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Synergistic flame retardancy of carbon fibre-reinforced polyimine vitrimer composites via vitrimer-based intumescent coating

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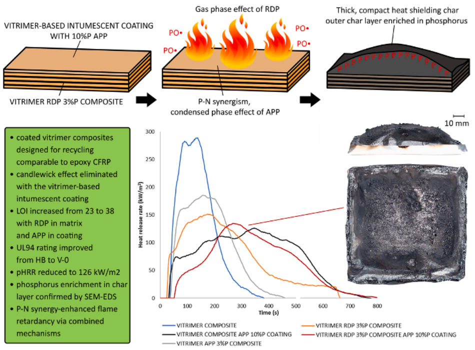
HIGHLIGHTS

- Candlewick effect was eliminated with the vitrimer-based intumescent coating.
- LOI increased from 23 to 38 with RDP in the matrix and APP in the coating.
- pHRR reduced to 126 kW/m^2, UL 94 rating improved from HB to V-0.
- Phosphorus enrichment in the outer char layer was confirmed by SEM-EDS.
- P–N synergy enhanced flame retardancy via combined mechanisms.

GRAPHICAL ABSTRACT



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ABSTRACT

We developed sustainable, recyclable carbon fibre-reinforced polyimine vitrimer composites with enhanced flame retardancy via a combination of resorcinol bis(diphenyl phosphate) (RDP) in the matrix and a 10 %P ammonium polyphosphate (APP) intumescent coating, offering a promising alternative to conventional epoxy systems for advanced applications. Fire performance was evaluated using Limiting Oxygen Index (LOI), UL94, and mass loss calorimetry (MLC) tests. The APP coating acted via a condensed-phase mechanism, forming a dense, phosphorus oxide-rich char that reduced the peak heat release rate (pHRR) from 289 kW/m^2 to 126 kW/m^2—the lowest observed among the tested formulations. Scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS) analysis revealed significant phosphorus enrichment in the outer char layer and, notably, an increased phosphorus content in the inner char when RDP was incorporated into the matrix. This synergistic effect indicates that RDP's gas-phase action effectively complemented APP's condensed-phase

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mechanism, further enhancing LOI, extending time to ignition (TTI), and reducing total heat release (THR), significantly improving overall fire resistance. Although benchmark epoxy composites exhibited higher tensile strengths, the vitrimer systems maintained competitive mechanical properties alongside superior recyclability, the ability to apply the intumescent coating via hot pressing, and intrinsic repairability. Overall, the dual-action flame retardant strategy achieved by combining RDP and APP significantly improved fire performance, demonstrating the potential of these advanced composites for multifunctional material applications.

1. Introduction

Vitrimers offer a unique solution with their associative covalent adaptable networks (CANs) as they exhibit crosslinked properties below a vitrimer transition temperature and can be melted and recycled above it, resembling thermoplastics [1–9]. Polyimine-type vitrimers, formed through heat-triggered imine exchange reactions, have gained attention for their recyclability [10–14]. Transimination reactions among the excess diamine monomers and the imine-linked network increase the number of end groups within the polymer, leading to the solubilisation of the polyimine network. Therefore, simple immersion of carbon fibre-reinforced composites (CFRPs) into diamines leads to the complete dissolution of the polyimine vitrimer and easy recovery of carbon fibre reinforcement with minimal residue on their surfaces [15,16]. Enhancing fire resistance is essential to make these recyclable crosslinked polymers more widely accessible [17–21]. Polyimines are typically synthesized through the simple reaction of aldehydes or ketones with amines, allowing for the straightforward substitution of individual components with heteroatom-containing compounds, such as phosphorus, which provide flame retardant properties. Therefore, recent studies have mainly explored inherently flame retarded polyimines [22–28].

Incorporating flame retardant components directly into the polyimine structure eliminates the need for additives, which could lead to filtration during the manufacturing of fibre-reinforced composites in the case of solid flame retardants [29,30]. Nevertheless, even in the case of reactive flame retardants, the condensed phase action of flame retardants is hindered by the fibre reinforcement [31,32]. A relevant strategy to eliminate these issues is to apply an intumescent coating on the top of fibre-reinforced composites. This way, not only the intumescence phenomena can fully develop, and the particle filtration can be avoided, but also the mechanical properties of the matrix can be preserved. Nevertheless, if the coating itself does not provide sufficient fire performance, additional gas phase flame retardants can be introduced to the matrix. The fact that the vitrimers can be melted above their vitrimer transition temperature, also predicts that if a vitrimer-based flame retardant coating is used, instead of brushing or spraying, the coating can be applied by simple hot pressing. Furthermore, the self-healing properties of the vitrimers predict good adhesion between the vitrimer matrix and vitrimer-based coating through chemical bonds, enabling easy repair of the coating via local heating if damaged.

In our previous research we performed a comprehensive study of the flame retardancy of a polyimine-based vitrimer system using additive and reactive flame retardants, acting in gas-, condensed- and combines phases [33]. We applied ammonium polyphosphate (APP), acting in condensed phase [34,35], resorcinol bis(diphenyl phosphate) (RDP), acting mainly in gas phase [34,35] as additive, and *N,N',N''*-tris(2-aminoethyl)-phosphoric acid triamide (TEDAP) [36], with combined phase action [37,38], as reactive flame retardant. We tested the flame retarded vitrimer matrices and carbon fibre-reinforced composites and compared their fire performance to a benchmark pentaerythritol-based aliphatic epoxy resin systems [39]. In addition to fire performance, we previously assessed the curing behaviour, thermal stability and thermomechanical properties of these systems using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). While the recyclability of the vitrimer composites and coating materials was addressed in another previous study, where the effect of chemical recycling on reinforcement recovery and material properties were analysed in detail [16]. The practical applicability of the vitrimer composites was also demonstrated through orthogonal machining experiments, confirming their processability with conventional technologies [40]. Based on these previous findings, we concluded that to achieve effective flame retardancy in vitrimer composites, it is necessary to incorporate at least 3 % phosphorus from APP or RDP in the matrix to prevent dripping by rapid charring of the matrix. Additionally, as observed in other carbon fibre-reinforced composites, the intumescent effect of APP is hindered by the reinforcement, making an APP-containing intumescent coating a more favourable approach.

Therefore, this study examines the use of APP and RDP as additive flame retardants in the vitrimer matrix and the application of an APP-containing vitrimer-based intumescent flame retardant coating. Both the composite and the coating are made from vitrimer, offering the advantage of recyclability through their dynamic covalent bonds, which align with the principles of design for recycling [41,42]. This work represents an innovative approach by combining fully vitrimer-based matrices and flame retardant coatings, enabling a unified, recyclable composite structure with enhanced fire safety. We evaluate the flame retardancy and mechanical properties of carbon fibre-reinforced polyimine composites and their coated versions, comparing their performance to benchmark epoxy resin composites.

2. Materials and methods

2.1. Materials

We used tetrafunctional pentaerythritol-based epoxy resin (PER), IPOX MR 3016 (supplier: IPOX Chemicals Ltd, Budapest, Hungary; main component: tetraglycidyl ether of pentaerythritol; viscosity at 25 °C: 0.9–1.2 Pa·s; density at 25 °C: 1.24 g/cm^3; epoxy equivalent: 156–170 g/eq) crosslinked with a cycloaliphatic amine, IPOX MH 3122 (supplier: IPOX Chemicals Ltd, Budapest, Hungary; main component: 3,3′-dimethyl-4,4′-diaminodicyclohexylmethane; viscosity at 25 °C: 80–120 mPa·s; density at 25 °C: 0.944 g/cm^3; amine number: 464–490 mg KOH/g) as reference epoxy resin.

We used the two-component Vitrimax T130 polyimine-type vitrimer system consisting of an epoxy resin component based on di-glycidyl ether of bisphenol A (DGEBA) and an amine-functional polyimine hardener (supplier: Mallinda Inc., Colorado, USA, viscosity of the mixed system at 50 °C: 54.8 Pa·s) [43].

In flame retarded compositions, we used two flame retardant additives: ammonium polyphosphate (APP; trade name: NORD-MIN JLS APP; supplier: Nordmann Rassmann, Hamburg, Germany; P content: 31–32 %; average particle size: 15 μm), and resorcinol bis(diphenyl phosphate) (RDP; trade name: Fyrolflex RDP; supplier: ICL Industrial Products, Beer Sheva, Israel; P content: 10,7%).

The composite samples were made with unidirectional carbon fibre reinforcement (PX35FBUD030 consisting of Panex 35 50 k rovings with an areal weight of 300 g/m^2; supplier: Zoltek Ltd, Nyergesújfalu, Hungary).

2.2. Methods

2.2.1. Preparation of polymer composite samples

PER epoxy resin composite laminates were made in $[0]_5$ layup by

Table 1
The processing parameters and average fibre content of prepared composite samples.

Composite	Layup	Preparation method	Heat treatment	Fibre content (mass%)
PER COMPOSITE HL	$[0]_5$	hand lamination	1 h at 80 °C and1 h at 100 °C	42 ± 1
PER APP 3 %P COMPOSITE HL				42 ± 1
PER RDP 3 %P COMPOSITE HL				42 ± 1
PER COMPOSITE WCM	$[0]_5$	wet compression moulding	1 h at 80 °C and1 h at 100 °C	60 ± 1
PER APP 3 %P COMPOSITE WCM				60 ± 1
PER RDP 3 %P COMPOSITE WCM				60 ± 1
VITRIMER COMPOSITE	$[0]_5$	prepregging followed by hot pressing	1 h at 150 °C, 1 h at 180 °C and15 min at 160 °C	43 ± 1
VITRIMER APP 3 %P COMPOSITE				45 ± 1
VITRIMER RDP 3 %P COMPOSITE				42 ± 1

HL: hand lamination, WCM: wet compression moulding.

hand lamination and wet compression moulding. The ratio of the epoxy resin component to the hardener was 100:40. We added the hardener to the epoxy resin component and mixed them at room temperature in a crystallising dish until the mixture was homogeneous. In the hand lamination process, the fibre layers were successively deposited onto a glass plate, with each layer being impregnated with resin using a brush. After the fifth layer, a second glass plate was positioned on top to ensure even distribution of the resin and to achieve a more even surface. The 2 mm thick composite laminates were then cured at 80 °C for 1 h and subsequently at 100 °C for 1 h. In the case of wet compression moulding, each fibre layer was separately impregnated with the resin by hand lamination in a press mould. The prepared laminates were then compressed with a hydraulic pressure of 200 bar (which is equal to a pressure of 28 bar on the laminate) in a T30 temperable platen press (Metal Fluid Engineering s.r.l., Verdello Zingonia, Italy). The curing process involved a two-step heat treatment inside the mould, with an initial 1 h cycle at 80 °C, followed by 1 h at 100 °C.

In the case of vitrimer composites, the mixing ratio of the epoxy resin component and polyimine hardener was 1:2. Before mixing, we heated the polyimine hardener to 100 °C for 1 h to lower its viscosity. Composite manufacturing involved the individual impregnation of each carbon fibre layer, and then the so prepared prepregs were cured for 1 h at 150 °C and 1 h at 180 °C, as suggested by the producer. The cured prepregs were then subjected to a hot pressing at 160 °C for 15 min, with a hydraulic pressure of 15 bars (which is equal to a pressure of 1 bar on the laminate). The fibre content of the composites was determined by measuring the mass of the dry fibre layers before processing and the mass of the crosslinked composite sample. The fibre content of the samples was calculated as the ratio of the dry fibre mass to the total composite mass.

Flame retarded composites containing 3 % phosphorus (P) in the matrix were prepared using APP or RDP, alongside reference epoxy resin and vitrimer composites. In this case, the flame retardant was first added into the epoxy component, followed by the addition of the hardener. The curing procedure for the flame retarded composites was identical to that used for the composites without flame retardants. The processing parameters and average fibre content of the composite samples is shown in Table 1.

2.2.2. *Preparation of vitrimer-based flame retardant coatings*

We developed a novel coating technology based on the thin-film processing technology leveraging the dynamic bond exchange reactions of vitrimers that enable thermoformability and reprocessability. The steps of the novel coating technology are the following (see Fig. 1): (a) mixing the polyimine and epoxy components of the vitrimer system with APP (to achieve 10 %P content) at an elevated (100 °C) temperature for lower viscosity; (b) pouring the mixture into a mould with PTFE foil; (c) homogenising the film thickness in a heated press with 100 °C and 10 bar hydraulic pressure for 10 min; (d) curing the film at room temperature (25 °C) for 72 h (which can be further reduced for process optimisation); (e) heating the vitrimer film above the vitrimer transition temperature (T_v) locally (for preventing the cracking of the rigid vitrimer film) with a hot air blower and separating the mould and the film;

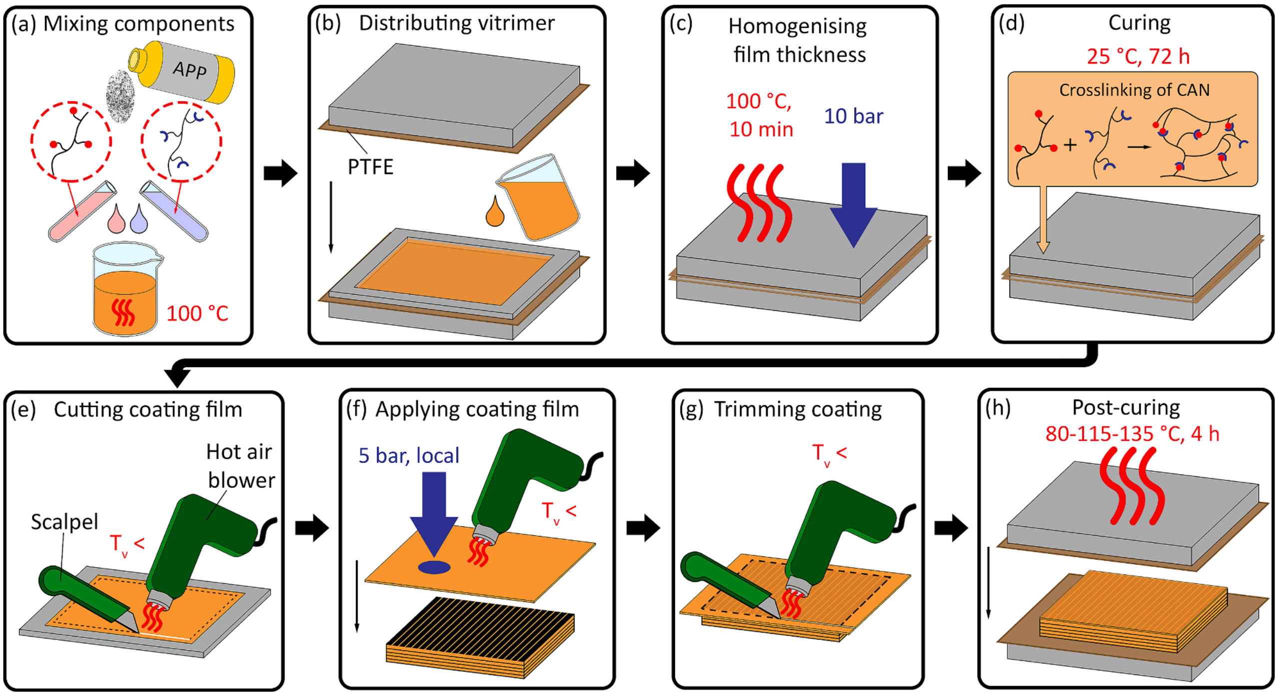


Fig. 1. Preparation of vitrimer-based flame retardant coatings and their application onto the composite.

(f) joining the vitrimer film with the vitrimer composite (made with and without 3 %P RDP) by exploiting the dynamic bond exchange reactions of the vitrimer network and heating the coating film and composite above T_v locally with 5 bar pressure; (g) trimming the excess material of the coating's edges above T_v by local heating; (h) post-curing of the coating (placed on the composite) in a mould (for preventing coating separation) in a drying oven at 80 °C for 20 min, 115 °C for 20 min and 135 °C for 3 h, according to the manufacturer's specification.

2.2.3. Fire performance

We performed standard horizontal and vertical UL 94 tests based on ISO 9772 and 9773 to classify the epoxy resin and vitrimer formulations based on their flammability. The composite sample size was 120 mm x 15 mm x 2 mm. UL 94 ratings in increasing order are HB, V-2, V-1, V-0. The flammability of the matrices was also investigated with limiting oxygen index tests (LOI, tests based on ISO 4589–2:2017). The LOI value expresses the lowest volume fraction of oxygen in a mixture of oxygen and nitrogen that supports the flaming combustion of the material under specified test conditions. 120 mm x 15 mm x 2 mm composite samples were used for the test. We performed mass loss type cone calorimetry (MLC) on the composite samples with an instrument made by FTT Inc. (East Grinstead, UK), according to the ISO 13927 standard. The samples were subjected to a heat flux of 50 kW/m^2. The composite sample size was 100 mm x 100 mm x 2 mm. Heat release values and mass reduction were continuously recorded during burning.

2.2.4. Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS)

After MLC testing, the residues of the reference and flame retardant-coated composites were examined using a JEOL JSM 6380LA scanning electron microscope (SEM, Jeol Ltd., Tokyo, Japan). The samples were gold-coated to avoid charging using a Jeol JPC1200 cathodic sputtering gold plating apparatus (Jeol Ltd., Tokyo, Japan). The residues were mapped using scanning electron microscopy with energy dispersive spectrometry (SEM-EDS) at 500x magnification. In the elemental analysis, both the inner and outer layers of the residue were analysed.

2.2.5. Mechanical characterisation

To compare the mechanical properties of the vitrimer and thermoset composites, we conducted tensile tests on a Zwick Z250 universal tensile tester (Zwick, Ulm, Germany). The tensile tester was equipped with a 100 kN tensile head, and the tests were performed based on the ISO 527–4:2023 standard. The dimensions of the PER composite specimens were 225x25x2 mm, and the dimensions of the vitrimer composite specimens were 225x25x3 mm; five specimens were tested from each material type. We applied a testing speed of 5 mm/min, a 125 mm clamping distance and 1 MPa of pre-load.

We performed dynamic mechanical analysis (DMA) tests with a TA Instruments DMA Q800 instrument (New Castle, DE, USA) to determine storage modulus (*E'*) and the glass transition temperature (T_g) from the peak values of the $tan\delta$ signals using the TA Universal Analysis 2000 software. A 3-point bending setup was employed, with the oscillation frequency set to 1.00 Hz, a static force of 0.10 N, a minimum oscillation force of 0.00 N, a 1.25 force track, an oscillation strain of 0.02 mm, a temperature range of 35–200 °C, and a heating rate of 3 °C/min. The nominal composite sample dimension was 60x10x4 mm, and the support span was 50 mm.

We carried out Charpy impact tests according to ISO 179–1:2023 to investigate the differences in energy-absorbing ability between PER and polyimine vitrimer CFRPs and to reveal the influence of flame retardants (APP and RDP) on material toughness. We also analysed the impact resistance increasing properties of the applied flame retardant coatings. A Resil Impactor Junior (Ceast Srl., Turin, Italy) impact tester with a 15 J hammer was used for the tests, the specimens were un-notched, and the blow direction was flatwise normal. In the case of coated composites, the blow direction was from the coating side.

2.2.6. Adhesion and scratch resistance

The quality of the coating technology was validated by means of a pull-off adhesion test based on ISO 4624–2023. For the pull-off adhesion tests, we used a DeFelsko PosiTest AT-A tester (St. Lawrence, New York, USA) with ø20 mm dollies fixed on the coating with Araldite 2011 (cured at room temperature for 24 h). The measured pull-off adhesion strength values were corrected with a 0.7 MPa pre-load according to the handbook of the machine.

We evaluated the scratch resistance of the vitrimer coating using a grid-cut method using a Zehntner ZMG2151 type multi-purpose gauge according to EN ISO 2409:2020. We placed the template on the coating and held it down to execute the cuts. Eleven parallel cuts with the desired spacing of 1 mm were made through the film to the composite substrate. After that, we turned the template for 90° and made the same number of cuts with the same spacing span. After the cross-cut, an adhesive tape (provided in the Zehntner kit) was applied to the cut surface and removed carefully. The classification of the samples was determined according to the standard.

3. Results and discussion

3.1. Comparison of carbon fibre-reinforced epoxy and vitrimer composites

In the following sections, a comparative analysis is conducted on the fire performance and tensile properties of carbon fibre-reinforced polyimine type vitrimer composites and benchmark epoxy resin composites. The investigation aims to assess the potential of vitrimers as a recyclable alternative to epoxy resins.

Table 2
Limiting oxygen index (LOI), UL 94 classification and mass loss type cone calorimetry results of reference and flame retarded epoxy resin and vitrimer matrices [33].

Matrix sample	LOI (vol %)	UL 94	TTI (s)	pHRR (kW/m^2)	Time to pHRR (s)	THR (MJ/m^2)	Residue (%)
PER	23	HB23 mm/min	17	706	67	100.5	0
PER APP 1 %P	27	HB	31	547	106	108.5	10
PER APP 2 %P	32	HB	40	539	99	71.5	13
PER APP 3 %P	32	HB	28	421	139	82.5	12
PER RDP 1 %P	25	HB	26	516	99	95.8	6
PER RDP 2 %P	26	HB	22	402	132	84.9	8
PER RDP 3 %P	29	HB	23	458	162	113.6	15
VITRIMER	21	no rate 60 mm/min	13	841	113	118.0	1
VITRIMER APP 1 %P	26	HB	13	251	124	99.0	14
VITRIMER APP 2 %P	26	HB	11	191	416	107.5	6
VITRIMER APP 3 %P	27	V-0	7	175	234	57.6	15
VITRIMER RDP 1 %P	24	HB	10	325	180	118.9	8
VITRIMER RDP 2 %P	25	HB	6	238	234	89.3	12
VITRIMER RDP 3 %P	28	V-0	11	290	207	75.2	20

TTI: time to ignition; pHRR: peak of heat release rate; THR: total heat release. Average standard deviation of the measured burning rate: ±1 mm/min; standard deviation of the LOI: ±1 vol%, TTI: ±3 s; pHRR: ±32 kW/m^2; time to pHRR: ±10 s; residue: ±2 %.

Table 3
LOI and UL 94 results of reference and flame retarded epoxy resin and vitrimer composites.

Composite sample	LOI (vol%)	UL 94 (burning rate)
PER COMPOSITE HL	27	HB
PER APP 3 %P COMPOSITE HL	27	HB
PER RDP 3 %P COMPOSITE HL	24	HB
PER COMPOSITE WCM	31	HB
PER APP 3 %P COMPOSITE WCM	36	HB
PER RDP 3 %P COMPOSITE WCM	29	HB
VITRIMER COMPOSITE	23	HB (25.4 mm/min)
VITRIMER APP 3 %P COMPOSITE	34	HB
VITRIMER RDP 3 %P COMPOSITE	27	HB

HL: hand lamination, WCM: wet compression moulding, Average standard deviation of the measured burning rate: ±1 mm/min; standard deviation of the LOI: ±1 vol%.

Table 4
Mass loss type cone calorimetry results of reference and flame retarded epoxy resin and vitrimer composites.

Composite sample	TTI (s)	pHRR (kW/m^2)	Time to pHRR (s)	THR (MJ/m^2)	Residue (%)
PER COMPOSITE HL	30	467	72	45.9	44
PER APP 3 %P COMPOSITE HL	26	359	70	37.2	51
PER RDP 3 %P COMPOSITE HL	28	292	67	35.4	50
PER COMPOSITE WCM	23	351	39	24.1	47
PER APP 3 %P COMPOSITE WCM	20	247	35	15.9	50
PER RDP 3 %P COMPOSITE WCM	26	200	45	15.8	56
VITRIMER COMPOSITE	36	289	140	44.6	43
VITRIMER APP 3 %P COMPOSITE	37	186	158	41.3	49
VITRIMER RDP 3 %P COMPOSITE	23	152	176	48.4	51

HL: hand lamination, WCM: wet compression moulding, TTI: time to ignition; pHRR: peak of heat release rate; THR: total heat release. Average standard deviation of the measured mass loss calorimeter values: TTI: ±3 s; pHRR: ±32 kW/m^2; time to pHRR: ±10 s; residue: ±2 %.

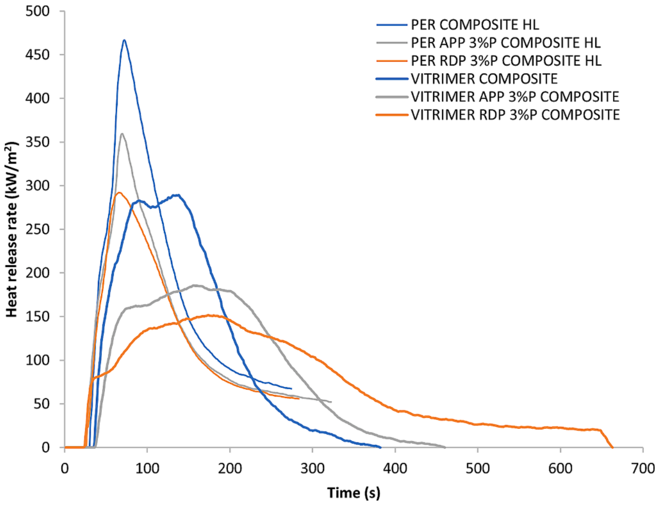


Fig. 2. The heat release rate of reference and flame retarded vitrimer and hand-laminated (HL) epoxy resin composites.

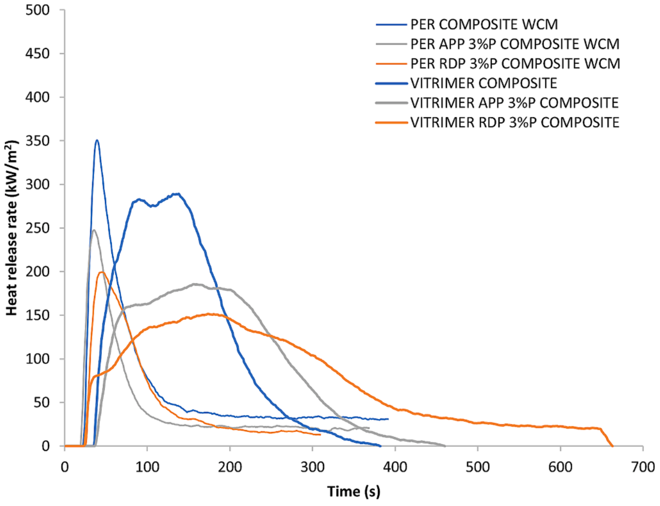


Fig. 3. The heat release rate of reference and flame retarded vitrimer and wet-compressed (WCM) epoxy resin composites.

As with the currently available composite manufacturing method, the highest achievable carbon fibre content in vitrimer composites is in the range of 42–45 mass%, benchmark epoxy composites were not only prepared by wet compression moulding, resulting in a fibre content of 60 mass%, but also with hand lamination method that led to a similar fibre content (42 mass%) as prepregging followed by hot pressing in the case of vitrimers.

3.1.1. Comparison of fire performance of carbon fibre-reinforced epoxy and vitrimer composites

In our previous work, we investigated the flame retardancy of reference and flame retarded PER epoxy resin and vitrimer systems by limiting oxygen index (LOI), UL 94 and mass loss calorimetry tests [33]. The main results that served as a starting point for this research are summarised in Table 2.

Based on the matrix results, we prepared carbon fibre-reinforced composites from the reference and flame retarded polymers containing 3 % phosphorus. The LOI and UL 94 results of the epoxy and vitrimer composites are summarised in Table 3.

The addition of carbon fibres reduces the proportion of combustible matrix, generally making carbon fibre-reinforced composites less flammable than the matrix material alone. In the case of PER, the LOI value increased from 23 vol% to 27 vol% in hand-laminated composite and to 31 vol% in wet-compressed composite, whereas for vitrimer, the addition of carbon fibres increased the LOI value from 21 vol% to only 23 vol %. In the hand-laminated systems, neither APP nor RDP could further improve the LOI or the UL 94 classification. In contrast, in wet-compressed PER and vitrimer systems, APP significantly increased the LOI values compared to the reference samples. In vitrimers, the addition of inert carbon fibre reinforcement reduced the flame propagation rate from 60 mm/min to 25.4 mm/min; however, similarly to all other samples, the UL 94 classification remained HB. This is likely due to the so-called “candlewick effect,” whereby during combustion, carbon fibres can channel the flammable pyrolysis products of the matrix to the flame zone through capillary action. This accelerates heat feedback and increases the mass loss of the matrix. As a result, despite the slower flame propagation rate observed during testing, the samples burned completely to the clamps.

The mass loss type cone calorimetry results of the epoxy and vitrimer composites can be seen in Table 4, Figs. 2 and 3.

Although the PER as matrix has better fire performance than the vitrimer system, the PER composites prepared either by HL or WCM ignite earlier and have a higher pHRR than the vitrimer composites. Similarly to the matrices, the flame retarded vitrimer composites outperform the epoxy composites regarding the relative pHRR reduction related to their reference composite counterparts. Contrary to the matrix, the lowest pHRR (152 kW/m^2 in the case of vitrimer composite) was achieved in all cases with RDP, acting mainly in the gas phase. As previously discussed in our publication [30], the reason behind this phenomenon is that carbon fibres interfere with the condensed phase action of APP, because the reinforcement hinders the intumescence by physically blocking the formation of a continuous protective layer when embedded in the matrix material and therefore, APP cannot fully develop its flame retardant effect. The THR values of the vitrimer composites are closer to the results of the hand-laminated PER composites, as these systems have a higher ratio of the burnable polymer matrix than the wet-compressed PER composites [44]. Even though the lower fibre content, the vitrimer composites had lower absolute pHRR than their wet-compressed epoxy counterparts.

3.1.2. *Comparison of tensile properties of carbon fibre-reinforced epoxy and vitrimer composites*

The tensile strength (σ_{max}) and Young's modulus (E) values of the composites are listed in Table 5 and are shown in Fig. 4**.** The results show that the wet-compressed PER composite has a remarkably higher σ_{max}, which can be explained by the higher carbon fibre content of the material, as carbon fibres are the main load-bearing elements of UD-composites during tensile testing. For better comparability and to assess result extensibility, we also analysed hand-laminated PER composites and benchmarked them against DGEBA composites from previous research [31]. The hand-laminated PER composite with a similar fibre content to the vitrimer composites has higher σ_{max} and E; however, the hand-laminated benchmark DGEBA composite with 40 mass% fibre content has lower σ_{max}, suggesting that increasing fibre content through improved processing could make polyimine vitrimer composites a viable substitute for certain epoxy composites. It is worth to highlight, that despite the RDP content can decrease the mechanical properties of the composite (as its molecules containing large aromatic rings form a stearic barrier during crosslinking, forming fewer crosslinks), the application of RDP can be advantageous in some cases. In the case of hand lamination technology, as the addition of RDP decreases the viscosity of the epoxy system, the quality of impregnation will be significantly better, influencing the mechanical properties in an advantageous way. In the case of hand lamination, the better processing technology is more dominant than the effect of fewer crosslinks. However, the effect of APP on the mechanical properties is highly dependent on the quality of distribution in the epoxy system. When the APP is distributed homogenously, as it is a spherical additive, it increases σ_{max} and E of materials; but the agglomeration of APP's small particles will form defects in the material, decreasing the mechanical properties. The measured strength values suggest more homogeneous dispersion of the APP particles in the vitrimer system, which could also be related to the different production method (i.e. prepregging layer by layer). The tensile tests also show that Young's modulus of vitrimer composites is substantially lower than the epoxy composites', resulting in higher flexibility of the composites.

Table 5
Tensile test results of reference and flame retarded epoxy resin and vitrimer composites.

Composite	σ_{max} (MPa)	E (GPa)
PER COMPOSITE HL	959 ± 58	16.5 ± 0.78
PER APP 3 %P COMPOSITE HL	654 ± 37	14.1 ± 0.34
PER RDP 3 %P COMPOSITE HL	986 ± 17	16.8 ± 0.49
PER COMPOSITE WCM	1284 ± 191	23.7 ± 0.36
PER APP 3 %P COMPOSITE WCM	911 ± 77	18.1 ± 1.54
PER RDP 3 %P COMPOSITE WCM	1012 ± 84	20.4 ± 0.26
VITRIMER COMPOSITE	497 ± 20	9.3 ± 0.45
VITRIMER APP 3 %P COMPOSITE	591 ± 20	11.1 ± 0.79
VITRIMER RDP 3 %P COMPOSITE	497 ± 51	9.0 ± 0.91
DGEBA COMPOSITE HL [31]	424 ± 14	18.5 ± 0.82

HL: hand lamination, WCM: wet compression moulding.

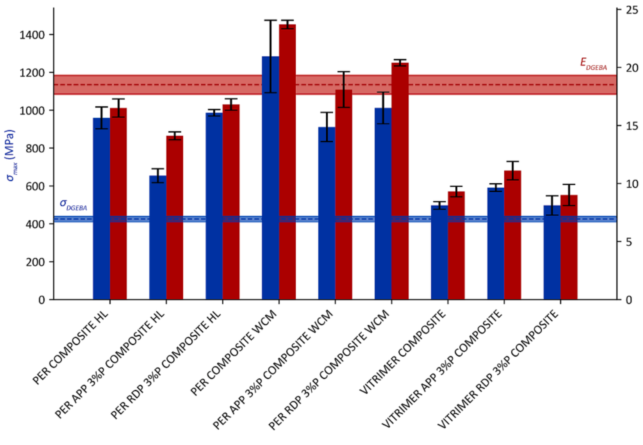


Fig. 4. Tensile test results of reference and flame retarded epoxy resin and vitrimer composites compared to benchmark DGEBA hand-laminated composite [31].

3.2. *Coated composites*

As discussed in chapter 3.1, the effectiveness of condensed phase flame retardants in composites is limited. To address this limitation, we applied RDP as a flame retardant in the vitrimer matrix material, as it primarily exerts its flame retardant effect in the gas phase; additionally, we prepared a vitrimer coating flame retarded with APP on the surface of the composites, functioning as an intumescent coating.

3.2.1. *Fire performance of coated vitrimer composites*

The LOI and UL 94 results of the reference and flame retarded vitrimer composites without and with intumescent coatings are summarised in Table 6.

The vitrimer coating containing 10 %P APP increased the LOI of the reference vitrimer composite from 23 vol% to 28 vol%, which is less than the LOI of composite flame retarded with 3 %P APP, but the coating itself ameliorated the UL 94 classification form HB to V-0 classification, with no flame propagation observed during testing. In the case of vitrimer composite flame retarded with 3 %P RDP, the vitrimer coating containing 10 %P APP increased the LOI even more significantly, from 27 vol% to 38 vol% (a 41 % improvement), indicating a synergism of the common application of RDP in the matrix and APP in the vitrimer-based coating. The previously observed "candlewick effect" was absent, and the sample proved non-ignitable in UL 94 testing.

The mass loss type cone calorimetry results of the reference and flame retarded vitrimer composites without and with intumescent coating are summarised in Table 7 and Fig. 5.

Table 6
LOI and UL 94 results of the uncoated and coated vitrimer composites.

Composite sample	LOI (volume %)	UL 94 (burning rate)
VITRIMER COMPOSITE	23	HB (25.4 mm/min)
VITRIMER APP 3 %P COMPOSITE	34	HB
VITRIMER RDP 3 %P COMPOSITE	27	HB
VITRIMER COMPOSITE APP 10 %P COATING	28	V-0
VITRIMER RDP 3 %P COMPOSITE APP 10 %P COATING	38	V-0

Average standard deviation of the measured burning rate: ±1 mm/min; standard deviation of the LOI: ±1 vol%.

Table 7
Mass loss type cone calorimetry results of reference and flame retarded epoxy resin and vitrimer composites.

Composite sample	TTI (s)	pHRR (kW/m^2)	Time to pHRR (s)	THR (MJ/m^2)	Residue (%)	MARHE (kW/m^2)	EHC (MJ/kg)
VITRIMER COMPOSITE	36	289	140	44.6	43	518	29.70
VITRIMER APP 3 %P COMPOSITE	37	186	158	41.3	49	136	16.92
VITRIMER RDP 3 %P COMPOSITE	23	152	176	48.4	51	187	23.58
VITRIMER COMPOSITE APP 10 %P COATING	32	126	349	56.3	43	95	17.98
VITRIMER RDP 3 %P COMPOSITE APP 10 %P COATING	52	135	272	48.2	47	82	16.10

TTI: time to ignition; pHRR: peak of heat release rate; THR: total heat release, MARHE: maximum average rate of heat emission, EHC: effective heat of combustion. Average standard deviation of the measured mass loss calorimeter values: TTI: ±3 s; pHRR: ±32 kW/m^2; time to pHRR: ±10 s; residue: ±2 %.

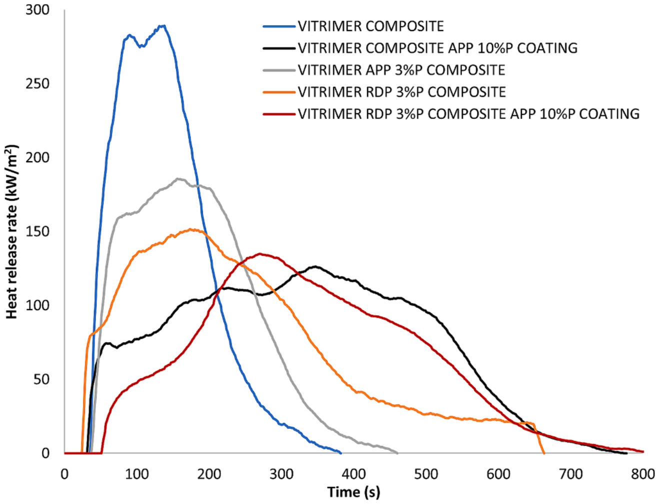


Fig. 5. The heat release rate of reference and flame retarded vitrimer composites without and with intumescent coating.

Although RDP alone significantly reduced the time to ignition (TTI) in the vitrimer composites from 36 s to 23 s due to its gas-phase mechanism initiated at low temperatures, a different behaviour was observed when combined with the APP-containing coating: The reference vitrimer composite with the coating ignited after 32 s, while the coated composite with RDP in the vitrimer matrix ignited only after 52 s. This demonstrates that the combined effect of RDP and APP effectively delays ignition.

Regarding peak heat release rate (pHRR), the coating with APP achieved a substantial 56 % reduction for the reference vitrimer composite and an 11 % reduction in the vitrimer composite containing RDP. This smaller improvement is attributed to the already relatively low pHRR of the RDP-containing composite without the coating. The coating also significantly delayed the time to peak heat release, which is critical for increasing evacuation times in real fire scenarios. The shape of the heat release curves indicates significantly reduced peaks that occur with a delay. In both cases, controlled, low heat-release combustion was observed due to the unlimited formation of an intumescent charred layer from the coating.

The total heat release (THR) slightly increased for the reference sample with the coating but remained unchanged for the RDP-containing composite. The residual mass showed a slight decrease, explained by the additional matrix layer without carbon fibres applied to the composite. This layer, activated as an intumescent barrier during combustion, leaves less residue than the base composite with 43 mass% fibre content. However, the residual mass of the composite itself, representing the original product, was higher. The top and side view of the MLC residues is shown in Fig. 6. When both the composite and the coating contained flame retardant, the surface of the coating became more homogeneous, and the side view photo clearly shows that the edges of the delaminated layers were also coated with the intumescent char, in contrast to the sample without RDP in the composite matrix.

MARHE (maximum average rate of heat emission) and EHC (effective heat of combustion) are essential parameters for analysing the efficiency and mechanisms of flame retardants. MARHE represents the maximum of the average heat release rate during combustion, indicating the overall flammability of the material. Low MARHE values suggest that the material emits less heat during combustion, thereby reducing the intensity of the burning process. EHC measures the ratio of combustion energy to the amount of material burned, reflecting the efficiency of the combustion process. A decrease in EHC indicates the formation of non-combustible components, such as char layers or inert gases, during combustion. Analysing these parameters helps determine whether flame retardant mechanisms operate in the condensed or gas phase, and this information is critical for designing and optimising flame retardant systems.

The MARHE and EHC results calculated from MLC measurements show that APP and RDP enhance the fire performance of vitrimer matrix carbon fibre composites through different but complementary mechanisms. In vitrimer composites containing 3 %P APP, MARHE decreased by approximately 74 % compared to the reference vitrimer composite, while EHC was reduced by 43 %. This is attributed to APP's condensed-phase mechanism, which leads to the formation a phosphorus oxide-rich protective layer, reducing heat release and increasing the residual mass ratio. For vitrimer composites containing 3 %P RDP, MARHE decreased by about 64 %, while EHC showed a smaller reduction of 21 %. This indicates that RDP primarily acts through a gas-phase mechanism, reducing the amount of heat released during combustion. Overall, the combination of APP and RDP reduces heat release and increases the residual mass ratio through a synergistic effect. APP provides protection to the outer layers via its condensed-phase mechanism, while RDP activates gas-phase mechanisms in the inner layers, significantly enhancing the fire resistance of the composites.

Following MLC measurements, the structure of the residues was analysed using scanning electron microscopy (SEM) (Fig. 7).

The analysis revealed significant differences between the structure of the inner and outer layers of the intumescent char. In both cases, the inner layers were less compact, with larger and more homogeneous pores compared to the outer layers. In the reference coated vitrimer composite, this can be attributed to the high nitrogen content of the vitrimer, which contributes to the flame retardant process through intense gas evolution during combustion. In the coated vitrimer composite with a matrix flame retarded with RDP, a more varied pore size distribution was observed, probably caused by gases released during RDP decomposition. The outer layers were in both cases more compact, denser, and featured smaller pores, resulting from the formation of phosphorus oxides and a char layer through condensed phase mechanism of APP. In the RDP-containing sample, a “bubblier” structure was evident, indicating more intense gas evolution.

In the inner and outer layers of the combustion residues, the amounts of carbon (C), oxygen (O), and phosphorus (P) were determined by energy-dispersive X-ray spectroscopy (EDS) (Fig. 8).

In both coated vitrimer composites, the inner layers have higher

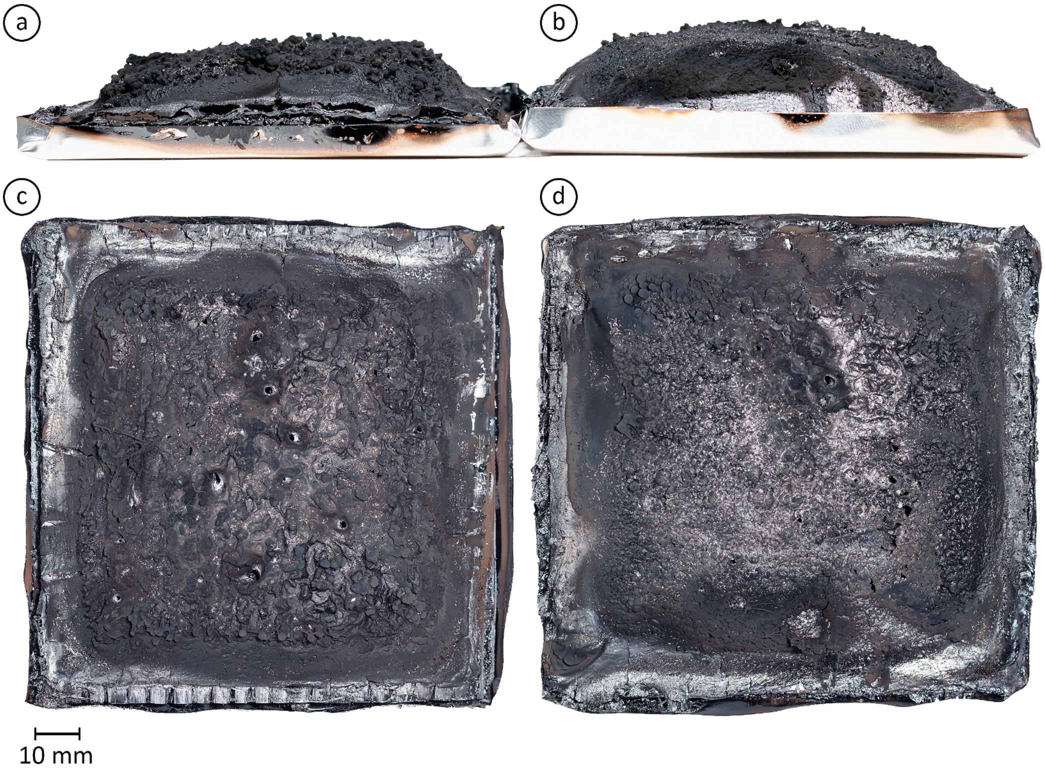


Fig. 6. The residue of composites with intumescent coating: (a) front view of VITRIMER COMPOSITE APP 10 %P COATING, (b) front view of VITRIMER RDP 3 %P COMPOSITE APP 10 %P COATING, (c) top view of VITRIMER COMPOSITE APP 10 %P COATING, (d) top view of VITRIMER RDP 3 %P COMPOSITE APP 10 % P COATING.

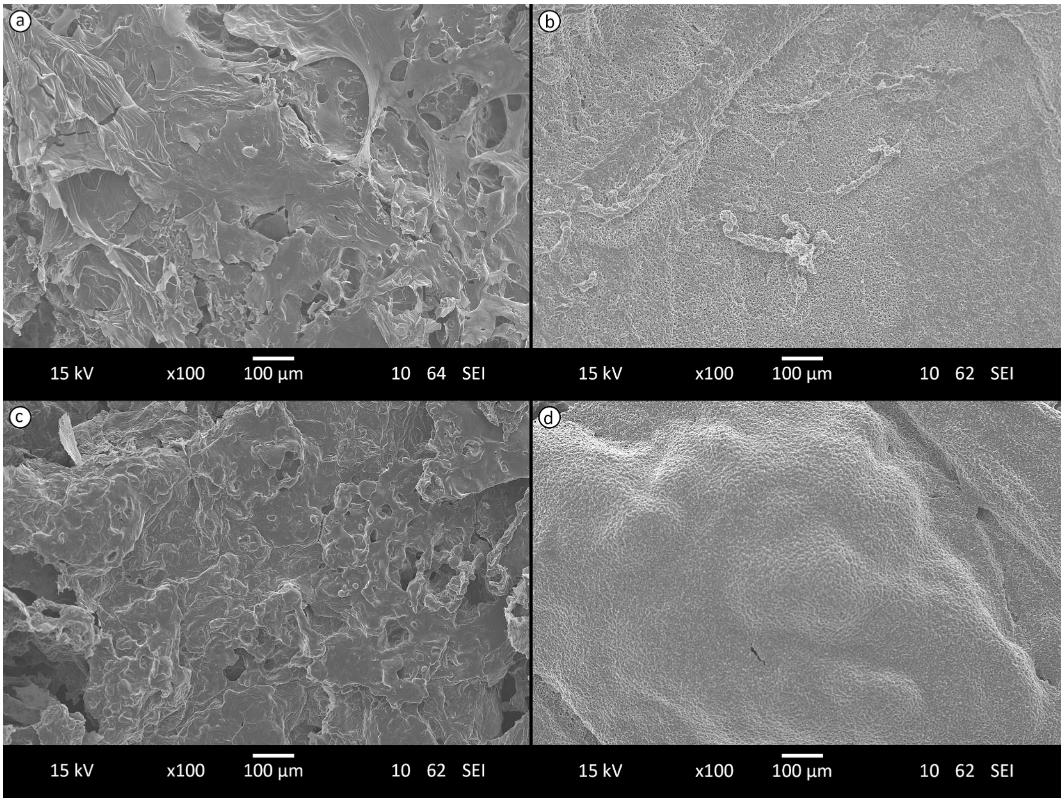
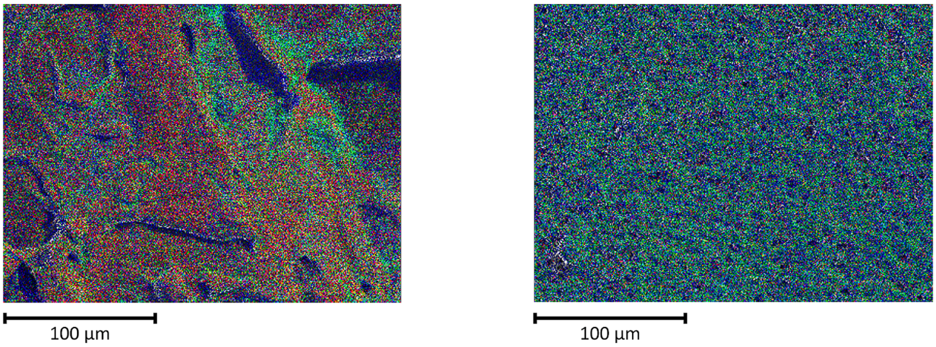


Fig. 7. Typical SEM images of the combustion residues (a) inner and (b) outer layers of the coated reference vitrimer composite (VITRIMER COMPOSITE APP 10 %P COATING), (c) inner and (d) outer layers of the coated vitrimer composite flame retarded with RDP (VITRIMER RDP 3 %P COMPOSITE APP 10 %P COATING).

	VITIRMER COMPOSITE APP 10%P COATING inner	VITIRMER COMPOSITE APP 10%P COATING outer
Element	(mass%)	(mass%)
C	50.1	15.3
O	35.1	55.8
P	14.8	28.9



	VITIRMER RDP 3%P COMPOSITE APP 10%P COATING inner	VITIRMER RDP 3%P COMPOSITE APP 10%P COATING outer
Element	(mass%)	(mass%)
C	37.3	14.7
O	40.4	53.7
P	22.2	31.6

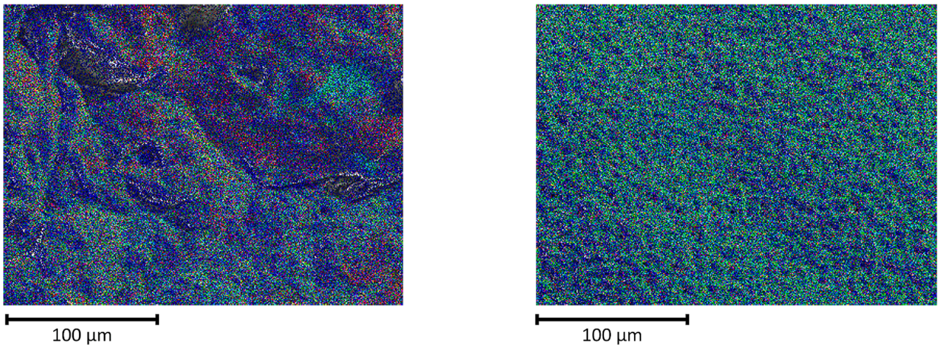


Fig. 8. Elemental composition of the inner and outer part of the mass loss type cone calorimetry residues of coated vitrimer composites by SEM-EDS (colour coding of elemental maps: carbon – red, oxygen – green, phosphorus – blue.).

carbon content and lower oxygen and phosphorus contents compared to the outer layers. This indicates that during the intumescent mechanism, the phosphorus-containing decomposition products of APP primarily migrate to the outer layers, where the phosphorus- and oxygen-rich oxides form an effective and stable heat-protective layer. In the vitrimer composite containing RDP in the matrix, the inner layer contains more phosphorus, indicating RDP's contribution to activating the gas phase flame retardant mechanisms. In the outer layers, phosphorus oxides dominate in both samples, but the presence of RDP leads to an additional increase in phosphorus concentration, enhancing the effectiveness of the protective layer. For the reference vitrimer composite base, the condensed phase mechanism dominates in the outer layers, while the samples combined with RDP provide more complex and efficient flame retardancy through a combination of gas- and condensed phase mechanisms. These results support the idea that the presence of RDP, complementing APP's mechanisms, significantly improves the flame retardant properties of both the inner and outer layers.

In conclusion, the results show that APP and RDP flame retardants activate different mechanisms in the inner and outer layers, which, through their synergistic effect, significantly improve the fire resistance of the samples. APP's condensed phase mechanism aids in the formation of a compact, phosphorus oxide-rich, heat-protective char layer in the outer layers, while RDP contributes to the gas-phase flame retardant mechanism in the inner layers, resulting in more intense gas evolution and higher phosphorus content. The EDS results confirmed that APP mainly enhances the protection of the outer layers, while RDP strengthens the gas-phase mechanisms of the inner layers. These results clearly support the effectiveness of the combination of RDP and APP, which increases both the complexity and efficiency of the flame retardancy mechanisms.

3.2.2. *Adhesion of the vitrimer-based flame retardant coatings to the vitrimer composites*

We have chosen a gel-coated PER epoxy composite from previous research [45] to illustrate comparatively the adhesion strength of the novel vitrimer coating. However, it must be highlighted that there are different adhesion mechanisms in the case of the PER and vitrimer composites. In the case of conventional thermosetting systems, the adhesion is formed by the secondary chemical bonds between the coating and the thermoset composite, which is affected by the contact surface area. Uneven surfaces can also increase the bonding between the coating and the sample via mechanical locking of the surfaces. On the other hand, in the case of the novel vitrimeric coating, primary chemical bonds can be formed between the coating and the composite, thanks to the dynamic covalent bonds in the covalent adaptable network. Since both the coating and the matrix are based on polyimine vitrimer chemistry, dynamic imine exchange reactions occur at the interface, enabling interfacial chemical bonding above the vitrimer transition

Table 8
The adhesion strength of the flame retarded coatings to composites.

Composite	Adhesion strength (MPa)
PER COMPOSITE APP 10 %P COATING	1.16 ± 0.20
PER 3 %P RDP COMPOSITE APP 10 %P COATING	0.53 ± 0.22
VITRIMER COMPOSITE APP 10 %P COATING	0.94 ± 0.29
VITRIMER 3 %P RDP COMPOSITE APP 10 %P COATING	0.54 ± 0.24

temperature (T_v). The adhesion strength values of the samples are shown in Table 8. The vitrimer and RDP flame retarded vitrimer composites have approximately the same adhesion strength with the 10 %P APP vitrimer coating as the gel coated PER composites, respectively, which confirms the effective usability of the vitrimer based flame retarded coatings on vitrimer composites and facilitates future applications. Similarly to the PER-based epoxy system, RDP behaves as a stearic barrier due to the large aromatic rings in its molecule: it decreases the ability to form a strong crosslinked network (which is proved by lower crosslinking enthalpy measured by differential scanning calorimetry [33]) which also decreases the adhesion strength.

Additionally, we evaluated the scratch resistance of the APP 10 %P vitrimer coating both on reference vitrimer composite and on vitrimer composite flame retarded with RDP using a grid-cut method. During the test, we investigated the pattern after the adhesive peel-off and found in both coated composites that only small flakes of the coating detached at the intersection of the cuts. The affected area within the cross-cut was less than 4 %, which means these coatings reached Class 1 type results (the second best amongst the classifications). These results provide further evidence of the mechanical robustness of the vitrimer layer and its potential for industrial use in multifunctional, repairable, and recyclable composite systems.

3.2.3. *Dynamic mechanical analysis of the coated vitrimer composites*

We conducted dynamic mechanical analysis (DMA) on the coated composites to assess the effect of flame retardants on the glass transition temperature (T_g), and their influence on the temperature-dependent mechanical properties. During the three-point bending tests, we measured the samples with the coating applied to both the compression and tension sides. The DMA curves can be seen in Fig. 9., T_g and storage modulus (*E'*) values are in Table 9. The results indicate that the RDP increased T_g and enhanced the *E'*, leading to a stiffer material in accordance with the tensile tests. Without RDP, *E'* decreased by 95–96 % with increasing temperature, whereas in RDP-containing samples, the decrease was only 83–88 %, indicating improved thermal stability. When the intumescent coating was applied on the compression side, composite stiffness increased, which is relevant for practical applications.

Table 9
DMA results of reference and flame retarded vitrimer composites with intumescent coating.

composite	$E'_{35^\circ C}$ (MPa)	$E'_{120^\circ C}$ (MPa)	T_g (°C)
VITRIMER COMPOSITE APP 10 %P COATING (coating compression side)	8028	348	73
VITRIMER COMPOSITE APP 10 %P COATING (coating tension side)	7119	344	71
VITRIMER 3 %P RDP COMPOSITE APP 10 %P COATING (coating compression side)	10,406	1199	89
VITRIMER 3 %P RDP COMPOSITE APP 10 %P COATING (coating tension side)	6496	1077	87

$E'_{35^\circ C}$ storage modulus at 35 °C, $E'_{120^\circ C}$ storage modulus at 120 °C, T_g glass transition temperature.

3.2.4. *Charpy impact test of the coated vitrimer composites*

The energy-absorbing ability of the PER, polyimine vitrimer and coated vitrimer composites (with 10 %P APP vitrimer coating) was inspected with Charpy impact test. The material toughness and the absorbed energy in the case of dynamic loads are key material properties from the perspective of the applicability of “high-tech” composites. As can be seen from the results depicted in Fig. 10**.** the vitrimer and flame retarded vitrimer composites generally have higher Charpy impact strength than PER and flame retarded PER composites, making them more suitable for high dynamic load applications. However, it is important to highlight that the flame retardants, both APP and RDP decreased the toughness of vitrimer composites. The APP agglomerates (coming from inefficient homogenising of APP and high viscosity vitrimer resin) may create defects in the matrix and starting locations for cracks, making the composite easier to damage. The RDP’s softening effect can also decrease the toughness of the composite, due to the large aromatic rings in the RDP’s molecule, which form a stearic barrier during crosslinking. Nevertheless, in the case of the coated composites (containing 10 %P APP), these generally unfavourable effects become advantageous and increase the energy absorption. Thanks to the high APP content, the coating shatters during impact, absorbing a lot of energy. Also, RDP decreased the adhesion strength between the coating and the composite (analysed with the pull-off adhesion tests), making the coating separate more easily at impact. This easier-separating and

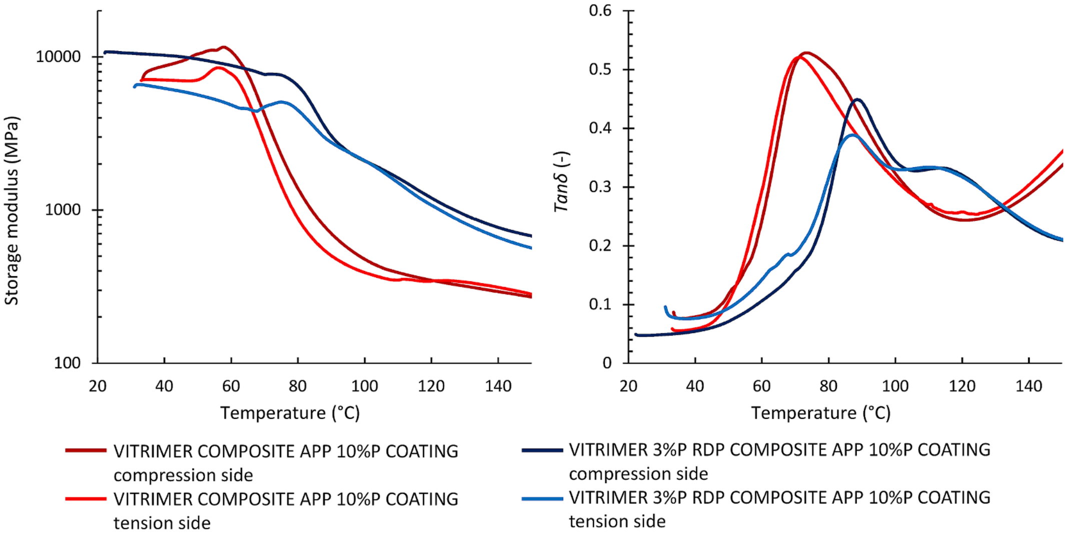


Fig. 9. Storage modulus and tanδ graphs of the reference and RDP flame retarded vitrimer composites with intumescent coating.

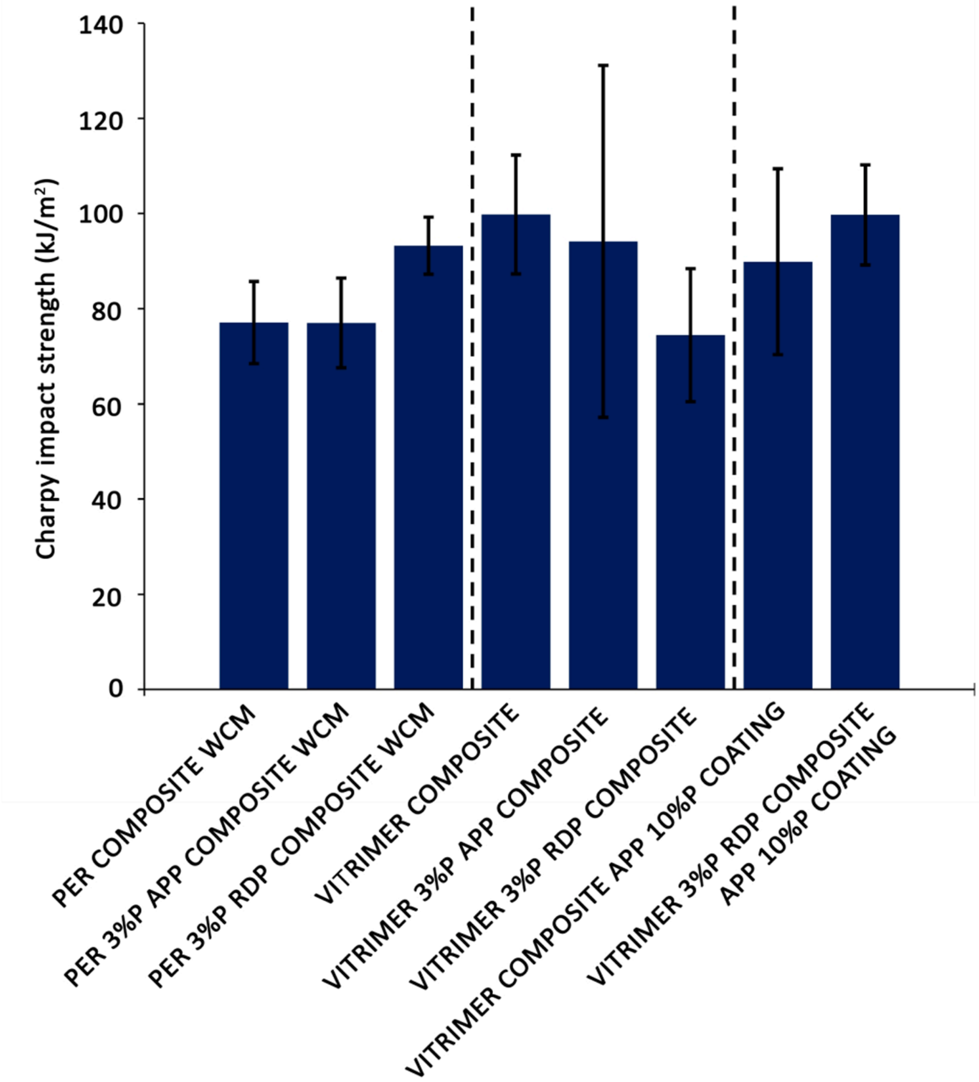


Fig. 10. Charpy impact test results of the reference and flame retarded vitrimer composites without and with intumescent coating compared to PER epoxy resin benchmark composite.

shattering coating may have a similar effect as the "crumple zone" in the case of car crashes from the perspective of energy absorption.

4. Conclusions

This study demonstrated the potential of recyclable polyimine vitrimer-based carbon fibre-reinforced composites as alternatives to epoxy systems, with a special focus on their fire performance and mechanical properties. A key challenge identified in vitrimer composites was the limited effectiveness of condensed-phase flame retardants in the presence of carbon fibre reinforcement. Carbon fibres, while enhancing the mechanical properties of composites, interfered with the intumescent mechanism of APP by hindering the migration of decomposition products necessary for forming a continuous protective char layer.

To compensate for the reduced efficiency of condensed-phase flame retardancy in the composite bulk, we introduced an APP-based vitrimer coating. This coating significantly improved fire resistance, achieving a UL 94 V-0 classification and eliminating the "candlewick effect" previously observed in uncoated vitrimer composites. The coating acted through an intumescent mechanism, forming a phosphorus oxide-rich char that protected the composite surface. When applied to RDP-containing vitrimer composites, the coating further extended the time to ignition and enhanced LOI values, demonstrating a strong synergistic effect between the gas-phase action of RDP and the condensed-phase mechanism of APP. Further analysis using MARHE and EHC parameters confirmed the complementary roles of APP and RDP in fire protection. APP primarily reduced MARHE by forming a robust char layer, while RDP contributed to lowering EHC by promoting the release of flame-inhibiting gases. Microscopic and elemental analyses of the residual char structure revealed that phosphorus migration occurred predominantly toward the outer layers, reinforcing the heat-resistant char. In RDP-containing composites, additional phosphorus accumulation in the inner char layers was observed, further supporting its role in gas-phase flame retardancy.

The tensile strength of vitrimer composites, ranging from 497 MPa to 591 MPa, is smaller than that of the PER epoxy composites but still comparable to the hand-laminated DGEBA epoxy composite (424 MPa). Based on the comparison of tensile test results of hand-laminated and wet-compressed PER composites, the mechanical properties of vitrimer composites could be significantly enhanced with improved processing techniques, resulting in increased fibre content. The lower Young's modulus of vitrimer composites, ranging from 9.0 GPa to 11.1 GPa, indicates higher flexibility, which could be advantageous in applications where improved impact resistance or flexibility is required. The adhesion strength of the vitrimer-based coating to the vitrimer composites was found to be comparable to conventional gel coatings applied to epoxy composites. This adhesion is attributed to the dynamic covalent bonding capabilities of the vitrimer network, allowing primary chemical bonds to form between the coating and substrate. In addition, the coating exhibited excellent scratch resistance, as confirmed by the grid cut test, achieving a Class 1 rating. This feature enhances the durability and integrity of the flame retardant system, facilitating its application in advanced fire-resistant composite structures. Charpy impact tests showed that reference and flame-retarded vitrimer composites had higher impact strength than the epoxy resin-based ones, indicating improved energy absorption under dynamic loads. Although APP and RDP reduced toughness in uncoated vitrimer composites, the coating with high APP-content enhanced impact resistance by acting similarly to a crumple zone.

Overall, this study highlights the benefits of integrating gas-phase and condensed-phase flame retardants into vitrimer composites, successfully addressing the challenges posed by carbon fibre reinforcement. The combination of RDP in the matrix and an APP-containing coating provides a promising strategy for achieving superior fire performance while maintaining mechanical integrity and recyclability. The development of an entirely vitrimer-based composite and coating system marks a novel contribution to the field, offering a recyclable and multifunctional alternative to traditional thermoset composites. These findings support the development of next-generation multifunctional composite materials with enhanced safety and sustainability.

CRediT authorship contribution statement

Andrea Toldy: Formal analysis, Methodology, Resources, Visualization, Writing – review & editing, Conceptualization, Funding acquisition, Project administration, Supervision, Writing – original draft. **Dániel István Poór:** Investigation, Visualization, Data curation, Validation, Writing – review & editing, Conceptualization, Methodology, Writing – original draft. **Beáta Szolnoki:** Visualization, Validation, Investigation, Writing – review & editing. **Norbert Geier:** Resources, Project administration, Writing – review & editing, Funding acquisition, Supervision. **Ákos Pomázi:** Investigation, Visualization, Data curation, Validation, Conceptualization, Methodology, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

References

[1] Türel T, Dağlar Ö, Eisenreich F, Tomović Ž. Epoxy thermosets designed for chemical recycling. Chem Asian J 2023;18:e202300373. https://doi.org/10.1002/asia.202300373.

[2] Maes S, Badi N, Winne JM, Du Prez FE. Taking dynamic covalent chemistry out of the lab and into reprocessable industrial thermosets. Nat Rev Chem 2025. https://doi.org/10.1038/s41570-025-00686-7.

[3] Toldy A. Safe and sustainable-by-design: Redefining polymer engineering for a greener future. Express Polym Lett 2025;19:350. https://doi.org/10.3144/expresspolymlett.2025.25.

[4] Kloxin CJ, Scott TF, Adzima BJ, Bowman CN. Covalent adaptable networks (CANs): a unique paradigm in cross-linked polymers. Macromolecules 2010;43:2643–53. https://doi.org/10.1021/ma902596s.

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

[6] Denissen W, Winne JM, Du Prez FE. Vitrimers: permanent organic networks with glass-like fluidity. Chem Sci 2016;7:30–8. https://doi.org/10.1039/C5SC02223A.

[7] Kissounko DA, Taynton P, Kaffer C. New material: vitrimers promise to impact composites. Reinf Plast 2018;62:162–6. https://doi.org/10.1016/j.repl.2017.06.084.

[8] Zhang ZP, Rong MZ, Zhang MQ. Polymer engineering based on reversible covalent chemistry: a promising innovative pathway towards new materials and new functionalities. Prog Polym Sci 2018;80:39–93. https://doi.org/10.1016/j.progpolymsci.2018.03.002.

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

[10] Taynton P, Yu K, Shoemaker RK, Jin Y, Qi HJ, Zhang W. Heat- or water-driven malleability in a highly recyclable covalent network polymer. Adv Mater 2014;26:3938–42. https://doi.org/10.1002/adma.201400317.

[11] Belowich ME, Stoddart JF. Dynamic imine chemistry. Chem Soc Rev 2012;41:2003–24. https://doi.org/10.1039/C2CS15305J.

[12] Zhao S, Abu-Omar MM. Recyclable and malleable epoxy thermoset bearing aromatic imine bonds. Macromolecules 2018;51:9816–24. https://doi.org/10.1021/acs.macromol.8b01976.

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

[14] Zhang H, Cui J, Hu G, Zhang B. Recycling strategies for vitrimers. Int J Smart Nano Mater 2022;13:367–90. https://doi.org/10.1080/19475411.2022.2087785.

[15] Taynton P, Ni H, Zhu C, Yu K, Loob S, Jin Y, et al. Repairable woven carbon fiber composites with full recyclability enabled by malleable polyimine networks. Adv Mater 2016;28:2904–9. https://doi.org/10.1002/adma.201505245.

[16] Pomázi Á, Poór DI, Geier N, Toldy A. Optimising recycling processes for polyimine-based vitrimer carbon fibre-reinforced composites: a comparative study on reinforcement recovery and material properties. Materials 2024;17:2372. https://doi.org/10.3390/ma17102372.

[17] Hervieu C, Sekar A, Poilvet G, Dul S, Lehner S, Jovic M, et al. Reprocessable flame retardant amino-ester thermoset. Chem Eng J 2025;503:158190. https://doi.org/10.1016/j.cej.2024.158190.

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

[19] Abdur Rashid M, Liu W, Wei Y, Jiang Q. Review of reversible dynamic bonds containing intrinsically flame retardant biomass thermosets. European Polym J 2022;173:111263. https://doi.org/10.1016/j.eurpolymj.2022.111263.

[20] Guo Y, Yang Q, Huo S, Li J, Jafari P, Fang Z, et al. Recyclable fire-retardant bio-based thermosets: from molecular engineering to performances and applications. Prog Polym Sci 2025;162:101935. https://doi.org/10.1016/j.progpolymsci.2025.101935.

[21] Wu Klingler W, Bifulco A, Polisi C, Huang Z, Gaan S. Recyclable inherently flame-retardant thermosets: Chemistry, properties and applications. Compos Part B: Eng 2023;258:110667. https://doi.org/10.1016/j.compositesb.2023.110667.

[22] Wang S, Ma S, Li Q, Yuan W, Wang B, Zhu J. Robust, fire-safe, monomer-recovery, highly malleable thermosets from renewable bioresources. Macromolecules 2018;51:8001–12. https://doi.org/10.1021/acs.macromol.8b01601.

[23] Zhang X, Eichen Y, Miao Z, Zhang S, Cai Q, Liu W, et al. Novel Phosphazene-based flame retardant polyimine vitrimers with Monomer-Recovery and high performances. Chem Eng J 2022;440:135806. https://doi.org/10.1016/j.cej.2022.135806.

[24] Wang Y, Jin B, Ye D, Liu Z. Fully recyclable carbon fiber reinforced vanillin-based epoxy vitrimers. Eur Polym J 2022;162:110927. https://doi.org/10.1016/j.eurpolymj.2021.110927.

[25] Liu T, Peng J, Liu J, Hao X, Guo C, Ou R, et al. Fully recyclable, flame-retardant and high-performance carbon fiber composites based on vanillin-terminated cyclophosphazene polyimine thermosets. Compos B Eng 2021;224:109188. https://doi.org/10.1016/j.compositesb.2021.109188.

[26] Nabipour H, Niu H, Wang X, Batool S, Hu Y. Fully bio-based epoxy resin derived from vanillin with flame retardancy and degradability. React Funct Polym 2021;168:105034. https://doi.org/10.1016/j.reactfunctpolym.2021.105034.

[27] Xie W, Huang S, Liu S, Zhao J. Imine-functionalized biomass-derived dynamic covalent thermosets enabled by heat-induced self-crosslinking and reversible structures. Chem Eng J 2021;404:126598. https://doi.org/10.1016/j.cej.2020.126598.

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

[29] Toldy A. Flame retardancy of carbon fibre reinforced composites. Express Polym Lett 2018;12:186. https://doi.org/10.3144/expresspolymlett.2018.17.

[30] Toldy A, Pomázi Á, Szolnoki B. The effect of manufacturing technologies on the flame retardancy of carbon fibre reinforced epoxy resin composites. Polym Degrad Stab 2020;174:109094. https://doi.org/10.1016/j.polymdegradstab.2020.109094.

[31] Toldy A, Szolnoki B, Marosi Gy. Flame retardancy of fibre-reinforced epoxy resin composites for aerospace applications. Polym Degrad Stab 2011;96:371–6. https://doi.org/10.1016/j.polymdegradstab.2010.03.021.

[32] Perret B, Schartel B, Stöß K, Ciesielski M, Diederichs J, Döring M, et al. Novel DOPO-based flame retardants in high-performance carbon fibre epoxy composites for aviation. Eur Polym J 2011;47:1081–9. https://doi.org/10.1016/j.eurpolymj.2011.02.008.

[33] Toldy A, Poór DI, Szolnoki B, Devecser B, Geier N, Pomázi Á. Comparative study of flame retardancy in polyimine vitrimers and composites:evaluating additive and reactive flame retardants acting via gas-, solid-, and combined-phase mechanisms. J Mater Sci Technol 2024:S1005030224002354. https://doi.org/10.1016/j.jmst.2024.01.047.

[34] Pomázi Á, Szolnoki B, Toldy A. Flame retardancy of low-viscosity epoxy resins and their carbon fibre reinforced composites via a combined solid and gas phase mechanism. Polymers 2018;10:1081. https://doi.org/10.3390/polym10101081.

[35] Szolnoki B, Bocz K, Marosi G, Toldy A. Flame retardancy of sorbitol based bioepoxy via combined solid and gas phase action. Polymers 2016;8:322. https://doi.org/10.3390/polym8090322.

[36] Toldy A, Szolnoki B, Csontos I, Marosi G. Green synthesis and characterization of phosphorus flame retardant crosslinking agents for epoxy resins. J Appl Polym Sci 2014;131:app.40105. https://doi.org/10.1002/app.40105.

[37] Toldy A, Anna P, Csontos I, Szabó A, Marosi Gy. Intrinsically flame retardant epoxy resin – Fire performance and background – Part I. Polym Degrad Stab 2007;92:2223–30. https://doi.org/10.1016/j.polymdegradstab.2007.04.017.

[38] Toldy A, Szabó A, Novák Cs, Madarász J, Tóth A, Marosi Gy. Intrinsically flame retardant epoxy resin – Fire performance and background – Part II. Polym Degrad Stab 2008;93:2007–13. https://doi.org/10.1016/j.polymdegradstab.2008.02.011.

[39] Szolnoki B, Toldy A, Konrád P, Szebényi G, Marosi G. Comparison of additive and reactive phosphorus-based flame retardants in epoxy resins. Per Pol Chem Eng 2013;57:85. https://doi.org/10.3311/PPch.2175.

[40] Poór DI, Tobey M, Taynton P, Pomázi Á, Toldy A, Geier N. A comparative machinability analysis of polyimine vitrimer, epoxy and polycarbonate polymers through orthogonal machining experiments. Int J Adv Manuf Technol 2024;131:1361–76. https://doi.org/10.1007/s00170-024-13087-9.

[41] Toldy A. Recyclable-by-design thermoset polymers and composites. Express Polym Lett 2021;15:1113. https://doi.org/10.3144/expresspolymlett.2021.89.

[42] Toldy A. Challenges and opportunities of polymer recycling in the changing landscape of European legislation. Express Polym Lett 2023;17:1081. https://doi.org/10.3144/expresspolymlett.2023.81.

[43] Gargiuli JF, Board RG, Shaffer MSP, Hamerton I. Evaluation of healable epoxy matrices as covalent adaptive networks in uniaxial compression. React Funct Polym 2023;192:105725. https://doi.org/10.1016/j.reactfunctpolym.2023.105725.

[44] Pomázi Á, Krecz M, Toldy A. The effect of the combined application of solid- and gas-phase flame retardants in epoxy gelcoats on the thermal stability, fire performance and adhesion of coated carbon fibre–reinforced epoxy composites. J Therm Anal Calorim 2023;148:257–70. https://doi.org/10.1007/s10973-022-11770-1.

[45] Pomázi Á, Krecz M, Toldy A. Thermal behaviour and fire and mechanical performance of carbon fibre-reinforced epoxy composites coated with flame-retardant epoxy gelcoats. J Therm Anal Calorim 2023;148:2685–702. https://doi.org/10.1007/s10973-022-11710-z.