Research Article

Comparative study of flame retardancy in polyimine vitrimers and composites: Evaluating additive and reactive flame retardants acting via gas-, solid-, and combined-phase mechanisms

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ABSTRACT

We developed flame retarded polyimine type vitrimers and carbon fibre reinforced composites using two additive and a reactive flame retardant containing phosphorus: ammonium polyphosphate (APP), resorcinol bis(diphenyl phosphate) (RDP); and *N,N',N''*-tris(2-aminoethyl)-phosphoric acid triamide (TEDAP). We characterised the vitrimer matrix materials by differential scanning calorimetry (DSC), thermal analysis (TGA), limiting oxygen index (LOI), UL-94 test and mass loss calorimetry (MLC), while the vitrimer composites by LOI, UL-94 test, MLC and dynamic mechanical analysis (DMA). We compared the performance of the vitrimer systems to a benchmark pentaerythritol-based aliphatic epoxy resin system (PER). The vitrimer reference had higher thermal stability but lower fire performance than the PER aliphatic reference epoxy. At lower phosphorus content, the vitrimer systems exhibited a melting above their vitrimer transition temperature, which negatively affected their LOI and UL-94 results. From 2% phosphorus content, rapid charring and extinguishing of vitrimers prevented the softening and deforming. The superior performance of these same flame retardants in vitrimer systems could be attributed to the high nitrogen content of imine-based vitrimers in combination with phosphorus flame retardants, exploiting nitrogen-phosphorus synergism. In both matrices, flame retardants with solid phase action lead to better fire performance, while in composites, the lowest peak heat release rates (152 kW/m^2 in vitrimer composite) were achieved with RDP acting predominantly in the gas phase, as carbon fibres hindered the intumescent phenomenon.

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1. Introduction

Implementing the circular economy approach to polymers includes not just mitigating their environmental impact but also essentially changing the approaches polymers are designed [1]. The circularity of the polymers is driven by their tailored chemical structure that enables recycling. While the mechanical recycling of thermoplastic polymers by melting and reprocessing is an established method in the industry, developing crosslinked polymers designed for recycling is still challenging [2]. Unlike thermoplastics, thermosetting polymers form crosslinked structures with irreversible primary covalent bonds, necessitating distinct production, processing, and recycling technologies. Despite being used in smaller quantities, such as in engineering plastics, and having a longer lifespan than thermoplastics, the recycling of thermosetting polymers has become essential due to their increasing usage, higher costs, and growing demand for carbon fibres. Notwithstand-
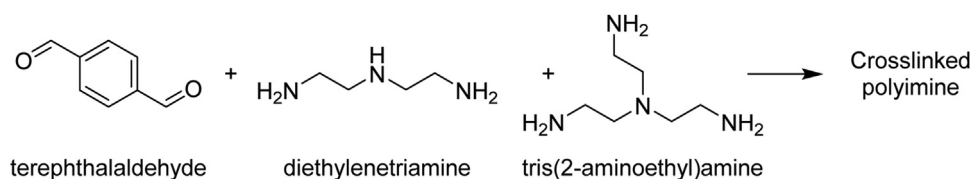
Fig. 1. Synthesis of the crosslinked polyimine (based on [13]).

ing the obvious barriers, various recycling solutions are being developed, including mechanical, thermal and chemical methods [3]. Among these, only mechanical recycling and pyrolysis (anaerobic thermal decomposition at high temperatures) are presently implemented on an industrial scale. On the other hand, some innovative concepts are striving to create recyclable-by-design thermoset polymers and composites. In 2011, Leibler and co-workers [4] developed a new class of thermosetting materials based on associative covalent adaptable networks (CANs)—called vitrimers. Below their so-called vitrimer transition temperature, they act like conventional crosslinked systems with excellent mechanical and thermal properties; but can be melted or recycled above it similarly to thermoplastics [4], as they can flow like viscoelastic fluids since the bond exchange reaction takes place rapidly. Covalent adaptable networks (CANs) have a sufficient quantity and topology of reversible covalent bonds that allow the crosslinked network to respond chemically when subjected to an external stimulus [5]. Based on their bond exchange mechanism, these dynamically rearranging networks can be classified into dissociative and associative [6]. In dissociative CANs, e.g. polymers based on Diels-Alder reactions, the breaking of the bonds precedes their regeneration, leading to a sudden decrease in viscosity when the bonds break, which compromises the dimensional stability of the polymer. While in associative CANs, e.g. vitrimers, the creation of new bonds takes place before the bond-breaking, thereby maintaining the crosslink density throughout the bond exchange. Recent reviews [8–10,33] categorise the CANs into several groups based on their bond exchange mechanism, including, among others, transesterification, imine exchange, disulphide exchange, Diels-Alder reaction, olefin metathesis, transalkylation exchange, boronic ester exchange, diketoenamine bonds. Many of these bond exchange mechanisms are triggered by specific catalysts, which implies limitations on their use and hinders their widespread uptake [11]. Among the catalyst-free solutions, polyimines [12], synthesised in the condensation reaction of aldehydes or ketones and primary amines, have been widely used and studied as the heat-triggered imine exchange reaction provides easy reprocessing. Imine exchange reactions are based on the rearrangement of the weak covalent C=N bond, also called Schiff base, which can undergo three different heat-triggered reactions: hydrolysis (reaction with water), transamination (reaction with a primary amine), and imine metathesis (reaction with

Table 1
Mechanical properties and T_g of polyimine networks [14].

Network	T_g (°C)	Tensile strength (MPa)	Elastic modulus (GPa)
Polyimine A	18	10	0.13
Polyimine B	56	40	1
Polyimine C	145	64	0.96

another imine). In 2014, Taynton and co-workers [13] prepared a catalyst-free polyimine network by the reaction of terephthaldehyde, diethylenetriamine, and tris(2-aminoethyl)amine (Fig. 1).

The obtained polymer had T_g of 56 °C and an elastic modulus of approx. 1 GPa, with a breaking stress of 40 MPa. They characterised the heat-induced malleability of the polyimine network by the measurement of the time and temperature-dependent relaxation modulus. The temperature required for fast bond exchange in the network was 80 °C, which is beyond the operating conditions in most applications.

In their 2016 study, Taynton and co-workers [14] prepared polyimine networks from terephthaldehyde and tris(2-aminoethyl)amine (TREN) and three other amines (Fig. 2) with different chain lengths and functionalities. Since the length of the amine backbone directly affects the network mobility, the mechanical properties of the resulting vitrimer could be tuned by adding different hardeners (Table 1).

The authors prepared one and two-ply carbon fibre-reinforced composite (CFRC) samples from both B and C polyimines with 65 m/m% fibre content and found that their mechanical properties directly correlate to the properties of the polyimine network and the fibre content of the composite. They also explored the recyclability of these polyimine composites. When they immersed composite sample B in diethylenetriamine (DETA) or a mixture of ethanol and DETA, the vitrimer matrix completely dissolved, and clean carbon fibre plies were recovered after rinsing away the matrix residue with ethanol.

To make these recyclable crosslinked polymers widely available in the future, it is not only necessary to approach the properties of the benchmark epoxy resins but also to increase their fire resistance. The achievements in the flame retardancy of vitrimers so far are well-summarised in recent review articles [15–
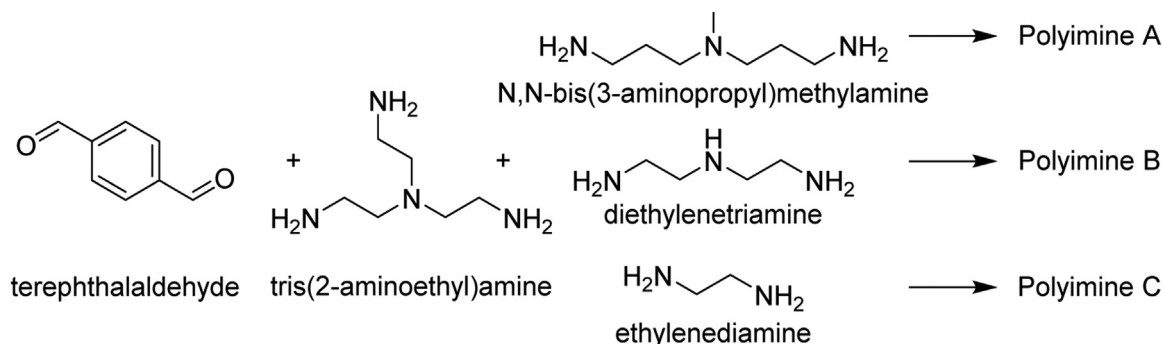

Fig. 2. Synthesis of polyimine thermosets [14].

17]. In the case of polyimine-type vitrimers, a reactive type of flame retardancy is typically used, presumably because of the wide range of chemical reactions that can be used to introduce the flame retardant moiety into the polyimine structure. Wang et al. [18] developed inherently flame-retarded polyimine-type vitrimers from vanillin derived from lignin. They synthesised a novel trialdehyde monomer from vanillin and phosphorus oxychloride, which was then used to create polyimine CANs by curing with hexamethylenediamine, 4,4-diaminodicyclohexylmethane and 4,4-diaminodiphenylmethane. The polyimines exhibited glass transition temperatures in the range of 87–178 °C, V-1 and V-0 UL-94 ratings, LOI of 30 V/V%, tensile strength of about 69 MPa, and tensile modulus of about 1925 MPa. Zhang et al. [7] synthesised polyimines from cyclophosphazene bearing three aldehyde groups, terephthalaldehyde, and diaminodiphenyl methane. Due to the phosphazene skeleton and high content of aromatic ring structure, the new polyimines exhibited high glass transition temperature (146 °C), LOI of 40 V/V% and V-0 UL-94 rating, as well as tensile strength of about 56 MPa. Yang et al. [32] synthesised inherently flame-retarded vanillin-based epoxy-functional polyimine via in situ condensation reaction of vanillin with diamino diphenylmethane (DDM) and addition reaction with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), followed by the epoxidation by epichlorohydrin. The vitrimer exhibited a V-0 UL-94 rating and LOI value of 27.0 V/V% with only 0.66% phosphorus content.

Since, based on the literature review, mainly reactive flame retardants have been used in polyimine-type vitrimers, we aimed to perform a comprehensive study using additive and reactive flame retardants, acting in gas-, solid- and both phases in polyimine-type vitrimers and their carbon fibre-reinforced composites as well. This strategic selection aims to enhance the understanding and application of flame retardants in polyimine-type vitrimers and their carbon fibre-reinforced composites, ultimately contributing to a more comprehensive understanding of flame retardancy in vitrimer systems. We used ammonium polyphosphate (APP), acting in solid phase [19,20], resorcinol bis(diphenyl phosphate) (RDP), acting predominantly in gas phase [19,20] as additive, and *N,N',N"*-tris(2-aminoethyl)-phosphoric acid triamide (TEDAP) [21], acting is both phases [22,23], as reactive flame retardant. We tested the vitrimer matrix materials by differential scanning calorimetry (DSC), thermal analysis (TGA), limiting oxygen index (LOI), UL-94 test and mass loss calorimetry (MLC), while the vitrimer composites by LOI, UL-94 test, MLC and dynamic mechanical analysis (DMA) and compared their performance to a benchmark pentaerythritol-based aliphatic epoxy resin systems [24].

2. Materials and methods

2.1. Materials

As a reference epoxy resin, we used a tetrafunctional pentaerythritol-based epoxy resin, 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).

We used the two-component Vitrimax T130 polyimine-type vitrimer system consisting of an epoxy resin component and a polyimine hardener (supplier: Mallinda Inc., Colorado, USA, viscosity of the mixed system at 50 °C: 54.8 Pa·s).

For the preparation of flame retarded compositions we used two additive flame retardants: ammonium polyphosphate (APP;

trade name: NORD-MIN JLS APP; supplier: Nordmann Rassmann, Hamburg, Germany; P content: 31%–32%; average particle size: 15 μm), resorcinol bis(diphenyl phosphate) (RDP; trade name: Fyrolflex RDP; supplier: ICL Industrial Products, Beer Sheva, Israel; P content: 10.7%) and a reactive flame retardant, a phosphorus-containing reactive amine, TEDAP (*N,N',N"*-tris(2-aminoethyl)-phosphoric acid triamide, amine number: 590–620 mg KOH/g; viscosity at 20 °C: 400 mPa s), synthesised according to previous publication of the authors [21].

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

The chemical structures of the reference epoxy monomer and hardener and additive and reactive flame retardants used can be seen in Fig. 3.

2.2. Methods

2.2.1. Preparation of polymer matrix samples

In the reference epoxy resin, 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. The samples were cured in appropriately sized silicon moulds. The curing procedure consisted of two isothermal heat steps (determined based on differential scanning calorimetry (DSC)): 1 h at 80 °C and 1 h at 100 °C in a Heraeus UT20 drying oven.

In the vitrimer system, the mixing ratio of the epoxy resin component and polyimine hardener was 1:2. Before mixing, we heated the polyimine hardener to 80 °C for 1 h to lower its viscosity. Then, the polyimine hardener was mixed with the epoxy resin component and poured into a silicone mould. The samples were allowed to cure for 20 min at 80 °C, 20 min at 115 °C, and 3 h at 135 °C according to the instructions of the producer.

Besides the reference epoxy resin and vitrimer samples, we prepared flame retarded samples with incremental phosphorus (P) content (1%, 2%, 3%) from APP, RDP or TEDAP, respectively. In the flame retarded samples, first, the flame retardant was mixed with the component, and then the hardener was added. The curing procedure was the same as in the case of samples without flame retardants.

The composition of the samples is listed in Table 2.

2.2.2. Preparation of polymer composite samples

PER epoxy resin composite laminates were made in [0]$_5$ layup by wet compression moulding: each fibre layer was separately impregnated with the resin by hand lamination in a press mould, then the prepared laminates were 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). A two-step heat treatment was used for curing: 1 h at 80 °C followed by 1 h at 100 °C. In the case of vitrimer composites, each carbon fibre layer was impregnated individually, and then the so prepared prepregs were cured for 1 h at 150 °C followed by 1 h at 180 °C. After the curing process, the cured prepregs were hot pressed together at 160 °C for 15 min with a hydraulic pressure of 15 bars. To determine the fibre content of the composites, we measured the mass of the dry fibre layers before processing and the mass of the crosslinked composite sample. We calculated the fibre content of the samples as a percentage by mass (1):

$$\text{Fibre content (mass\%)} = \frac{m_{\text{dry fibre}}}{m_{\text{composite}}} \times 100 \qquad (1)$$

The average fibre content of the composite samples and their properties are shown in Table 3.
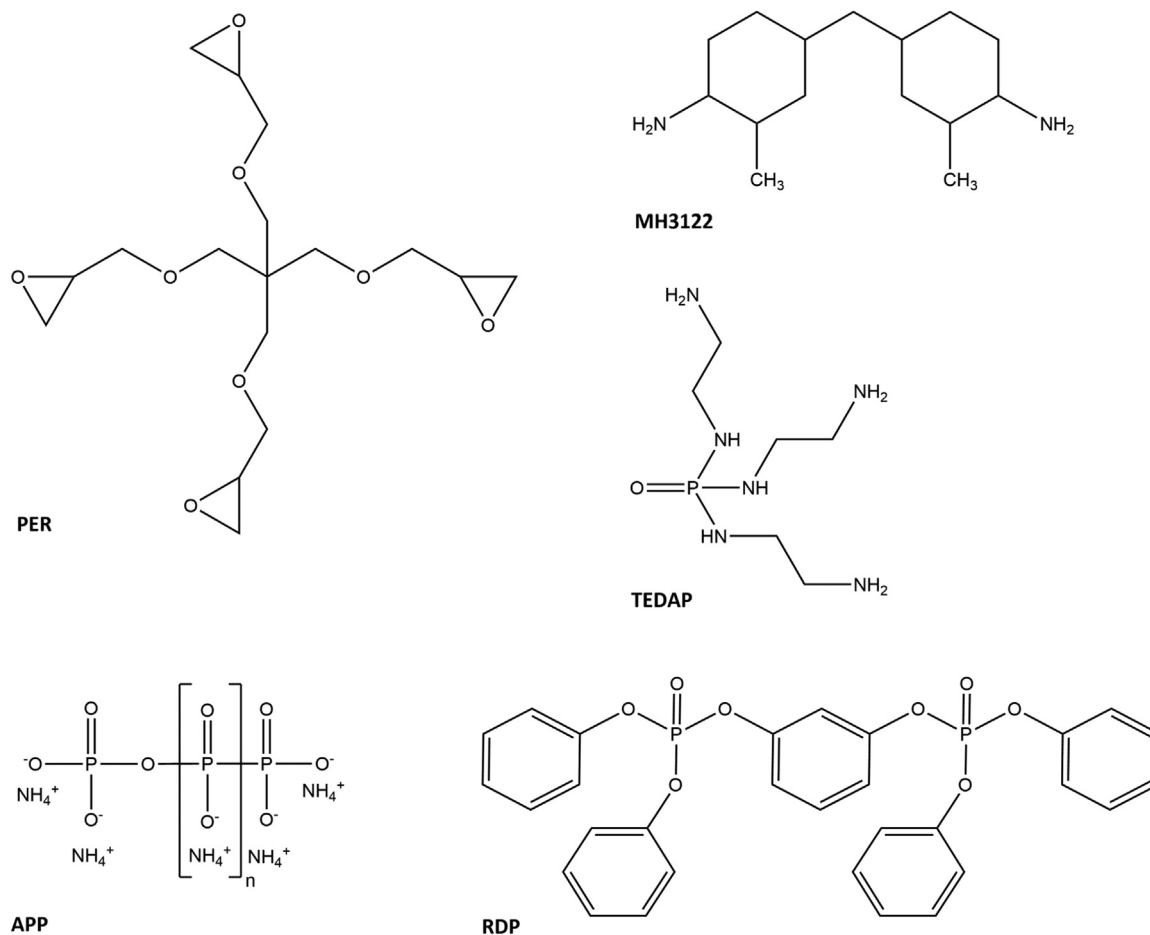
Fig. 3. The chemical structures of the reference epoxy monomer (PER), hardener (MH 3122), additive (APP and RDP) and reactive (TEDAP) flame retardants.

Table 2
Composition of reference and flame retarded epoxy resin and vitrimer samples.

Sample	Epoxy (%)	Hardener (%)	APP (%)	RDP (%)	TEDAP (%)	P content (%)
PER	71.43	28.57	0	0	0	0
PER APP 1%P	69.16	27.66	3.17	0	0	1
PER APP 2%P	66.89	26.76	6.35	0	0	2
PER APP 3%P	64.63	25.85	9.52	0	0	3
PER RDP 1%P	64.75	25.90	0	9.35	0	1
PER RDP 2%P	58.08	23.23	0	18.69	0	2
PER RDP 3%P	51.40	20.56	0	28.04	0	3
PER TEDAP 1%P	75.81	16.97	0	0	7.23	1
PER TEDAP 2%P	77.08	8.47	0	0	14.45	2
PER TEDAP 3%P	78.33	0	0	0	21.67	3
VITRIMER	33.33	66.67	0	0	0	0
VITRIMER APP 1%P	32.28	64.55	3.17	0	0	1
VITRIMER APP 2%P	31.22	62.42	6.35	0	0	2
VITRIMER APP 3%P	30.16	60.32	9.52	0	0	3
VITRIMER RDP 1%P	30.22	60.44	0	9.35	0	1
VITRIMER RDP 2%P	27.10	54.21	0	18.69	0	2
VITRIMER RDP 3%P	23.99	47.98	0	28.04	0	3
VITRIMER TEDAP 1%P	48.06	44.71	0	0	7.23	1
VITRIMER TEDAP 2%P	63.43	22.12	0	0	14.45	2
VITRIMER TEDAP 3%P	78.33	0	0	0	21.67	3

2.2.3. Differential scanning calorimetry (DSC)

The DSC tests were performed with a TA Instruments Q2000 device (New Castle, DE, USA) in a 50 mL/min nitrogen flow with Tzero aluminium pans. The sample mass was 5–16 mg. We investigated the curing process of the polymers with a three-step temperature program consisting of heat/cool/heat cycles. In the first cycle, we used a linear ramp from 25 °C to 250 °C with a heating rate of 3 °C/min. After that, the sample was cooled down to 0 °C at a cooling rate of 50 °C/min (second cycle), which was followed by a second heating ramp from 0 °C to 250 °C at a heating rate of 10 °C/min. The curing enthalpy was determined from the first heating, while the glass transition temperature (T_g) of the material

Table 3
The properties of prepared composite samples.

Composite	Flame retardant	Overall P content (%)	Layup	Preparation method	Heat treatment	Fibre content (mass%)
PER COMPOSITE	–	–	$[0]_5$	wet compression moulding	1 h at 80 °C 1 h at 100 °C	60 ± 1
PER 3%P APP COMPOSITE	APP	3	$[0]_5$	wet compression moulding	1 h at 80 °C 1 h at 100 °C	60 ± 1
PER 3%P RDP COMPOSITE	RDP	3	$[0]_5$	wet compression moulding	1 h at 80 °C 1 h at 100 °C	60 ± 1
VITRIMER COMPOSITE	–	–	$[0]_5$	prepregging followed by hot pressing	1 h at 150 °C 1 h at 180 °C, 15 min at 160 °C	43 ± 1
VITRIMER 3%P APP COMPOSITE	APP	3	$[0]_5$	prepregging followed by hot pressing	1 h at 150 °C 1 h at 180 °C, 15 min at 160 °C	45 ± 1
VITRIMER 3%P RDP COMPOSITE	APP	3	$[0]_5$	prepregging followed by hot pressing	1 h at 150 °C 1 h at 180 °C, 15 min at 160 °C	42 ± 1

was determined from the second heating, defined as the inflexion point of the transition curve.

2.2.4. Thermogravimetric analysis (TGA)

The thermal stability of the samples was investigated with a TA Instruments Q500 device (New Castle, DE, USA) in the range of 25 °C to 800 °C, with a heating rate of 20 °C/min, under a nitrogen gas flow rate of 40 ml/min. We used platinum-HT pans, and the mass of the samples was 3–12 mg in each case.

2.2.5. Fire performance

We performed standard UL-94 tests according to ASTM D3801-20a and ASTM D635-22 to classify the epoxy resin and vitrimer formulations based on their flammability in horizontal and vertical test setups. The matrix sample size was 120 mm × 15 mm × 3 mm, while the composite sample size was 120 mm × 15 mm × 2 mm. UL-94 ratings in increasing order are as follows: HB, V-2, V-1, V-0. The fire performance of the matrices was also investigated with limiting oxygen index tests (LOI, according to ASTM D2863-19). 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 × 15 mm × 3 mm matrix samples and 120 mm × 15 mm × 2 mm composite samples were used for the test. We performed mass loss type cone calorimetry (MLC) on the polymer and composite samples with an instrument made by FTT Inc. (East Grinstead, UK), according to the ISO 13927 standard. The samples were subjected to a constant heat flux of 50 kW/m². We used a metal frame with aluminium foil backing. The sample size was 100 mm × 100 mm × 4 mm in the case of the matrix samples and 100 mm × 100 mm × 2 mm in the case of the composites. Heat release values and mass reduction were continuously recorded during burning.

2.2.6. Dynamic mechanic

We performed dynamic mechanical analysis (DMA) tests by TA Instruments DMA Q800 device (New Castle, DE, USA) to determine storage modulus (E') and the glass transition temperature (T_g) from the peak values of the tanδ signals with the TA Universal Analysis 2000 software. We applied a 3-point bending setup, the oscillation frequency was 1.00 Hz, the static force was 0.10 N, the minimum oscillation force was 0.00 N, a 1.25 force track was applied, the oscillation strain was 0.02 mm, the examined temperature range was 35–200 °C, and the heating rate was 3 °C/min. The nominal composite sample dimension was 60 mm × 10 mm × 4 mm, and the support span was 50 mm.

3. Results and discussion

3.1. Crosslinking enthalpy and the glass transition temperature of reference and flame retarded epoxy resin and vitrimer samples

We examined the effect of flame retardants on the crosslinking process and the glass transition temperature (T_g) by DSC. Table 4 shows the results of the DSC analysis.

The reaction enthalpy of the epoxy and vitrimer matrix systems decreased when we used additive flame retardants (APP and RDP) as the ratio of epoxy resin capable of crosslinking decreased. Even if we compare the reaction enthalpy related to the mass of epoxy (i.e. we disregard the amount of flame retardants), we can see that this effect was much more pronounced in the case of RDP. Due to the lower phosphorus content of RDP, 28.04% of RDP was necessary to reach 3% phosphorus content (in the case of APP, only 9.52% was needed), and the steric hindrance of RDP molecules during the crosslinking is the reason behind the lower reaction enthalpy and glass transition temperature [25]. As TEDAP is a reactive phosphorus-containing flame retardant and amine-type hardener at the same time, in samples containing TEDAP, no such effect was measured; TEDAP even increased the reaction enthalpy, decreased the temperature of the exothermic peak and significantly increased the glass transition temperature of both systems. Both in the epoxy and the vitrimer system, all the original hardener has to be replaced to reach a phosphorus content of 3%, therefore, the chemical structure of the crosslinked system changed fundamentally. In the PER epoxy system, the T_g increased from 122 °C to 127 °C, which may be attributed to the fact that the original hardener is bifunctional, while TEDAP is trifunctional, which may lead to a denser 3D-network and lower molecular mobility, nevertheless, the increase is not significant. In the vitrimer system, the T_g increased from 80 °C to 136 °C. In this case the original low functional polyimine hardener is replaced by TEDAP.

3.2. Thermal stability of reference and flame retarded epoxy resin and vitrimer samples (TGA)

The thermal stability of the reference and flame retarded epoxy resin and vitrimer samples was investigated by thermogravimetric analysis; Table 5, Fig. 4 show the TGA results.

If we compare the reference PER epoxy resin and vitrimer samples, we can conclude that the thermal degradation of the vitrimer, indicated by the temperature at 5% mass loss ($T_{-5\%}$), started at about 10 °C higher temperature. The temperature at 50% mass loss ($T_{-50\%}$) of the vitrimer sample was also 70 °C higher than in the reference epoxy resin case, indicating superior thermal stabil-

Table 4
DSC results of reference and flame retarded epoxy resin and vitrimer samples.

Sample	Glass transition temperature (°C)	Reaction enthalpy		Temperature of exothermic peak (°C)
		(J/g)	(J/g epoxy)	
PER	122	283	396	100
PER APP 3%P	100	266	412	102
PER RDP 3%P	60	160	311	87
PER TEDAP 3%P	127	305	389	75
VITRIMER	80	184	552	113
VITRIMER APP 3%P	86	120	398	117
VITRIMER RDP 3%P	103	63	263	100
VITRIMER TEDAP 3%P	136	246	314	86

Table 5
TGA results of the reference and flame retarded epoxy resin and vitrimer samples.

Sample	$T_{-5\%}$ (°C)	$T_{-50\%}$ (°C)	dT_{Gmax} (%/ C)	T_{dTGmax} (°C)	Char yield at 800 °C (%)
PER	287	333	2.47	289	4.1
PER APP 3%P	291	339	1.73	293	8.5
PER RDP 3%P	269	323	1.11	292	7.9
PER TEDAP 3%P	265	328	1.13	312	9.7
VITRIMER	298	423	0.62	436	7.6
VITRIMER APP 3%P	285	398	0.55	360	12.7
VITRIMER RDP 3%P	277	400	0.68	405	13.1
VITRIMER TEDAP 3%P	278	349	1.12	337	13.5

$T_{-5\%}$: temperature at 5% mass loss; $T_{-50\%}$: temperature at 50% mass loss; dT_{Gmax}: maximum mass loss rate; T_{dTGmax}: the temperature belonging to the maximum mass loss rate.
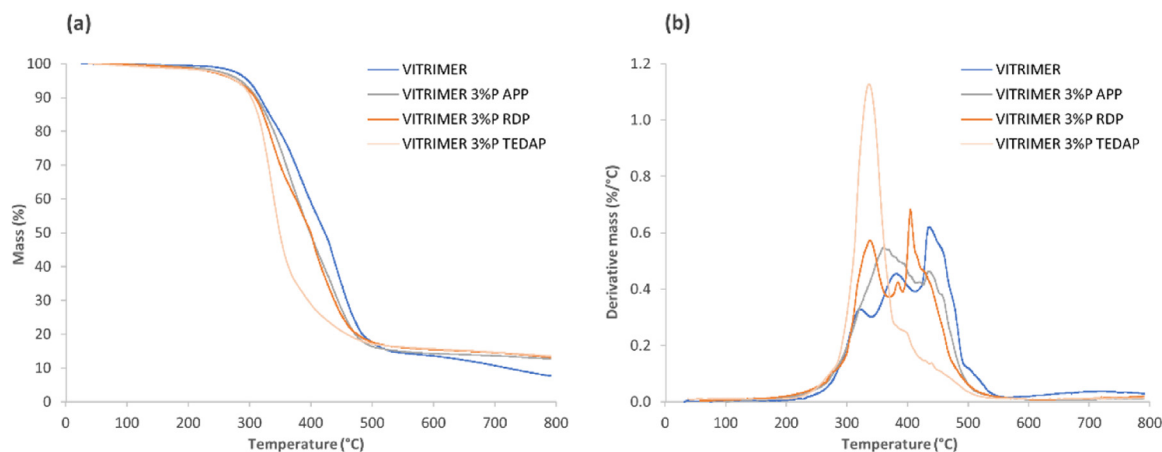
Fig. 4. The mass curves (a) and derivative mass curves (b) of vitrimer matrices with 3% P content from APP, RDP and TEDAP compared to the vitrimer reference.

ity. The maximum mass loss rate of the vitrimer was 4 times lower and occurred at about 70 °C higher temperature than in the reference epoxy resin, which indicates a more controlled and elongated degradation at a higher temperature. The vitrimer had almost double amount of char which may be explained by the high nitrogen content of the imine-type vitrimer. As for the flame retardants, APP acts predominantly in the solid phase [19,20], RDP mainly in the gas phase [19,20], while TEDAP exhibits a combined-phase action [22,23]. Accordingly, the samples which contained additives active in the gas phase lost 5% of their mass at lower temperatures than the samples containing APP. In the epoxy samples, the $T_{-50\%}$ values were not significantly affected by the flame retardants, while in the vitrimer samples, we observed a decrease of 20 °C in the case of the additive flame retardants (APP, RDP) and 50 °C in the case of reactive flame retardant (TEDAP). The addition of the flame retardants significantly decreased the maximum mass loss rate in PER, but these values remained higher than in the case of the vitrimer reference. The lowest mass loss rate was reached with 3%P from APP in vitrimer. In the epoxy systems, the flame retardants increased the temperature of maximum mass loss rate to some ex-

tent, while in the vitrimer systems, the initially highest value of 436 °C was lowered but remained above the values of the epoxy systems in all cases. The flame retardants approximately doubled the original char yields, the best results were achieved with TEDAP in both systems, and the VITRIMER TEDAP 3%P has the highest char yield (13.5%). The results generally indicate superior thermal stability and more controlled degradation of the vitrimer samples compared to the epoxy resin systems.

3.3. Fire performance of reference and flame retarded epoxy resin and vitrimer samples (LOI, UL-94 and MLC)

We investigated the fire performance of reference epoxy resin and vitrimer samples by limiting oxygen index (LOI), UL-94 and mass loss calorimetry (MLC) tests. Table 6 contains the LOI and the UL-94 test results.

If we compare the fire performance of the epoxy resin and vitrimer systems, we can conclude that the LOI of the PER reference is higher than the LOI of the vitrimer reference, and this initial difference also remains in the flame retarded samples. In PER, the

Table 6

Limiting oxygen index (LOI) and UL-94 classification of reference and flame retarded epoxy resin and vitrimer samples.

Sample	LOI (vol%)	UL-94	Sample	LOI (vol%)	UL-94
PER	23	HB (23 mm/min)	VITRIMER	21	no rate (60 mm/min)
PER APP 1%P	27	HB	VITRIMER APP 1%P	26	HB (41 mm/min
PER APP 2%P	32	HB	VITRIMER APP 2%P	26	HB
PER APP 3%P	32	HB	VITRIMER APP 3%P	27	V-0
PER RDP 1%P	25	HB (15 mm/min)	VITRIMER RDP 1%P	24	HB (39 mm/min)
PER RDP 2%P	26	HB	VITRIMER RDP 2%P	25	HB
PER RDP 3%P	29	HB	VITRIMER RDP 3%P	28	V-0
PER TEDAP 1%P	25	V-2	VITRIMER TEDAP 1%P	24	HB (11 mm/min)
PER TEDAP 2%P	30	V-1	VITRIMER TEDAP 2%P	28	V-0
PER TEDAP 3%P	33	V-0	VITRIMER TEDAP 3%P	29	V-0

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

highest LOI values were achieved with APP and TEDAP, which both exhibit solid phase action and better UL-94 ratings than HB were achieved at these phosphorus contents only with TEDAP, which is a reactive flame retardant and crosslinking agent designed for the flame retardancy of PER with combined solid and gas phase action. Overall, the best result was achieved with the self-extinguishing PER TEDAP 3%P system. The samples softened and deformed during the test in the vitrimer-based systems at 0% and 1% phosphorus content. This may be explained by their vitrimeric properties, namely, after reaching their vitrimer transition temperature in the region of 150–200 °C, they start to behave like thermoplastic materials and undergo a melting process. From 2% phosphorus content, the vitrimer samples exhibited intensive charring and extinguished before they started to soften and deform. All vitrimer samples containing 3% phosphorus and the sample with 2% phosphorus content from TEDAP reached a self-extinguishing V-0 UL-94 rate. In general, the vitrimer systems exhibit somewhat lower LOI values than the benchmark system, but contrary to PER, the V-0 rate could be achieved with all flame retardants at 3% phosphorus content.

Table 7 shows the MLC results. The flame retardancy index (FRI), calculated from TTI, pHRR and THR [26], was solely used for the comparison of the samples with the same matrix, without the intention to compare them to other formulations. Fig. 5 shows the heat release rate of vitrimer matrices in the function of P content in samples flame retarded with APP, RDP and TEDAP, respectively, and the heat release rate of epoxy resin and vitrimer matrices with 3% P content from APP and RDP.

In accordance with the LOI and UL-94 results, the PER reference sample performed better than the vitrimer reference. The vitrimer had a 135 kW/m^2 higher peak heat release rate (pHRR); nevertheless, it occurred 46 s later than in the case of the PER epoxy system. If we compare the flame retardant effect of APP, RDP and TEDAP in these two systems, we can conclude that—except for the PER TEDAP 3%P system—the flame retardants reduced the pHRR values to a much greater extent in the vitrimer system than in the PER epoxy systems. APP acting in the solid phase and TEDAP with combined phase action were more effective in reducing the pHRR in vitrimers than RDP with predominant gas phase action. Nevertheless, the differences are minor; in all cases, the original pHRR of 841 kW/m^2 was reduced to 175–293 kW^2, which is equivalent to a reduction of 65%–79%. All flame retarded samples exhibited reasonable charring, even the ones flame retarded with RDP. If we compare the flame retardancy index (FRI), based on

Table 7

MLC results of reference and flame retarded epoxy resin and vitrimer samples .

Sample	TTI (s)	pHRR (kW/m^2)	Time to pHRR (s)	THR (MJ/m^2)	Residue (%)	FRI (-)
PER	17	706	67	100.5	0	–
PER APP 1%P	31	547	106	108.5	10	2.18
PER APP 2%P	40	539	99	71.5	13	4.33
PER APP 3%P	28	421	139	82.5	12	3.36
PER RDP 1%P	26	516	99	95.8	6	2.20
PER RDP 2%P	22	402	132	84.9	8	2.69
PER RDP 3%P	23	458	162	113.6	15	1.85
PER TEDAP 1%P	22	668	104	97.5	7	1.41
PER TEDAP 2%P	17	244	159	59.4	26	4.90
PER TEDAP 3%P	95	111	110	28.0	40	127.57
VITRIMER	13	841	113	118.0	1	–
VITRIMER APP 1%P	13	251	124	99.0	14	3.99
VITRIMER APP 2%P	11	191	416	107.5	6	4.09
VITRIMER APP 3%P	7	175	234	57.6	15	5.30
VITRIMER RDP 1%P	10	325	180	118.9	8	1.98
VITRIMER RDP 2%P	6	238	234	89.3	12	2.16
VITRIMER RDP 3%P	11	290	207	75.2	20	3.85
VITRIMER TEDAP 1%P	2	178	223	52.1	11	1.65
VITRIMER TEDAP 2%P	9	235	294	95.2	13	3.07
VITRIMER TEDAP 3%P	19	218	260	53.5	20	12.44

TTI: time to ignition; pHRR: peak of heat release rate; THR: total heat release; FRI: flame retardancy index [26] related to PER and VITRIMER matrix sample, respectively. 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 %.
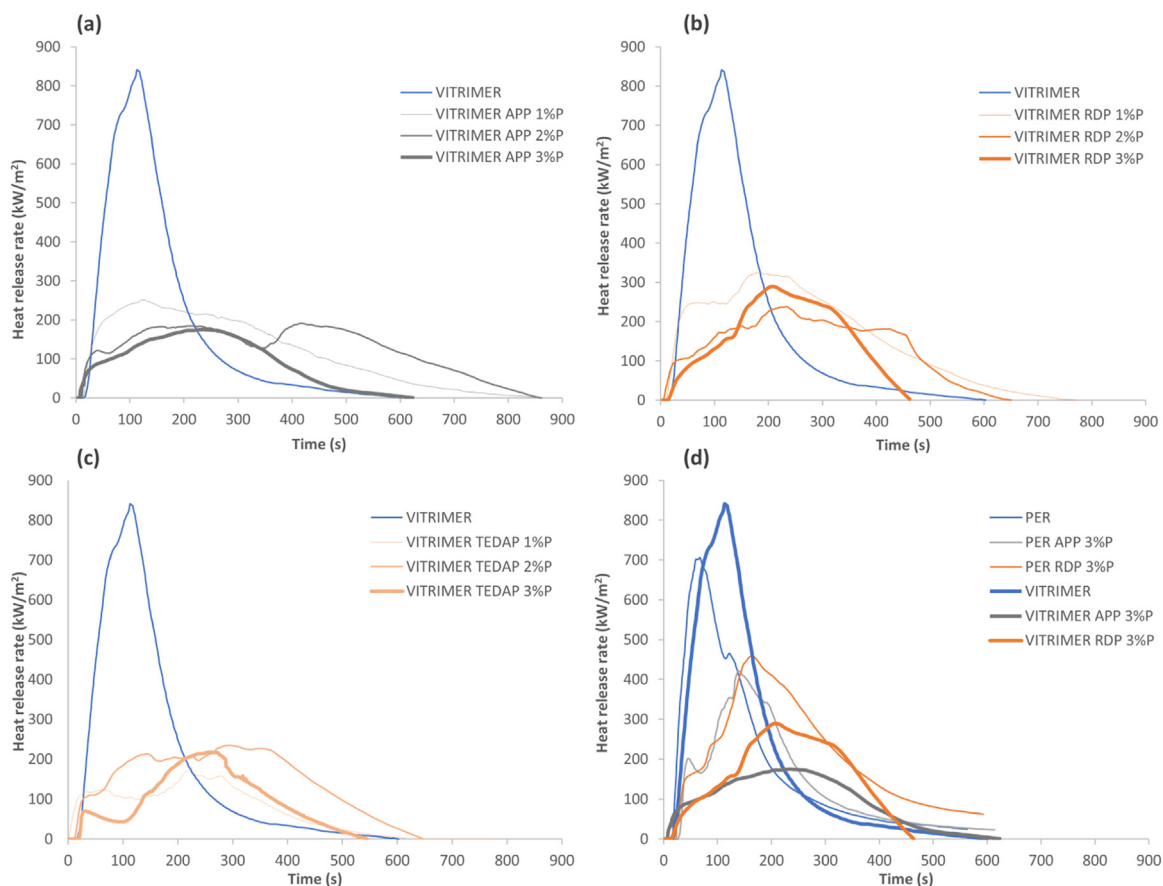
Fig. 5. The heat release rate of heat release rate of vitrimer matrices flame retarded with (a) APP, (b) RDP and (c) TEDAP in the function of P content, (d) the heat release rate of epoxy resin and vitrimer matrices with 3% P content from APP and RDP compared to the PER and vitrimer reference.

time to ignition, peak of heat release rate and total heat release rate, we can conclude that by increasing the amount of phosphorus, the fire performance of the flame retarded samples gradually increased to a small extent. To compare the fire performance of the epoxy and vitrimer systems, we depicted the heat release curves of the reference and flame retarded matrix samples with 3% phosphorus content. In the PER-based system, the flame retardants decreased the pHRR in the order of RDP<APP<<TEDAP, while in the vitrimer system, the order was RDP<TEDAP<APP. The reason behind the better performance of the same flame retardants in the vitrimeric systems may be the high nitrogen content of the imine-based vitrimers in combination with phosphorus flame retardants, though exploiting the nitrogen-phosphorus synergism [27–29].

It has to be noted that in both systems with 3% phosphorus content from TEDAP, the original hardener (a cycloaliphatic amine in the PER and an imine type component with amine functions in the vitrimer system) was entirely replaced by TEDAP reactive flame retardant and hardener at the same time. This replacement led to the best fire performance in PER systems, with as low pHRR as 111 kW/m², the longest time to ignition (95 s) and the lowest total heat release rate. The outstanding flame retardancy index above 100 indicates the best overall fire performance. In the vitrimer-based systems, we had to completely replace the imine component with TEDAP to reach 3% phosphorus content; the sample named VITRIMER TEDAP 3%P cannot be considered as a vitrimeric material, as it contains only the epoxy part of this system crosslinked with TEDAP. (Because of this, in Fig. 5(d) only matrices flame retarded with APP and RDP were compared.) Therefore, in the next

step of the development, we prepared carbon fibre-reinforced composites only from the reference and best flame retarded polymers with APP and RDP.

3.4. Fire performance of reference and flame retarded epoxy resin and vitrimer composites (LOI, UL-94 and MLC)

We investigated the fire performance of reference epoxy resin and vitrimer composites by limiting oxygen index (LOI), UL-94 and mass loss calorimetry (MLC) tests. Table 8 contains the LOI and the UL-94 test results.

The LOI of the reference vitrimer composite increased from 21 vol% to 23 vol% only, while in the PER reference composite, it increased from 23 vol% to 31 vol%, probably due to the higher carbon fibre content of the latter (43mass% vs 60%). In both systems, only APP could increase the LOI values compared to LOI of the matrices. The burning rate of the vitrimer composite decreased from 60 mm/min to 25.4 mm, but similarly to all other samples, its UL-94 rate remained HB due to the candlewick effect caused by the UD carbon reinforcement: Although the burning times were sufficiently short V0-V2 rates, the flames reached the top of the composite samples in almost all cases.

The MLC results of the composites are shown in Table 9, and their heat release rate is plotted in Fig. 6.

Although the PER as matrix has better fire performance than the vitrimer system, the PER composite has a TTI lower by 13 s and a higher pHRR by 62 kW/m². Similar to the matrices, the flame retarded vitrimer composites outperform the epoxy composites regarding the relative pHRR reduction related to their refer-

Table 8

Limiting oxygen index (LOI) and UL-94 classification of reference and flame retarded epoxy resin and vitrimer composites.

Sample	LOI (vol%)	UL-94	Sample	LOI (vol%)	UL-94
PER COMPOSITE	31	HB	VITRIMER COMPOSITE	23	HB (25.4 mm/min)
PER APP 3%P COMPOSITE	36	HB	VITRIMER APP 3%P COMPOSITE	34	HB
PER RDP 3%P COMPOSITE	29	HB	VITRIMER RDP 3%P COMPOSITE	27	HB

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

Table 9

MLC results reference and flame retarded epoxy resin and vitrimer composites.

Sample	TTI (s)	pHRR (kW/m^2)	Time to pHRR (s)	THR (MJ/m^2)	Residue (%)	FRI (-)
PER COMPOSITE	23	351	39	24.1	47	11.35
PER APP 3%P COMPOSITE	20	247	35	15.9	50	21.25
PER RDP 3%P COMPOSITE	26	200	45	15.8	56	34.34
VITRIMER COMPOSITE	36	289	140	44.6	43	21.32
VITRIMER APP 3%P COMPOSITE	37	186	158	41.3	49	36.77
VITRIMER RDP 3%P COMPOSITE	23	152	176	48.4	51	23.87

TTI: time to ignition; pHRR: peak of heat release rate; THR: total heat release; FRI: flame retardancy index [26] related to PER and VITRIMER matrix samples, respectively.
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 %.
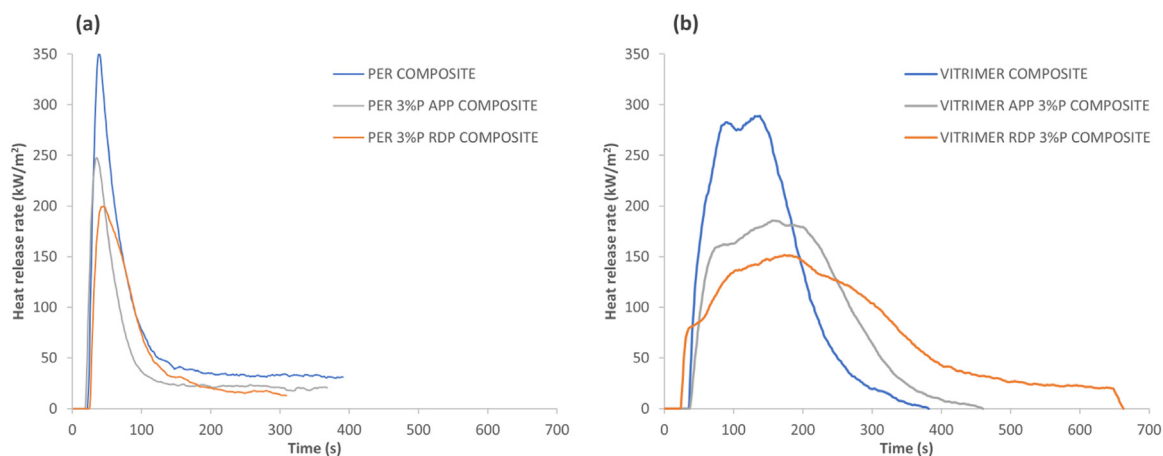
Fig. 6. The heat release rate of heat release rate of reference and flame retarded (a) epoxy resin and (b) vitrimer composites.

ence composite counterparts. Due to the introduction of 3%P APP and 3%P RDP, even though the absolute decrease due to FR compared to the composite reference is in the same range in the epoxy and vitrimer composites (APP: 104 vs 103 kW/m^2, RDP: 151 vs 137 kW/m^2, respectively), the relative decrease related to composite references is higher in the vitrimer systems (APP: 30% vs 36%, RDP 43% vs 53%, respectively). Contrary to the matrix, the lowest pHRR (152 kW/m^2) was achieved in both cases, with RDP acting mainly in the gas phase. As explored in detail in our previous publication [30], the reason behind this phenomenon is that the carbon fibres interfere with the solid phase action of APP, and therefore, it cannot fully develop its flame retardant effect. This is well-illustrated by comparing the mass loss calorimetry residues of vitrimer reference and flame retarded matrices and composites (Fig. 7). The higher THR values of the vitrimer composites are in connection with their lower carbon fibre content (in average 43 mass% vs 60% in PER) and, consequently, a higher ratio of the burnable polymer matrix [31]. With the current manufacturing method of the vitrimer composites (prepregging followed by pressing), a 43% fibre content is achievable, which is similar to the fibre content of the hand-laminated thermoset composites. As hand lamination is rarely used in the industry, we compared the results to the epoxy composites made by wet compression moulding, lead-

ing to a fibre content of 60%, which is a more realistic approach. Even though the fibre content was lower, the vitrimer composites had lower absolute pHRR than their epoxy counterparts. The development of the processing technology and deeper understanding of this novel vitrimer system may result in higher fibre content in the future.

3.5. Dynamical mechanical analysis of reference and flame retarded epoxy resin and vitrimer composites

The DMA results of the reference and flame retarded epoxy resin and vitrimer composites are shown in Table 10, and their loss modulus is illustrated in Fig. 8.

Based on the storage modulus results and glass transition temperatures (T_g) determined from the maximum of the loss factor curve, the softening effect of the flame retardants was much more expressed in the PER epoxy composites than in the vitrimers. In the VITRIMER RDP 3%P COMPOSITE sample, the initial lower storage modulus started to decrease at about 25 °C higher temperatures. APP did not affect the T_g of the composites notably, while RDP had a contrary effect in the two systems: in the PER composite, the T_g nearly halved, while in the vitrimer composite, the T_g increased by 35 °C to 113 °C.
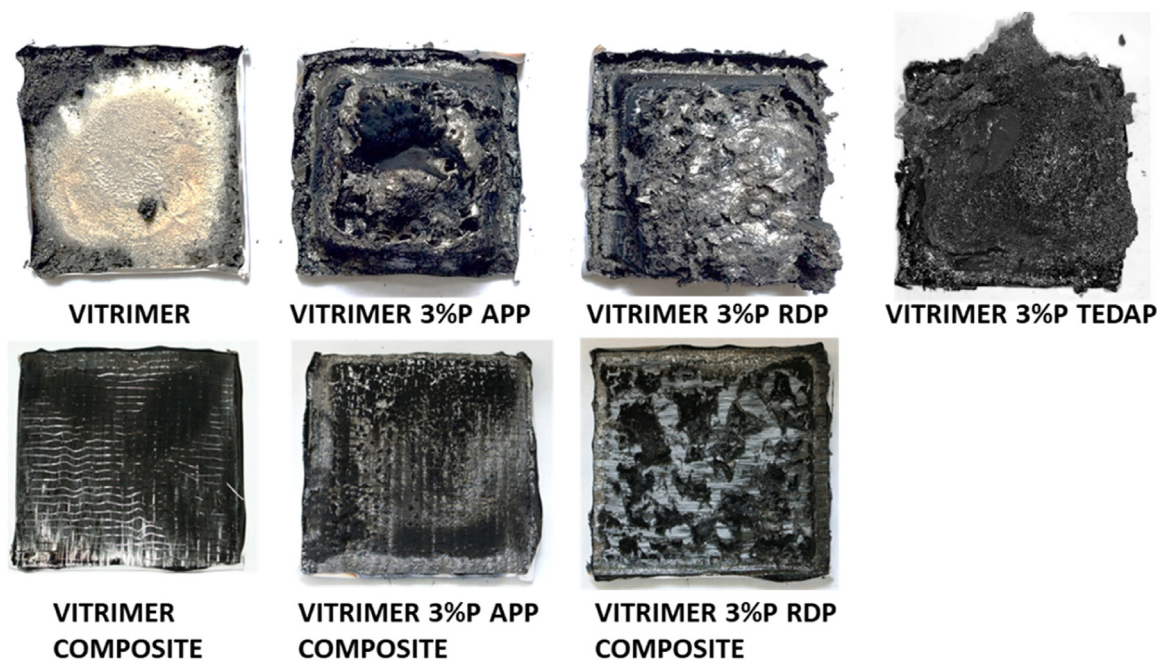
Fig. 7. Mass loss calorimetry residues of vitrimer reference and flame retarded matrices and composites.

Table 10
DMA results reference and flame retarded epoxy resin and vitrimer composites.

Sample	E' at 35 °C (MPa)	E' at 120 °C (MPa)	Max of tanδ (°C)
PER COMPOSITE	34,708	16,316	70
PER APP 3%P COMPOSITE	5864	1026	70
PER RDP 3%P COMPOSITE	1530	598	36
VITRIMER COMPOSITE	37,113	1191	78
VITRIMER APP 3%P COMPOSITE	27,865	1830	82
VITRIMER RDP 3%P COMPOSITE	21,653	4061	113

E' at 25 °C: storage modulus at 25 °C; *E'* at 75 °C: storage modulus at 75 °C; Max of tanδ: the temperature at the tanδ (loss factor curve) peak.
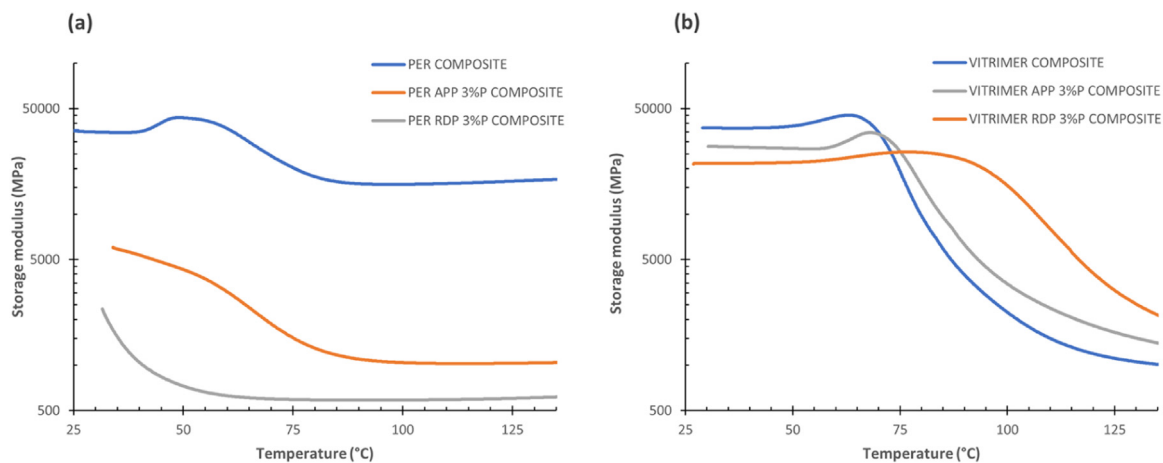
Fig. 8. The storage modulus of reference and flame retarded (a) epoxy resin and (b) vitrimer composites.

4. Conclusions

We developed flame retarded polyimine-based vitrimers and carbon fibre-reinforced vitrimer composites by incorporating two additive flame retardants and a reactive flame retardant containing phosphorus: ammonium polyphosphate (APP), resorcinol bis(diphenyl phosphate) (RDP), and *N,N',N''*-tris(2-aminoethyl)-phosphoric acid triamide (TEDAP). These flame retardants exhib-

ited different modes of action, either in the solid phase (APP), predominantly gas phase (RDP), or a combination of both (TEDAP). We compared the performance of vitrimer systems with an aliphatic epoxy resin system based on pentaerythritol (PER). The matrix materials were extensively characterised using techniques such as differential scanning calorimetry (DSC), thermal analysis (TGA), limiting oxygen index (LOI), UL-94 testing, and mass loss calorimetry (MLC). Additionally, the composites were analysed

through LOI, UL-94 test, MLC and dynamic mechanical analysis (DMA).

The DSC analysis showed that adding additive flame retardants decreased the crosslinking enthalpy of both epoxy resin and vitrimer systems. This effect was more pronounced in the case of RDP, as it required a higher amount to reach the same phosphorus-content. TEDAP, a reactive phosphorus-containing flame retardant and amine hardener, increased the reaction enthalpy and the glass transition temperature in both systems. The vitrimer systems exhibited greater thermal stability compared to PER epoxy resins, suggesting a more controlled degradation process.

In studying the flame retardancy of vitrimers, not enough emphasis has been placed on the issue that, despite being thermosetting materials, they exhibit thermoplastic behaviour above their vitrimer transition temperature. This has significant drawbacks in terms of flame retardancy with regard to melting and dripping. In the studied systems, the melting of vitrimer could be prevented by rapid charring from 2% phosphorus content. In epoxy systems, the self-extinguishing V-0 UL-94 rate was achieved only with TEDAP at 3% phosphorus content, while in the vitrimer system, all flame retardants led to a V-0 UL-94 rate at 3% phosphorus content. The flame retardants reduced the pHRR values more significantly in the vitrimer system than in the PER epoxy systems, except for the PER TEDAP 3%P system. In the PER system, the order of effectiveness for flame retardants was RDP<APP<<TEDAP, while in the vitrimer system, it was RDP<TEDAP<APP. RDP with predominant gas phase action was less effective in both matrices. The better performance of the same flame retardants in the vitrimeric systems can be attributed to the higher nitrogen content of the imine-based vitrimers in combination with phosphorus flame retardants, leveraging nitrogen-phosphorus synergism. Vitrimer composites outperformed epoxy composites in terms of relative pHRR reduction. Contrary to the epoxy and vitrimer matrices, in composites, the lowest pHRR (152 kW/m^2 in VITRIMER RDP 3%P COMPOSITE sample) was achieved with RDP, which mainly acts in the gas phase. This can be attributed to the fact that carbon fibres interfere with the solid-phase action of APP, preventing it from fully exerting its flame-retarding properties.

This study has shown that the vitrimer systems have certain benefits in terms of thermal stability and fire resistance compared to the epoxy resin systems, in addition to being easily recyclable. In the future, we plan to follow two development strategies. On the one hand, we plan to eliminate the negative effect of the carbon fibres by applying vitrimer-based intumescent flame-retardant coatings with APP. On the other hand, the phosphorus-nitrogen synergism could be further exploited by developing inherently flame retarded imine-type vitrimers using TEDAP.

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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