mechanical properties, healing, reprocessing, and recycling capacities (positive aspects and limitations) of such systems, also offering future insights and perspectives [156].

However, some other exhaustive reviews of strategies and technical aspects concerning the recycling of flame retardant thermosets based on CANs can be found in the recent literature [156,217,218].

5.2. Thermomechanical and chemical recycling strategies of FR thermosets based on CANs

The good fluidity of thermoplastics at high temperatures allows their manufacturing by extrusion, thermoforming, injection molding, and vacuum forming. However, most plastics exhibit poor resistance toward organic solvents and low mechanical properties, which limits their applications in industry and daily life. On the contrary, thermosets are composed of chemically cross-linked three-dimensional networks, therefore such materials are characterized by excellent mechanical behavior, dimensional stability, and chemical resistance. Owing to their properties, thermosets are widely employed in aerospace and windmills, though their chemical structure and insoluble nature make the recycling of thermosets full of hurdles. Moving to CANs, the possibility to choose among different dynamic covalent bonds (e.g., disulfide, imine, silicon-oxygen, boron-oxygen bonds) allows the design of vitrimers with specific characteristics (e.g., thermal ductility, reproducibility, viscoelastic behavior) and recycling features. The type of dynamic covalent bond influences the mechanical properties, chemical resistance, and thermostability of the final product and thus its recyclability, including the performances and potential applications of the recovered materials.

Due to the main features of vitrimers, these latter, at the end of their life, can be directly reprocessed through traditional manufacturing methods or used as filler after grinding them into powders or pellets [219]. Physical recycling mainly involves three thermomechanical approaches: hot pressing/compression molding, extrusion molding, and injection molding. Hot press recycling consists of the reduction of vitrimers into small pieces, usually through a cryo-grinding process, which is converted into recycled material by a hot press (Fig. 12) [218].

Hot pressing parameters strongly influence the properties of the recovered material. Proper conditions of temperature, pressure, and powder size must be selected for the hot press recycling of the EoL FR vitrimer to prevent the thermal degradation or oxidation of the FR polymer matrix and the damage of the filler (e.g., long fibers) [220]. These aspects are strong limitations for the application of such recycling technology to FR vitrimers, as many of them do not show high thermal stability, especially due to a thermolabile FR part [221,222]. Currently, most of the vitrimers are recycled and reprocessed by limited hot pressing, though this latter is an energy-consuming process and often provides recycled resin materials with lower mechanical properties [153,223]. Some important drawbacks of the hot pressing approach are (i) the difficulty of obtaining recycled products in a wide range of possible shapes, (ii) the vitrimers should be enough fluid to undergo a topological transformation, and (iii) the downgrade of long fibers in FRP composites due to pulverization process [224].

Thermosets based on CANs are able to flow like thermoplastics in a wide range of temperatures and thus can be recycled by injection molding, which is performed by injecting the vitrimer at a certain speed into a cooled mold of desired shape. Conversely, during extrusion molding, the material is thermal treated by the action of the extruder barrel and pushed forward by a screw into a designed mold cavity. A high thermal stability and an MFI index greater than 10 g (10 min)$^{-1}$, at the processing temperature (measured according to ASTM D1238 standard), are two of the main requirements that make a material suitable for injection or extrusion molding recycling. These aspects are strong limitations for the application of such recycling technologies to flame retardant vitrimers, as many of them do not show high thermal stability, mainly due to a thermolabile FR part, and proper MFI value [221,222]. Recently, some lower time-consuming and energy-demanding reprocessing processes are emerging and growing in importance [225,226]. Despite the negative effects on the mechanical properties of recycled prod-
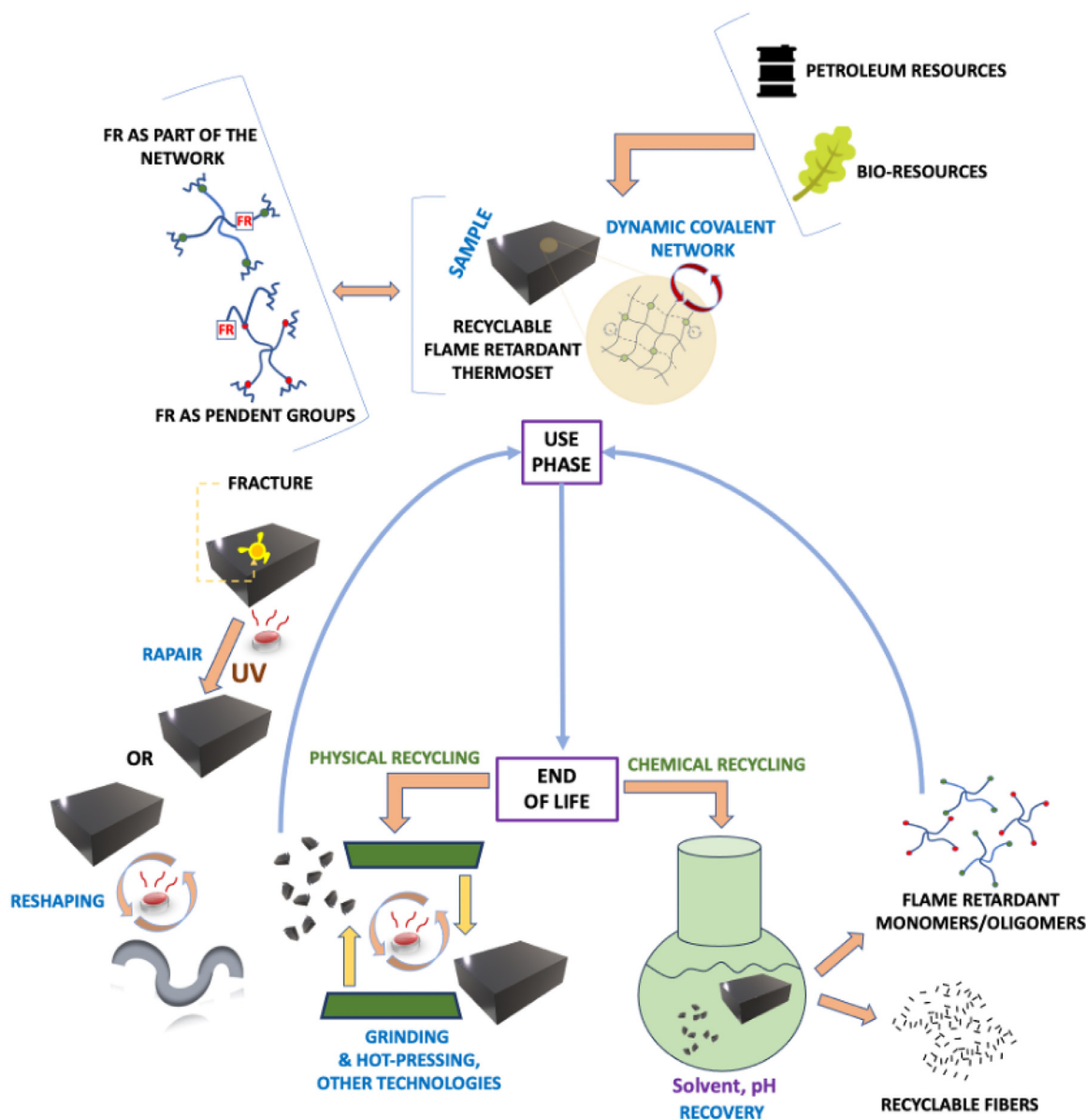
Fig. 12. FR vitrimers: synthesis procedures, main features, application (electronic component, building material, sensor, fire protection system, etc.), and main recycling strategies at the end-of-life. The reversible nature of vitrimers enables welding, molding, reshaping, and recycling of fully cured materials.

ucts and their energy-consuming approach, compression molding is still the most employed methodology for the recycling of vitrimers [153,223]. HealTech^{TM} is a technology that has been recently marketed by CompPair, an EPFL spin-off based in Switzerland, which allows the manufacturing of composite components to be quickly fixed on-site at low temperatures [225]. Mallinda is a startup company affiliated with the University of Colorado Boulder, which was founded in April 2014 to develop and produce malleable CFRPs for rapid production cycle times [155]. Mallinda co-founders invented a catalyst-free polyimine vitrimer exhibiting malleable behavior when heated above the Tg of a given formulation. Below the Tg, the polymer network of such vitrimer behaves like the one of a conventional thermoset [155].

Mallinda's malleable vitrimer can be used for the fabrication of pre-cured pre-impregnated laminates (prepreg) by a roll-to-roll process. As shown in Fig. 13, any number of plies of pre-cured prepreg malleable CF-reinforced laminates can be heated to a specific Tg and then laid up in a mold to the final thickness [155], and both consolidated and formed into a desired part through com-

pression forming. In 1 min the formed part can be demolded and handled to be used with its full rigidity or recycled in a solution-based process, wherein both fiber and resin are regained [155].

Despite the easier processing of physical recycling, the chemical recycling of FR thermosets based on CANs is usually preferred [157]. Unlike thermomechanical recycling, the chemical recycling of vitrimer as a single material allows for the recovery of monomers by solvents, containing small molecules with exchangeable functional groups, which are used for the degradation of vitrimers into recyclable oligomers. Concerning vitrimer-based composites, they are separated into multiple materials, filler (e.g., carbon fibers) and FR monomers/oligomers, during the recycling process (Fig. 12) [227]. When reinforced vitrimer-based composites undergo chemical recycling, the length and overall properties of fibers are often retained, facilitating the reuse of the recovered fibers in further manufacturing processes. Chemical recycling of vitrimers is possible thanks to the dynamic bond exchange reactions taking place when the material is exposed to a proper solvent at certain pH conditions. The dissolution of vitrimers may be time-consuming
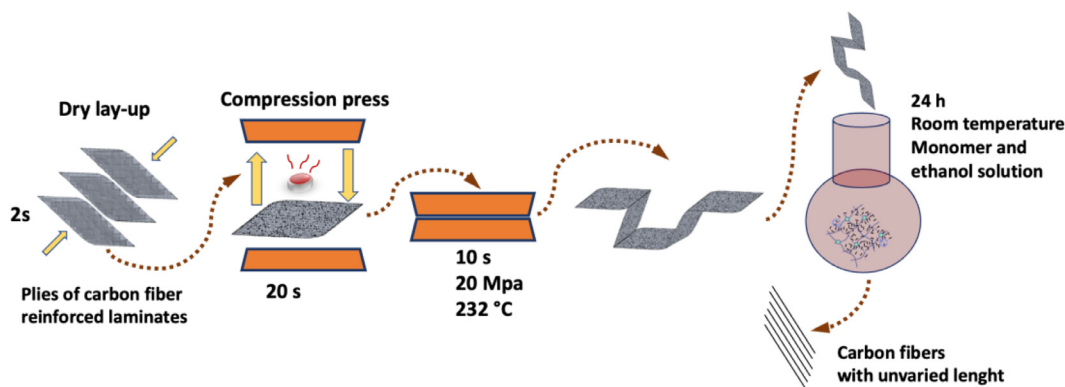
Fig. 13. Consolidation and molding process for Mallinda's malleable materials. Figure adapted from [155].
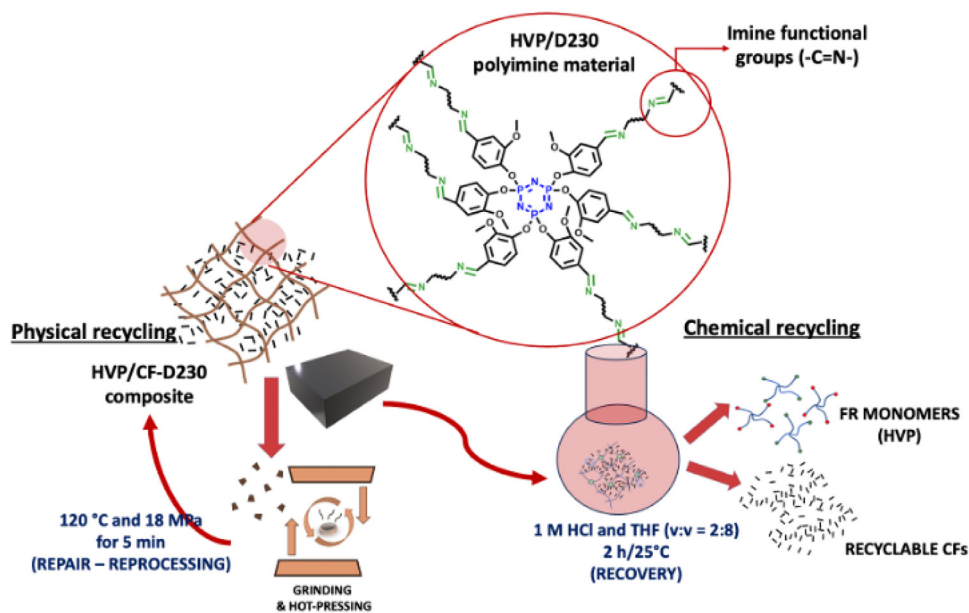

Fig. 14. Physical and chemical recycling strategies for fire-resistant vanillin-based polyimine composites containing carbon fibers.

and lead to mixtures from which FR oligomers/monomers are not easy to separate. In the next section, some recent recycling strategies of flame retardant thermosets based on CANs are reported.

5.2.1. Polyimine vitrimers

FR fiber-reinforced polyimides are often used to form lightweight fire-resistant composite materials for many applications in aerospace and electronics [228]. To reduce the production of EoL polymer waste based on polyimides, several synthesis routes and strategies have been applied for the development of fully chemically recyclable FR thermosetting polyimides based on CANs. Among the dynamic bonds, the imine bonds give reversible metathesis reactions [229]. Thermosets based on CANs can also offer easy and low-cost strategies for the recovery of valuable fillers, for example, CFs from EoL CFRPs (Fig. 12) [230]. Liu et al. [231] exploited HVP, a monomer derived from vanillin, to prepare self-extinguishing polyimine binder material cured with D230 through a catalyst-free Schiff base reaction. Then, the resulting material was used for the manufacturing of fully recyclable CFRPs [231]. HVP/CF-D230 could be degraded and dissolved in a mixed acidic solution containing THF to retrieve nearly 100 wt.% of the HVP. Small pieces of pristine HVP/D230 could be reshaped into a complete film by hot pressing (120 °C and 18 MPa for 5 min) (Table 1). Also, HVP/CF-D230 laminates could be reprocessed and

repaired at the same conditions within 15 min (Fig. 14) [231]. HVP/CF-D230 composites represent an example of bio-based recyclable fiber-reinforced thermosets, which may help to reduce the production of fire-safe high-performance wastes. The research group also compared the final properties and characteristics of HVP/CF-D230 to the ones of laminates made of an unmodified epoxy resin (E51/D230-CF, see Table 1).

Zhang et al. [232] modified HCCP through the introduction of three aldehyde groups (CP-3AP) to obtain polyimine vitrimers exhibiting a V0 rating in the UL-94 vertical burning test. Due to an effective metathesis mechanism between imine dynamic covalent bonds in the network, vitrimers showed more than 90 % recycling efficiency of mechanical properties, even after three thermo-mechanical recycling cycles. Monomers of vitrimers could be recovered by hydrolysis reaction under mild acidic conditions (1 M HCl and THF (v:v = 2:8), within 60 min at 25 °C) [233]. Polyimine vitrimers could be reprocessed into recycled smooth films by hot pressing small fragments under 15 MPa at 180 °C for 30 min (Table 1) [232]. Particularly, the first recycled samples of polyimine vitrimers kept their tensile strength almost unvaried compared to the values of the original materials, whereas mechanical strength and elongation at the break of samples slightly decreased after the second and third recycling cycles [232]. Such a decrease was attributed to partial oxidation and self-crosslinking

among imine bonds during the hot pressing [234]. Recently, Ding et al. [235] left to react vanillin with phosphorus oxychloride to obtain a trialdehyde monomer, which was cured using polyetherimide D230 and 4-aminophenyl disulfide via Schiff base reaction to synthesize a polyimine vitrimer with a dual dynamic network, including disulfide bonds (–S–S–) and reversible imine bonds (–C=N–). The polymine vitrimer showed a V0 rating in the UL-94 test and a high LOI value, it could be also thermomechanically recycled by hot pressing under 20 MPa at 150 °C for 10 min. As in the case for most Shiff base structures, the recyclable thermoset obtained by curing the trialdehyde monomer with D230 could be dissolved in 1 M HCl and THF (v:v = 2:8) mixed solution in only 4 min. The original monomer could be retrieved from the solution with high a recovery rate of 70.5 % [235].

5.2.2. Polyurethane vitrimers

Due to their versatility in several fields and high flammability, urethanes and vinylogous urethanes containing FRs largely contribute to the production of EoL plastic wastes [236]. Vitrimers based on vinylogous urethanes are attracting great attention in the preparation of recyclable materials showing similar mechanical properties and fire behavior of conventional analogs [237]. However, most of such vitrimers exhibit poor fire resistance and thus do not satisfy more stringent requirements. In this context, Markwart et al. [238] prepared phosphonate-based flame retardant vinylogous polyurethane vitrimers (poly-1), also reinforced with glass fibers, showing V2 rating in the UL-94 vertical burning test, high glass transition temperature, and very good recyclability. Poly-1, previously cut into small pieces, could be reprocessed by hot pressing in a mold at 10 kN for 30 min at 150 °C (Table 1). Recycled vinylogous polyurethane vitrimers showed a storage modulus of around 0.36 GPa, even after three reshaping cycles [238]. The good fire behavior of poly-1 was due to the incorporation of phosphorus moieties in the polymer network, whereas the presence of reversible imine bonds allowed for its easy reprocessing and physical recycling.

5.2.3. Epoxy vitrimers

As previously mentioned, ER is one of the most important thermosets. Most ERs are based on DGEBA, which is recognized as an endocrine-disrupting chemical. Unmodified ERs show high flammability, therefore the addition of FRs, such as halogen-based and P-based compounds, is required to achieve good performances [239]. The presence of FRs in the epoxy matrix influences the recycling method and the procedure steps. Epoxy vitrimers contain dynamic covalent bonds and can be used as matrices for the synthesis of FR composites showing high performances and recyclability [8]. Disulfide bonds are reversible covalent bonds that can impart healing functionality to ER at low temperatures [240,241]. Zhou et al. [242] prepared a self-extinguishing CTP-EP/DTDA able to be repaired by hot pressing, also exhibiting a healing efficiency of 97.5 % after 10 min of processing (200 °C and 10 MPa), owing to the presence of exchangeable disulfide bonds in the epoxy matrix (Fig. 15).

The research group demonstrated that it was possible to reshape CTP-EP/DTDA multiple times, similar to a thermoplastic. In 2012, the company Connora Technologies marketed ammine reagents, named Recyclamine[TM], based on sulfide points, which could be selectively cleaved in an aqueous solution at mild conditions [243]. Recyclamine[TM] allowed for the regain of clean reinforcing fibers and reusable thermoplastic matrix from the epoxy network of composites [170,243]. Life cycle analysis of bio-based epoxy monomers cured with Recyclamine[TM] confirmed their high sustainable and low-cost values [170,226].

The incorporation of ester bonds into the thermoset matrix leads to vitrimers showing high reprocessability. Ester bonds form a dynamic covalent network enabling topological rearrangement through transesterification [244] and exchange of β–hydroxy ester or boronic ester bonds [245]. The transesterification is typically activated by thermal stimulation and occurs in the presence of specific catalysts [224].

Chen et al. [246] cured DGEBA resin with AA and DDP, using TBD as a catalyst, to prepare flame-retardant epoxy vitrimers. With a 30 wt.% DDP content, these materials exhibited a V0 rating in the UL-94 vertical burning test, multiple shape memory capability, and could be reprocessed in 15 min at 200 °C without any detrimental impact on the mechanical properties and flame retardance, owing to the presence of exchangeable β–hydroxy ester bonds in the epoxy matrix enabling catalytic transesterification activity into the crosslinking network. The physical recycling of FR epoxy vitrimers by hot pressing did not significantly affect their Tg ($\sim$110.7 °C) and thermal stability, only resulting in a slighter increase of rigidity, due to partial oxidation during the reprocessing process [246]. Feng et al. [247] prepared PE-CANs by curing DGEBA resin (EPON-826) with HEMAP (i.e., phosphate ester). PE-CANs did not start burning even after 600 s of flame application and could be reduced into small pieces and then reshaped by hot pressing (110 °C for 1 h), owing to the presence of a dynamic β–hydroxy phosphate esters-based covalent adaptable network (Table 1) [247] (Fig. 16). PE-CANs could be chemically recycled by dissolution in ethanol (or other polar solvents) at 80 °C for 4 h without a catalyst [247]. PE-CANs prove that dynamic β–hydroxy phosphate ester chemistry allows for the synthesis of catalyst-free and recyclable vitrimers showing good mechanical properties and fire behavior.

Tian et al. [248] prepared flame retardant recyclable epoxy vitrimers starting from a bio-based GTE, as an epoxy monomer, modified with DOPO and cured by using a vanillin-derived imine compound. Vitrimers containing 6 wt.% DOPO showed a UL-94 V0 rating and lower peak heat release rate than unfilled material. Owing to the presence of exchangeable imine bonds in the polymer network, the self-extinguishing epoxy vitrimers could be easily chemically recycled through their dissolution in a 0.1 M EDA solution with DMF, as a solvent, after keeping samples at 80 °C for 3 h [248]. Flame retardant monomer and curing agent could be regained by removal of EDA and DMF via thermal treatment at 80 °C for 48 h, then used to fabricate recycled vitrimers. These latter could be physically recycled by compression molding under 15 MPa at 170 °C for 20 min to obtain thermosets showing a tensile strength similar to original vitrimers [248].

Recently, Klingler et al. [249] developed an inherently FR-recyclable phosphonated thermoset. More in detail, DGEBA resin was modified by reaction with a bis H-phosphite monomer (TDPSD) enabling fire resistance and transesterification reactions in a dynamic covalent network containing P–O ester moieties. The use of TDPSD allowed for the production of epoxy coatings showing damage reparability and excellent fire protection properties, making them suitable to be used in electronic and transportation applications. The cryo-grinded epoxy vitrimer could be thermomechanically recycled by physical methodology using hydraulic hot pressing for 5 min at varied temperatures (i.e., 150 or 160 °C) under a pressure of 6 MPa (Table 1). The phosphonated epoxy vitrimer was also employed for the fabrication by compression molding of flax fiber reinforced composites, exhibiting flexural strength $\sim$6 times more than the pristine thermoset [249].

CANs show the recyclability of thermoplastics and the durability of thermosets, due to their crosslinked network based on dynamic covalent bonds. The stimuli-driven reprocessability of such materials may allow us to solve many environmental problems and develop recyclable self-healing smart actuators and adhesives. However, most CANs are still made from petroleum resources, therefore there is the need to replace fossil-based raw materials with renewable feedstock, for example, biomass and natural rub-
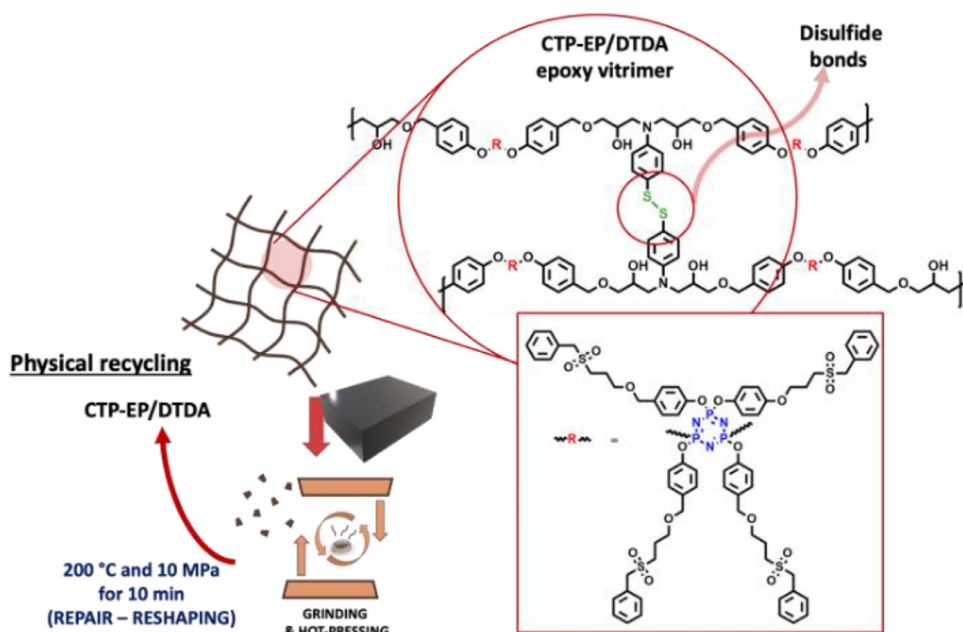
Fig. 15. Physical recycling strategy for a flame retardant cyclotriphosphazene-based epoxy vitrimer.
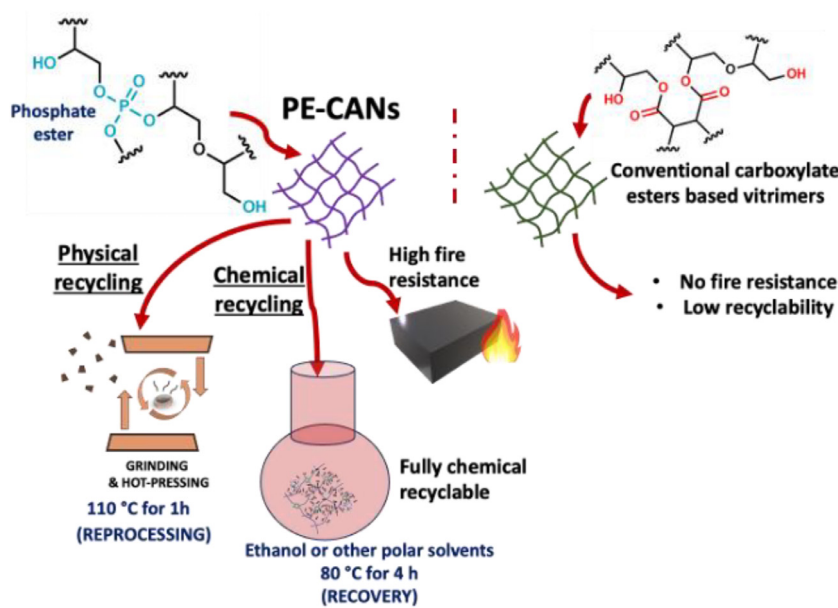

Fig. 16. Physical and chemical recycling of a β–hydroxy phosphate esters-based thermoset.

ber, and design synthesis procedures for the preparation of more sustainable products. CANs also have their drawbacks and limitations. For example, Schiff base CANs need the addition of FR additives to improve their fire performance and the recovery of a matrix involves the use of organic non-sustainable solvents (e.g., THF) [51]. CANs containing disulfide exchangeable bonds are good performing in terms of flame retardancy and mechanical properties, but their chemical recycling or combustion leads to the production of toxic sulphureous anhydrides [250]. Finally, CANs based on phosphate ester, boronates, and boroxines [251,252], are susceptible to hydrolysis, which deteriorates crosslinks in the FR monomers and matrices, making their recovery ineffective for reprocessing procedures. Despite the promising characteristics of FR CANs, the challenge for the scientific community is to overcome the above-mentioned drawbacks, together with optimizing

the processing techniques, scalability, and understanding the long-term stability and performance of these materials in real-world applications to open a new concept for recyclable materials.

As previously mentioned, the main outcomes for some of the most recent recycling strategies of inherently FR CANs and FR polymeric materials discussed in this review are summarized in Table 1.

6. Summary and perspectives

The scientific community is increasing attention to developing more effective technologies for recycling flame retardant (FR) polymeric wastes. Fig. 17 shows a typical recycling scenario and related options concerning the reprocessing of end-of-life FR plastic-based products.
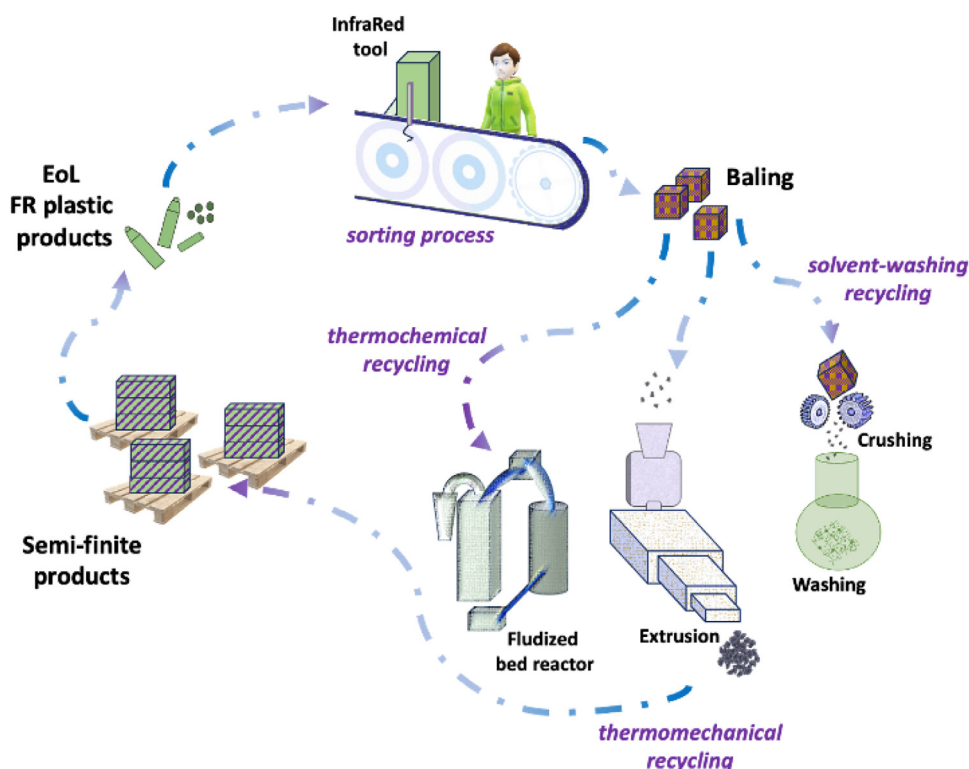
Fig. 17. Flame retardant plastic waste undergoes (i) a sorting process (manual sorting or digital sorting), followed by (ii) solvent-washing recycling or (iii) thermochemical recycling or (iv) thermomechanical recycling. The solvent-washing can also be performed before the thermomechanical/thermochemical recycling to dehalogenate the waste.

Due to the negative consequences on the environment, the direct incineration of plastic wastes containing halogen-based FRs (HFRs) cannot be considered a valuable disposal method. Since the use of many HFRs has been banned, it is now mandatory to remove halogenated plastic wastes, showing total bromine content higher than 2000 mg kg^{-1}, before mechanical recycling. This sorting process can be performed by high-resolution near-infrared devices, which are used to screen plastics filled with HFRs (Fig. 17(a)). Mechanical recycling of FR plastic waste mainly consists of upcycling it as filler in a new manufacturing process and may involve the thermal reprocessing (thermomechanical recycling) of waste (Fig. 17(b)). As an alternative to the sorting process, solvent-washing treatments can be employed for the dehalogenation (e.g., debromination) of plastic waste, resulting in the extraction of halogenated additives from the native plastic (Fig. 17(c)). Tertiary recycling of halogenated plastic wastes results in their conversion into lower molecular weight products or for energy recovery. Several techniques (e.g., gasification, thermolysis, photolysis, solvent-assisted depolymerization) may be implemented to perform tertiary recycling processes (Fig. 17(d)). However, the effective trapping of residual halogenated by-products during pyrolysis (thermochemical recycling) is still one of the major challenges of this route. Regarding halogen-free FR (HFFR) thermoplastics waste, mechanical recycling is the preferred strategy due to its sustainability and low costs, together with the possibility of keeping good mechanical performances and fire behavior for the reprocessed product. One drawback is linked to the thermal degradation of HFFR thermoplastics, often leading to a significant loss of mechanical properties and a potential decrease of flame retardancy during the thermomechanical recycling of such materials. The composition of the polymer matrix and its FRs strongly affect the optimal recycling method for a specific plastic waste stream. Mixed waste streams composed of HFFR thermoplastics are difficult to recycle by mechanical processes. To address this issue, tertiary recycling by chemical or thermochemical techniques may represent a valuable alternative.

Moving on to thermoset wastes, there is a pressing need to allocate greater focus on understanding the impact of FRs on their recycling. Currently, mechanical recycling of thermoset wastes mainly transforms them into sized flakes that can be upcycled as reinforcing fillers for the preparation of new polymeric composites through thermomechanical processes. On the other hand, thermochemical recycling is energy-demanding and often deteriorates the polymer matrix, which is detrimental from a circularity point of view. Solvolysis of FR thermosetting wastes allows for the recovery of more resistant fibers (e.g., carbon fibers), but it needs to be conducted at extreme operative conditions. Besides, the application of solvolysis to thermosetting wastes frequently results in the transformation of matrix and FR into species of different chemical nature that are difficult to separate and reuse. Conversely, EoL FRT based on CANs are re-processable and enable the full recovery of FR, though their upscaling and rapid steady-state processing still need additional research efforts and investigations. In summary, further research is expected to address these key challenges, some mentioned above, and open new avenues toward sustainable FR polymers.

Author statement

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Aurelio Bifulco reports financial support was provided by

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