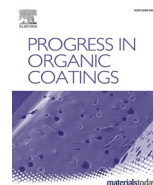Development of fire retardant epoxy-based gelcoats for carbon fibre reinforced epoxy resin composites

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Development of fire retardant epoxy-based gelcoats for carbon fibre reinforced epoxy resin composites

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ABSTRACT

This research article focuses on the development of multifunctional, flame retarded epoxy gelcoat formulations based on phosphorus-containing, intumescent flame retardant (FR). We prepared epoxy resin-based gelcoats with 5 %, 10 % and 15 % phosphorus (P) content using ammonium polyphosphate (APP), and compared their thermal stability, glass transition temperature, crosslinking reaction enthalpy and fire performance to the non-flame retarded reference and a commercial FR gelcoat. We coated carbon fibre reinforced pentaerythritol (PER)-based epoxy composites (non-FR, and FR) with these gelcoats in two thicknesses (0.5 mm and 1.0 mm). The APP-based gelcoats outperformed both the commercial reference and FR gelcoat in terms of thermal stability. When the APP concentration in the gelcoat was increased, the thermal stability and the limiting oxygen index (LOI) increased. All FR gelcoats reached the self-extinguishing (V-0) classification during the UL-94 test and showed remarkable char formation during the mass loss calorimetry (MLC) test even at a lower heat flux (25 kW/m^2). In terms of heat release rate, the gelcoat with 10 % P from APP behaved similarly, while the formulation with 15 % P from APP outperformed the commercial FR gelcoat. The tendency in the fire performance of the coated composites was similar to the behaviour of the gelcoat matrices: above 10 % P content, the coated sample outperformed the commercial FR gelcoat. The addition of a liquid, organophosphorus flame retardant (resorcinol bis(diphenyl phosphate) (RDP), acting mainly in the gas phase) to the epoxy matrix of the composite resulted in the further decrease of heat release rate. Non-FR gelcoats considerably deteriorated the fire performance of the fibre reinforced composites, even when applied in a thickness of 0.5 mm. If a gelcoat layer is necessary on the surface of the composite part, a substantial increase in heat release must be considered, or an FR multifunctional gelcoat should be used as an alternative. We reached a 67 % reduction in peak heat release rate when we replaced a 1 mm thick non-FR gelcoat with a gelcoat containing 15 % P on the PER reference composite.

1. Introduction

The application of composite structures has been steadily increasing in the last decades due to their excellent mechanical behaviour and light weight. However, these parts must comply with strict safety requirements, especially in the automotive and the aerospace industry, where these composites are used as structural and indoor elements. These applications often require special features, such as electrical and thermal conductivity or flame retardancy. Special features need special manufacturing technologies, special additives or both. For example, in the case of most unsaturated polyester (UP) and epoxy resin (EP) matrices, a significant disadvantage in aerospace applications is the flammability of the resins themselves [1,2]. The addition of additives

(usually solid particles) to the resin matrix could highly influence the viscosity of the resin, which can be disadvantageous during manufacturing. Traditional manufacturing technologies (e.g. hand lamination, wet compression moulding etc.) are not very sensitive to the latter phenomenon, but in the case of the highly productive infusion techniques, the increased viscosity could lead to defects during manufacturing. For example, if the applied flame retardant (FR) contains solid-phase particles, they can be filtered by the reinforcement layers during the infusion phase of liquid composite moulding techniques (e.g. resin transfer moulding [RTM] or vacuum assisted resin transfer moulding [VARTM]), which leads to a non-uniform particle distribution and thus uneven fire performance in the cross-section of the composite [3,4]. Another issue occurs when intumescent flame

retardant additives are applied: the fibre reinforcement can interfere with the solid phase action of the FRs by hindering char formation on the composite surface. Furthermore, the charring of the intumescent FR can lead to delamination between the reinforcement layers, which causes a sufficient loss in the post-fire mechanical properties of the composite [5–7]. A possible solution to avoid particle filtration and its disadvantageous side effects is the application of a liquid phase flame retardant in the matrix (the resin remains injectable, while no particle filtration occurs) and/or a flame retarded surface coating on the top of the composite [4,5].

Multifunctional surface coatings are also a widely studied field nowadays. Almost every industry applies gelcoats to provide a high-quality finish on the visible surface of composite parts [8]. Gelcoats are resin systems usually dissolved in easily evaporable organic solvents (such as styrene). The base material of the gelcoat should be chemically similar to the resin matrix of the composite base to provide good interfacial adhesion [9]. Gelcoats are usually applied on the inner side of the mould surface, where the evaporation of the solvent starts the crosslinking process. When the gelcoat material is partially crosslinked, the reinforcement layup is built and impregnated with the resin matrix (e.g. by hand lamination, vacuum infusion, etc.). For an even gelcoat thickness, these materials are usually brushed, rolled or sprayed on the mould surface (depending on the viscosity of the gelcoat system). However, these techniques mean an extra step during manufacturing [10,11]. Other methods do not require further steps during production and provide a fairly even gelcoat thickness on the surface. These manufacturing techniques are mainly based on different in-mould coating solutions [11–15]. Although these gelcoats are usually very thin (approx. below 500 μm), the material itself is also highly flammable such as the neat resin matrix of the composite, which means that in the case of a fire, the composite with a gelcoat on top of it means more flammable material. As mentioned above, the primary function of gelcoats is the mechanical protection and the aesthetic appearance of the composite, but individual needs can be satisfied with the addition of functional additives (e.g. FRs) into the gelcoat material. While gelcoats are widely used in the industry, it seems to be a good decision to apply multifunctional gelcoats on the composite surface where needed [16]. The properties of the ideal FR gelcoat are non-flammability, low thermal conductivity, similar heat expansion coefficient to the matrix material of the composite, strong interfacial adhesion between the gelcoat and the matrix resin, weather and wear resistance, low weight and cost-effectiveness [1].

Multifunctionality plays an increasingly important role in composite applications. Thus, light weight is not always enough for composites to compete with other high-tech materials, so the added functionality might be significant for the performance and added value of composite parts [17]. Multifunctional gelcoats are already commercially available, although these materials are mostly based on unsaturated polyester (UP)

resins, because of their wide use in several industrial fields and low cost. However, the development of functional coatings is a widely researched field in the world of thermoplastic polymers as well (e.g. anti-corrosion coatings [18]). Multifunctionality itself might sound like a bit too general, as it may include improved abrasion resistance [19], self-healing ability [20], antistatic behaviour [21], water-resistance [22,23], electric conductivity [24–26], flame retardancy and other properties. However, it is not always easy to find the proper combination of additives to produce the desired properties. One of the most critical functionalities is flame retardancy, especially in the aerospace, automotive and railway industries. Some of the commercially available FR gelcoats or FRs tested for application in gelcoats are listed in Table 1.

In our previous study, we investigated the effect of flame retardant particle filtration on the fire performance of carbon fibre reinforced epoxy composites made by different manufacturing technologies [36]. We found that the filtration phenomenon can be avoided by the application of a liquid phase flame retardant (acting mainly in the gas phase) in the composite matrix with a multifunctional coating on top filled with a high amount of phosphorus FR additive (acting in the solid phase). One of the most crucial issues is the strength of the interfacial adhesion between the coating and the composite substrate. The flame retardant function of the gelcoat can only be utilized if there is strong adhesion in the interface of the gelcoat and the composite [1,9]. The easiest way to achieve good interfacial adhesion is to apply the same base material in the gelcoat and the composite. For example, in the case of a carbon fibre reinforced epoxy composite, an epoxy resin-based FR gelcoat seems to be the right choice. However, most commercially available FR gelcoats are based on unsaturated polyester resins; only a few gelcoat systems are based on epoxy resins, and only a few of them contain phosphorus-based intumescent flame retardant additives. Our goal was to develop an epoxy resin-based FR gelcoat containing halogen-free, phosphorus-based, intumescent FR for carbon fibre reinforced epoxy composites. These composites play an important role in high-tech engineering applications, especially in the transportation industry. First, we chose a commercially available non-FR epoxy gelcoat as a reference and a FR commercial gelcoat. Our formulations were based on the non-FR gelcoat with different P content. We compared these gelcoats to the commercial FR gelcoat system focusing on the thermal behaviour of the gelcoat matrices and the fire properties of the coated composites.

2. Materials and methods

2.1. Materials

As the reference epoxy gelcoat component, we used Sicomin SG715 with Sicomin SD802 hardener, while Sicomin SGi128, which contains titanium-dioxide, was used as the commercial flame retarded epoxy gelcoat with the Sicomin SD228 hardener.

Table 1
Commercial FR gelcoat systems or FRs tested in gelcoats and their field of application.

Brand name	Producer	Matrix	Flame retardant	Manufacturing	Area of application
Crystic Fireguard series [27]	Scott Bader	UP	halogen-free, antimony-free	brushing, spraying	railway, marine, construction
FB2220, FB2330 [28]	CCP Composites	UP	halogen-free, antimony-free	brushing, spraying	automotive, aircraft, construction
SGi128 [29]	Sicomin	EP	halogen-free	brushing	automotive, railway, construction
Nuvopol, Nuvochryl, Giralithe [30]	Mäder Group	UP, urethane acrylate	inorganic hydroxides, intumescent systems	brushing, spraying	railway, marine
Hetron FR 1540 [31]	Ashland	UP	brominated	brushing, pultrusion	railway, construction
Exolit AP740 [32]*	Clariant	UP	ammonium polyphosphate	brushing, spraying, infusion	transportation, railway, construction
Exolit AP742 [33]*	Clariant	UP	ammonium polyphosphate	brushing, spraying, infusion	transportation, aerospace, construction
Exolit AP750 [34]*	Clariant	EP	ammonium polyphosphate	brushing, spraying, infusion	transportation, railway, construction

*Clariant Exolit flame retardants are ammonium polyphosphate-based additives, which were tested in UP-based and EP-based gelcoats [35]; these gelcoat formulations, however, are not yet commercial.

For composite preparation, as EP component, we used tetrafunctional pentaerythritol-based PER (MR 3016; supplier: IPOX Chemicals Ltd, Budapest, Hungary; main component: tetraglycidyl ether of pentaerythritol; viscosity: 0.9–1.2 Pa s at 25 °C; density: 1.24 g/cm^3 at 25 °C; epoxy equivalent: 156−170 g/eq). As hardener, we applied MH 3122 cycloaliphatic amine (supplier: IPOX Chemicals Ltd, Budapest, Hungary; main component: 3,3′-dimethyl-4,4′-diaminodicyclohexylmethane; viscosity: 80–120 mPa s at 25 °C; density: 0.944 g/cm^3 at 25 °C; amine hydrogen equivalent: 60 g/eq).

For the preparation of flame retarded gelcoats based on Sicomin SG715, we used ammonium polyphosphate as flame retardant (APP; supplier: Nordmann Rassmann, Hamburg, Germany; trade name: NORD-MIN JLS APP; P-content: 31–32 %; average particle size: 15 μm). We prepared gelcoat formulations with 5 %, 10 % and 15 % P-content APP. For the flame retardancy of the composite matrix material, we used resorcinol bis(diphenyl phosphate) (RDP) (supplier: ICL Industrial Products (Beer Sheva, Israel), trade name: Fyrolflex RDP, P-content: 10.7 %).

In the case of composites, the reinforcement was P X 35FBUD030 unidirectional carbon fibre (CF) fabric consisting of Panex 35 50 k rovings with an areal weight of 300 g/m^2 (supplier: Zoltek Ltd, Nyergesújfalu, Hungary).

The chemical structures of the EP monomer, hardener and FR additives used can be seen in Fig. 1.

2.2. Methods

2.2.1. The preparation of gelcoat matrix samples

In the case of reference SG715/SD802 and flame retarded SGi128/SD228 systems, we mixed the two components according to the stoichiometric ratio recommended by the distributor. In the case of the FR coating made with APP, the amount of solid flame retardant was added to the epoxy component (SG715) of the gelcoat system, stirred well, and then the hardener was added. Gelcoat materials were cured in a silicon mould for 24 h at room temperature. The SGi128/SD228 system was post-cured for 16 h at 60 °C in a Heraeus UT6 type drying oven (manufacturer: Heraeus Holding GmbH), as suggested by the technical datasheet. The reference and flame retarded gelcoat compositions are listed in Table 2.

Table 2
Reference and flame retarded gelcoat materials.

Sample	Mixing ratio [gelcoat:hardener]	Gelcoat [%]	Hardener [%]	APP [%]	P-content [%]
SG715 REF	100:27	79	21	0	0
SGi128 FR	100:70	59	41	0	0
SG715 5 % P APP	100:27	66	18	16	5
SG715 10 %P APP	100:27	53	15	32	10
SG715 15 %P APP	100:27	41	11	48	15

2.2.2. The preparation of composite samples coated with gelcoat

We prepared epoxy resin composites with 3% P content in the matrix by the addition of RDP by hand lamination in a press mould (wet compression moulding). Each carbon weave layer was separately impregnated. We compressed the prepared laminates with 180 bar of hydraulic pressure (which equals to approx. a 25 bar pressure on the laminate) in a T30 type platen press (Metal Fluid Engineering s. r. l., Verdello Zingonia, Italy) to achieve high and uniform fibre content in the composites. 2 mm thick laminates were made in [0]$_5$ layup. The heat treatment, determined on the basis of differential scanning calorimetry (DSC), consisted of the following isothermal heat steps: 1 h at 80 °C and 1 h at 100 °C, and it was carried out during pressing. The fibre content of the composites was 60 ± 1 mass%.

Composite plates were coated by brushing the gelcoat material onto the surface in a thickness of 400−500 μm and 900−1000 μm. The coatings were cured for 24 h at room temperature.

The applied composite processing and coating methods are schematically depicted in Fig. 2.

2.2.3. Differential scanning calorimetry (DSC)

We carried out DSC tests to determine the reaction enthalpy of the crosslinking process and the glass transition temperature (T_g) of the gelcoats. The DSC tests were performed with a TA Instruments Q2000 device (New Castle, DE, USA) in 50 mL/min nitrogen flow with the use of Tzero-type aluminium pans. Sample mass was 5−10 mg. We used heat/cool/heat cycles: after a linear ramp from 25 °C to 250 °C with a heating rate of 3 °C/min (first cycle), the sample was cooled down to
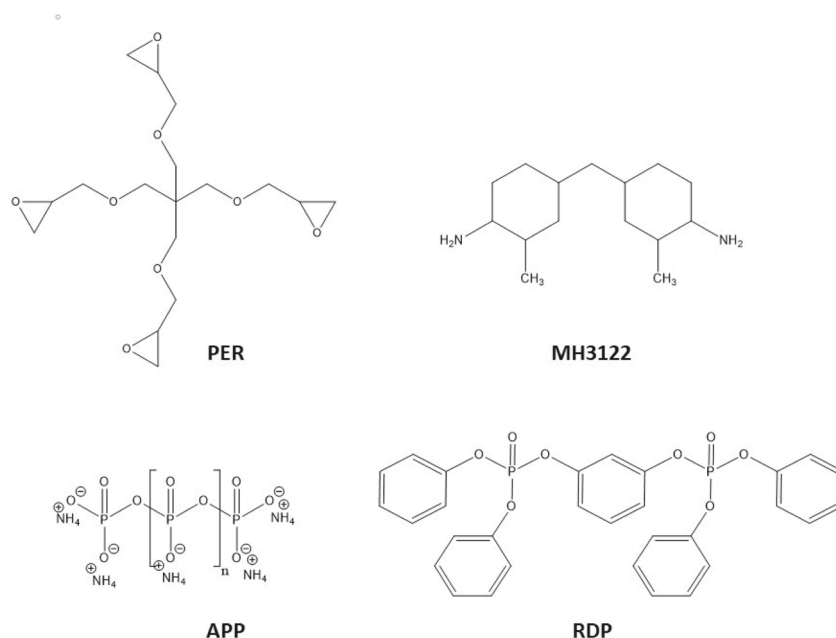

Fig. 1. The chemical structures of the EP monomer (PER), hardener (MH 3122) and FR additives (APP and RDP).

preparation of carbon fibre reinforced composites by hand lamination followed by hot pressing (wet compression moulding)

hand lamination in a mould

epoxy resin matrix
(+ liquid flame
retardant)

unidirectional carbon fibre
reinforcement layers in [0]₅ layup

hot pressing in a mould

1 h at 80 °C
1 h at 100 °C

application of gelcoats on the surface of composites by brushing

(flame retarded) gelcoat

**carbon fibre reinforced
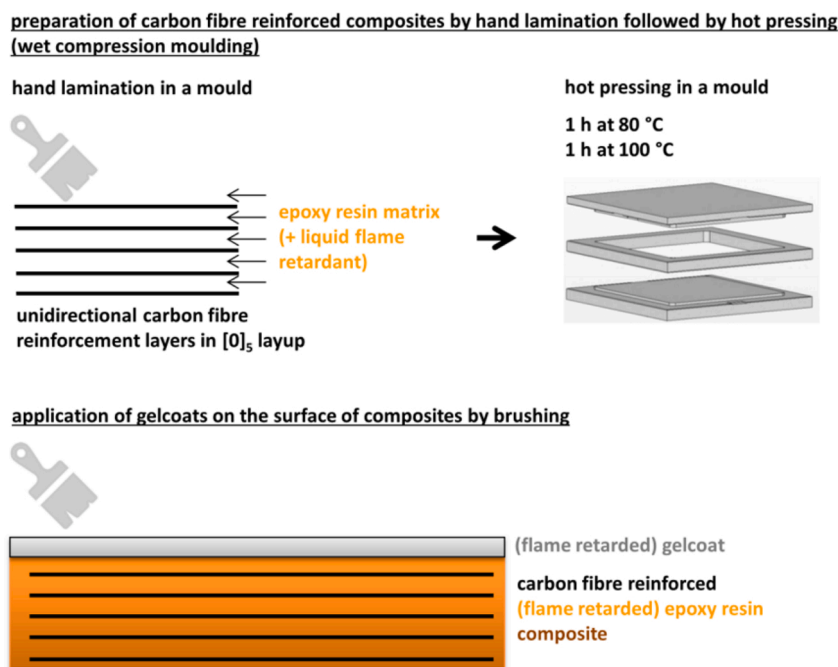(flame retarded) epoxy resin
composite**

Fig. 2. The preparation of coated composite samples.

0 °C at a cooling rate of 50 °C/min, followed by a second linear heating ramp from 0 °C to 250 °C at a heating rate of 10 °C/min (second cycle). The crosslinking reaction enthalpy values were determined from the first heating, while T_g values were determined from the second heating and were defined as the inflection point of the transition curve.

2.2.4. Thermogravimetric analysis (TGA)

We investigated the thermal stability of the gelcoats using a TA Instruments Q500 device (New Castle, DE, USA). Samples of 5−10 mg were heated in the range of 25−800 °C, with a heating rate of 20 °C/min under 30 mL/min nitrogen gas flow.

2.2.5. Fire behaviour

The fire behaviour of the reference and flame retarded gelcoats was characterized with limiting oxygen index tests (LOI, according to ASTM D2863). The LOI value expresses the lowest volume fraction of oxygen in a mixture of oxygen and nitrogen that supports flaming combustion of a material under specified test conditions. Sample size was 120 mm × 15 mm × 2 mm.

We also performed standard UL-94 flammability tests (according to ASTM D3801 and ASTM D635) in order to classify the gelcoat samples based on their flammability in horizontal and vertical test setups. Sample size was 120 mm × 15 mm × 2 mm. The increasing values of UL-94 ratings are as follows: HB, V-2, V-1, V-0.

Mass loss type cone calorimetry tests (MLC) of gelcoat materials and composites were carried out with an instrument made by FTT Inc. (East Grinstead, UK) using the ISO 13927 standard method. Gelcoat specimens (100 mm × 100 mm × 2 mm and 100 mm x 100 mm x 4 mm) were exposed to a constant heat flux of 25 kW/m² and ignited. In the case of composite specimens (100 mm × 100 mm × 2 mm), a constant heat flux of 50 kW/m² was applied. Heat release values and mass reduction were continuously recorded during burning. The average standard deviation of the method was calculated using the results of three parallel tests.

2.2.6. Dynamic mechanical analysis (DMA)

For the investigations of the dynamic mechanical properties and for the determination of the glass transition temperature (T_g) values DMA tests were carried out in three-point bending setup with TA Q800 device of TA Instruments (New Castle, DE, USA). The temperature range was

25−200 °C at 3 °C/min heating rate. The frequency was 1 Hz. The size of the specimens was 55 × 10 × 2 mm (length x width x thickness), and the support span was 50 mm. The amplitude was strain controlled with 0.1 % relative strain. Three parallel tests were carried out, and the results were evaluated with TA Instruments Universal Analysis 2000 4.7A version software.

3. Results and discussion

First, we characterized the gelcoat materials, then we chose reference and flame retarded composite substrates according to mechanical and fire behaviour. Finally, we investigated the coated composite samples focusing on fire performance.

3.1. The characterization of gelcoat matrix samples

This chapter summarizes the effect of flame retardant (FR) on the crosslinking process and the glass transition temperature (determined by DSC), thermal stability (TGA) and fire behaviour of the gelcoat matrix samples.

3.1.1. The effect of FR on the crosslinking enthalpy and glass transition temperature (DSC)

We performed DSC tests on the reference and flame retarded gelcoat

Table 3
DSC results of reference and FR gelcoat matrices.

Sample	Glass transition temperature [°C]	Reaction enthalpy		Temperature of exothermic peak [°C]
		[J/g]	[J/g epoxy]	
SG715 REF	97	188	188	75
SGi128 FR	108	198	198	78
SG715 5 % P APP	105	186	221	74
SG715 10 % P APP	120	174	255	73
SG715 15 % P APP	123	111	212	73

matrices to determine the effect of FR on the crosslinking process and glass transition temperature (T_g). Table 3 shows the results of the DSC analysis.

The commercial SGi128 FR gelcoat had higher T_g and crosslinking reaction enthalpy than the reference SG715 gelcoat due to the different base materials. The increasing APP content in the SG715 reference gelcoat led to higher T_g, which can be explained by the well-dispersed spherical APP particles in the gelcoat matrix [37–40]. The reaction enthalpy obviously decreased when the APP ratio was increased, as the ratio of epoxy resin matrix capable of crosslinking decreased. However, if the reaction enthalpy is related to the mass of epoxy (i.e. we disregard the amount of APP), the reaction enthalpy in J/g epoxy increased when the APP content was increased and had a maximum at 10 % P content. The sample with 5% P APP content showed the most similar characteristics to those of the commercial SGi128 FR gelcoat. For all samples, the exothermic peak temperatures were in the same range. The commercial SGi128 FR gelcoat had higher exothermic peak temperature than the SG715 reference gelcoat, but the increasing amount of APP did not influence the temperature of the exothermic peak.

3.1.2. The effect of FRs on thermal stability (TGA)

We investigated the impact of the FR on the thermal stability of gelcoat matrices. The results are listed in Table 4.

The SGi128 FR gelcoat started to decompose at the lowest temperature and had the lowest maximum mass loss rate, while the char yield at 800 °C was only 9% higher than in the case of the reference gelcoat. Gelcoat materials containing APP started to decompose in the same temperature range (ca. 300 °C) as the reference SG715 gelcoat, but all their other thermal characteristics were significantly changed by the addition of APP. The greatest improvement in thermal stability was observed in the case of the gelcoat containing 15 % P from APP: decomposition started at the highest temperature; $T_{-50\%}$ was almost twice as high as in the case of SG715 REF; it had the lowest mass loss rate among all the samples and a char yield of nearly 50 % at 800 °C.

3.1.3. The fire behaviour of gelcoat matrix samples

The fire performance of the gelcoat materials was tested with standard limiting oxygen index (LOI), UL-94 and mass loss calorimetry (MLC) tests. Table 5 shows the LOI and UL-94 results of the matrices.

Obviously, the reference gelcoat had the weakest fire performance: lowest LOI and worst UL-94 classification. Each flame retarded gelcoat matrix reached the self-extinguishing (V-0) classification during the vertical UL-94 test, which is favourable, considering their application as multifunctional surface coatings. The SGi128 FR matrix had a LOI twice as high as that of the reference gelcoat. The addition of APP increased the LOI values as expected: 5% P APP content resulted in 1.5x higher LOI, while 10 % P APP caused 3x higher LOI. The sample made with 15 % P APP had a LOI value of >85 V/V% (up to 4x higher than SG715 REF); this material reached the measuring range of the equipment.

We expected intensive char forming during the burning of the flame

Table 4
TGA results of the reference and FR gelcoat matrices.

Sample	$T_{-5\%}$ [°C]	$T_{-50\%}$ [°C]	dTG_{max} [%/°C]	T_{dTGmax} [°C]	Char yield at 800 °C [%]
SG715 REF	299	375	1.1	346	23.9
SGi128 FR	270	407	0.7	326	33.0
SG715 5 %P APP	299	408	1.0	332	38.2
SG715 10 % P APP	300	475	0.9	329	43.2
SG715 15 % P APP	304	717	0.7	331	47.3

$T_{-5\%}$: temperature at 5% mass loss; $T_{-50\%}$: temperature at 50 % mass loss; dTG_{max}: maximum mass loss rate; T_{dTGmax}: the temperature belonging to the maximum mass loss rate.

Table 5
Limiting oxygen index (LOI) and UL-94 classification of gelcoat materials.

Sample	LOI[V/V%]	UL-94[*]
SG715 REF	21	HB (23 mm/min)
SGi128 FR	42	V-0
SG715 5 %P APP	33	V-0
SG715 10 %P APP	62	V-0
SG715 15 %P APP	>85	V-0

[*] Average standard deviation of the measured burning rate: ±1 mm/min.

retarded gelcoat materials, thus we used a heat flux of 25 kW/m² during the MLC test. The dimensions of the samples were 100 × 100 × 4 mm, as required by the standard. Table 6 contains the results, while Fig. 3 shows the heat release rate of the 4 mm thick samples. Flame retardancy index (FRI) was defined on the basis of literature [41]:

$$FRI[-] = \frac{\left(\frac{THR\left[\frac{MJ}{m^2}\right]*pHRR\left[\frac{kW}{m^2}\right]}{TTI[s]}\right)_{REF\ gelcoat}}{\left(\frac{THR\left[\frac{MJ}{m^2}\right]*pHRR\left[\frac{kW}{m^2}\right]}{TTI[s]}\right)_{FR\ gelcoat}}$$

The FRI of the FR gelcoat samples was related to the SG715 reference gelcoat without FRs.

The SG715 reference sample reached the highest peak heat release rate (pHRR) and total heat release (THR), while the residue after burning was the lowest, as expected. There was no significant difference between the time to ignition (TTI) values of the samples. The FR gelcoats had intensive intumescent foaming during burning, which significantly reduced the heat release rate of the samples. The FR samples foamed into the cone during the test, thus the burning continued at a quite low heat release. This phenomenon caused the plateau of the heat release rate curves shown on Fig. 3. With increasing APP content, pHRR and THR decreased, and the residue after burning remained higher. Among the FR gelcoat matrices, the sample made with 5% P APP burned with the highest heat release. The sample made with 10 % P APP acted similarly to the commercial SGi128 FR gelcoat, while the gelcoat with 15 % P APP content exceeded the commercial material in fire performance and an FRI three times greater than that of the other FR gelcoats.

Because of the foaming into the cone, MLC tests were repeated with 2 mm thick samples. Results and heat release rate curves are shown in Table 7 and Fig. 4. Fire behaviour was similar to that of the 4 mm thick samples, although no charring into the cone was observed resulting in more realistic THR values. 5 % P APP content was not enough to outperform the commercial FR gelcoat, while the sample with 10 % P APP behaved similarly, and 15 %P APP outperformed the SGi128 FR gelcoat.

Table 6
MLC results of gelcoat matrices (sample thickness: 4 mm).

Sample	TTI [s]	pHRR [kW/m²]	Time to pHRR [s]	THR [MJ/m²]	Residue [%]	FRI [-]
SG715 REF	78	627	138	90.5	18.7	–
SGi128 FR	66	169	371	74.6	45.8	3.81
SG715 5 % P APP	69	242	134	61.1	35.1	3.39
SG715 10 %P APP	65	185	191	70.3	52.1	3.64
SG715 15 %P APP	85	129	945	39.3	66.2	12.20

TTI: time to ignition; pHRR: peak of heat release rate; THR: total heat release; FRI: flame retardancy index related to SG715 REF sample. Average standard deviation of the measured mass loss calorimeter values: TTI: ±3; pHRR: ±30; time to pHRR: ±5; residue: ±2.
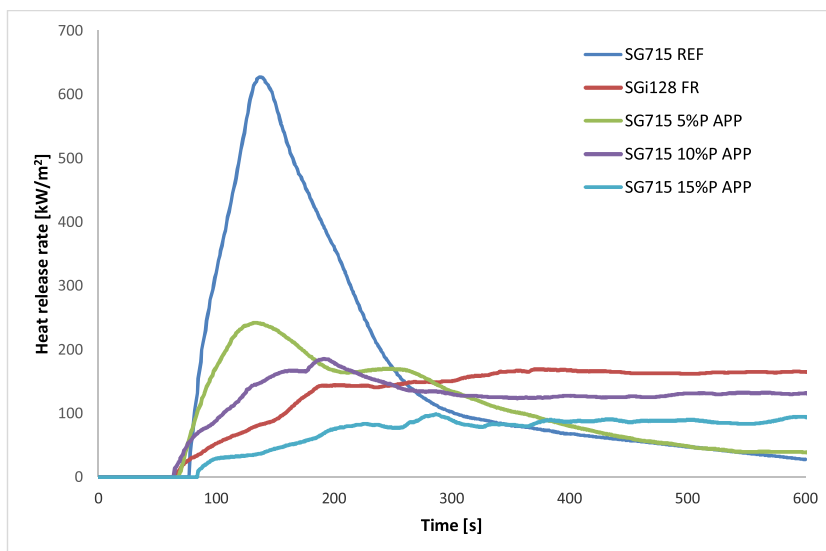
Fig. 3. Heat release rate of gelcoat matrices (sample thickness: 4 mm).

Table 7
MLC results of gelcoat matrices (sample thickness: 2 mm).

Sample	TTI [s]	pHRR [kW/m²]	Time to pHRR [s]	THR [MJ/m²]	Residue [%]	FRI [-]
SG715 REF	41	428	74	60.0	18.7	–
SGi128 FR	46	127	97	45.0	39.6	5.04
SG715 5 % P APP	29	200	74	42.1	32.1	2.16
SG715 10 %P APP	41	158	82	35.0	48.9	4.64
SG715 15 %P APP	36	133	84	27.3	62.1	6.21

TTI: time to ignition; pHRR: peak of heat release rate; THR: total heat release; FRI: flame retardancy index related to SG715 REF sample. Average standard deviation of the measured mass loss calorimeter values: TTI: ±3; pHRR: ±30; time to pHRR: ±5; residue: ±2.

3.2. Screening of FR compositions for the matrix of fibre reinforced composites

In addition to the reference carbon fibre reinforced composite, we also intended to test the gelcoat formulations on flame retarded composites to study the possible synergistic effects of FRs applied both in the gelcoat and in the composite matrix material.

The selection of the composite matrix formulation was based on two aspects:

- the applied epoxy resin matrix should be injectable even after the addition of flame retardants;
- the applied flame retardant should provide good FR performance and should not impair the mechanical properties of the composite significantly; and no particle filtration should occur during liquid composite moulding.

An epoxy resin with low enough viscosity satisfies the first condition. The tetrafunctional pentaerythritol-based PER epoxy resin is suitable for this application above 40 °C without any solid additives [42]. The
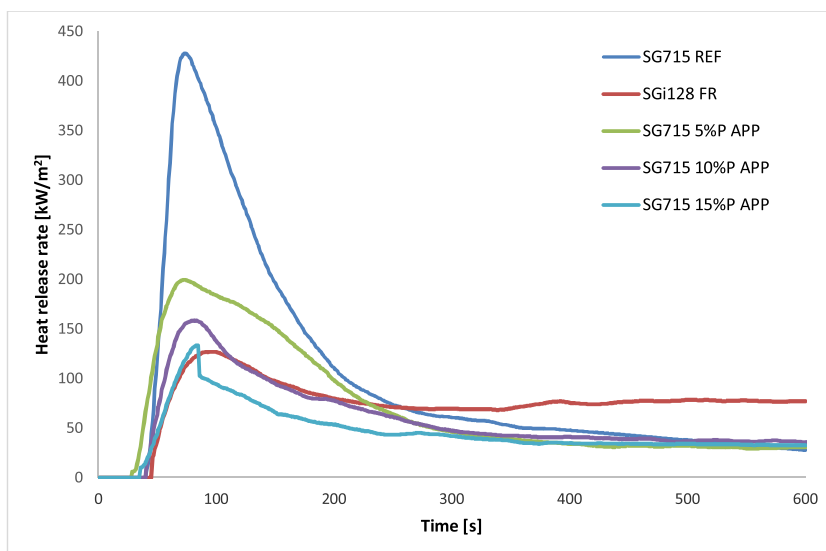

Fig. 4. Heat release rate of gelcoat matrices (sample thickness: 2 mm).

second condition can be satisfied with a proper amount of liquid resorcinol bis(diphenyl phosphate) (RDP). RDP decreases the viscosity of the resin, thus the matrix material remains injectable [42]. To determine the appropriate RDP content in the composite, we investigated the fire performance of the matrix, and the dynamic mechanical behaviour of the carbon fibre reinforced composites made with an increasing amount of RDP in the epoxy resin matrix.

3.2.1. The fire behaviour of the fibre reinforced composite matrix material

First, the fire behaviour of the epoxy resins, which we intended to use as composite matrix materials, was investigated with standard LOI and UL-94 tests. The oxygen index and UL-94 classification of the resins are listed in Table 8 below.

Higher RDP content in the PER matrix resulted in higher LOI and better UL-94 classification, as expected. Above 4 % P RDP content, LOI did not increase any more. Although the P content was higher in the case of the samples containing more RDP, the crosslinking density declined as RDP does not participate in the crosslinking process, which did not make any further improvement in fire performance, possible above 4 % P-content. For this reason and due to the significant softening effect of RDP, we only prepared composite specimens from PER matrices with a P content no more than 4%.

3.2.2. The dynamic mechanical analysis of the fibre reinforced composites

To select the proper composite substrate, we investigated the softening effect of RDP with regard to the T_g and the mechanical properties by dynamic mechanical analysis (DMA). Table 9 summarizes the glass transition temperatures and storage moduli.

The presence of RDP in the resin matrix decreased the glass transition temperature and storage modulus as well. The decrement was particularly drastic in the case of the PER 4 %P RDP composite.

Based on the fire performance and dynamic mechanical behaviour of the composites, we selected the PER 3 %P RDP composite as a flame retarded substrate besides the PER reference composite. The PER matrix containing 1% P RDP burned during the horizontal UL-94 test, while its LOI remained low. 4% P RDP already resulted in a V-0 self-extinguishing classification during the UL-94 test, and the LOI was also above 30 V/V %, but the mechanical properties of the composite made it unsuitable for any application. As there was no huge difference in the dynamic mechanical properties of the samples containing 2 % or 3-%P RDP, we chose PER 3-%P RDP because of its higher FR content, and consequent higher LOI. Because of the moderate T_g, the PER reference composite is not suitable for structural applications, e.g. in the aerospace industry, but it can be used as indoor elements. The selected PER 3%-P RDP matrix did not reach the self-extinguishing, V-0 classification during the vertical UL-94 test, therefore it provides room for improvement, if the composite is coated with a gelcoat having high P content. Furthermore, the combined application of RDP in the matrix, (acting mainly in the gas phase), and APP in the gelcoats, (acting in the solid phase), may have synergistic effects, as we showed earlier [42].

3.3. The fire performance of coated composite samples

The selected reference and flame retarded composite substrates were

Table 8

The LOI and UL-94 values of the reference and flame retarded PER matrices made with RDP.

Matrix	LOI [V/V%]	UL-94*
PER	23	HB (32 mm/min)
PER 1 %P RDP	25	HB (15 mm/min)
PER 2 %P RDP	26	HB
PER 3 %P RDP	29	HB
PER 4 %P RDP	32	V-0
PER 5 %P RDP	32	V-0

*Average standard deviation of the measured burning rate: ±1 mm/min.

Table 9

Dynamic mechanical behaviour of the reference and the flame retarded composites made with RDP.

Composite	T_g [°C]	E'(25 °C) [MPa]	E'(75 °C) [MPa]
PER	69	85857	48002
PER 1 %P RDP	74	54766	26035
PER 2 %P RDP	57	64828	13737
PER 3 %P RDP	56	63358	19005
PER 4 %P RDP	41	36146	7331

T_g: glass transition temperature; E'(25 °C): storage modulus at 25 °C; E'(75 °C): storage modulus at 75 °C.

coated with 0.5 and 1.0 mm thick reference and FR gelcoats by brushing as described in chapter 2.2.2. The coated samples were characterized, with special focus on fire performance.

3.3.1. The fire performance of reference and flame retarded composites coated with a 0.5 mm thick gelcoat

The fire behaviour of the coated composite sheets was investigated by MLC. During the test, a heat flux of 50 kW/m² was applied, which corresponds to a cabin fire [43] in an aircraft fire. Table 10 and 11 summarize the numerical MLC results, while Figs. 5 and 6 show the heat release rate of the coated reference and flame retarded composites with a gelcoat thickness of 0.5 mm.

Flame retardancy index (FRI) was defined on the basis of literature [41]:

$$FRI[-] = \frac{\left(\dfrac{THR\left[\frac{MJ}{m^2}\right]*pHRR\left[\frac{kW}{m^2}\right]}{TTI[s]}\right)_{composite}}{\left(\dfrac{THR\left[\frac{MJ}{m^2}\right]*pHRR\left[\frac{kW}{m^2}\right]}{TTI[s]}\right)_{reference\ matrix}}$$

The FRI of the FR gelcoat samples was related to the PER reference epoxy resin matrix (TTI: 17 s, pHRR: 706 kW/m², THR: 100, 5 MJ/m²) [42].

As for the coated reference composites, a 0.5 mm thick gelcoat without FR (SG715 REF) increased the pHRR of the PER composite by 23 % (from 351 to 430 kW/m²) (Table 10, Fig. 4). This significant increase was caused by the addition of a further flammable layer to the surface of the composite. The flame retarded gelcoats caused a lower pHRR than in the case of the uncoated reference composite; the amount of their residues after burning showed a slightly increasing tendency. On average, the 0.5 mm thick FR gelcoats lowered the pHRR of the PER composite by 22 %. The lowest pHRR (242 kW/m²) was reached by the PER composite

Table 10

MLC results of the coated reference composites with a 0.5 mm thick gelcoat.

Sample	TTI [s]	pHRR [kW/m²]	Time to pHRR [s]	THR [MJ/m²]	Residue [%]	FRI [-]
PER REF composite	23	351	39	24.1	47.4	15.28
PER REF_SG715 REF	33	430	57	32.6	45.7	13.23
PER REF_SGi128 FR	28	265	67	24.9	51.4	23.85
PER REF_SG715 5 %P APP	29	307	55	26.8	49.1	19.81
PER REF_SG715 10 %P APP	27	242	58	21.2	50.4	29.58
PER REF_SG715 15 %P APP	34	286	66	22.8	52.8	29.31

TTI: time to ignition; pHRR: peak of heat release rate; THR: total heat release; FRI: flame retardancy index related to PER REF sample. Average standard deviation of the measured mass loss calorimeter values: TTI: ±3; pHRR: ±30; time to pHRR: ±5; residue: ±2.

Table 11
MLC results of the coated FR composites with 0.5 mm gelcoat thickness.

Sample	TTI [s]	pHRR [KW/m^2]	Time to pHRR [s]	THR [MJ/m^2]	Residue [%]	FRI [-]
PER 3 %P RDP composite	26	200	45	15.8	56.2	46.25
PER 3 %P RDP_SG715 REF	35	283	61	24.6	47.8	28.26
PER 3 %P RDP_SGi128 FR	30	196	55	20.0	54.9	43.02
PER 3 %P RDP_SG715 5 %P APP	32	257	56	23.0	50.0	30.43
PER 3 %P RDP_SG715 10 %P APP	36	210	64	22.7	55.3	42.45
PER 3 %P RDP_SG715 15 %P APP	36	180	62	20.4	55.9	55.11

TTI: time to ignition; pHRR: peak of heat release rate; THR: total heat release; FRI: flame retardancy index related to PER REF sample. Average standard deviation of the measured mass loss calorimeter values: TTI: ±3; pHRR: ±30; time to pHRR: ±5; residue: ±2.

coated with the gelcoat containing 10 % P (SG715 10 %P APP), which is equivalent to a pHRR reduction of 31 % compared to the uncoated PER reference composite, and a 44 % reduction compared to the PER reference composite coated with a 0.5 mm thick non-FR gelcoat, respectively. PER composites coated with the gelcoat containing 10 % P and 15 % P had similar overall fire performance on the basis of FRI, and both of them outperformed the composite coated with the commercial SGi128 FR gelcoat.

The addition of RDP lowered the pHRR of the PER reference composite by 43 % (from 351 to 200 kW/m^2) (Table 11, Fig. 5). In comparison to the coated reference composites, the pHRR of the FR-coated composites was reduced by 19 % on average, due to the incorporation of RDP in the composite matrix, i.e. the additional FR effect in the FR coated composites was less than half the reduction experienced in the reference composite. Only the composites coated with the commercial FR gelcoat (SGi 128) and the gelcoat containing 15 % P APP had lower pHRR than the uncoated composite sheet. 5 % P and 10 % P APP was possibly not enough to compensate for the increase coming from the

addition of a further flammable layer onto the surface, which affected the pHRR values negatively. The lowest pHRR (180 kW/m^2) was reached by the FR composite coated with the gelcoat containing 15 % P (SG715 15 %P APP), which is equivalent to a pHRR reduction of 49 % compared to the uncoated PER reference composite, and a 58 % reduction compared to the PER reference composite coated with a 0.5 mm thick non-FR gelcoat, respectively. Based on the FRI values when the composite itself contained P-containing FR, at least 15 % P in the gelcoat was necessary to further ameliorate the overall fire performance.

3.3.2. Fire performance of the reference and flame retarded composites coated with a 1.0 mm thick gelcoat

We repeated the experiments with 1.0 mm thick gelcoats, hoping to further reduce the heat release rate. Table 12 and 13 summarize the numerical MLC results, while Figs. 7 and 8 show the heat release rate of coated reference and flame retarded composites with a gelcoat thickness of 1 mm.

As expected, the 1 mm thick gelcoat without FR (SG715 REF) increased the pHRR of the PER composite even more than the 0.5 mm thick gelcoat, by 30 % instead of 23 % (from 351 to 456 kW/m^2) (Table 12, Fig. 7). By increasing the APP ratio, the fire performance of the SG715-based gelcoats improved, and the amount of residue increased. On average, the 1 mm thick FR gelcoats lowered the pHRR of the PER composite by 44 %, which is twice the value calculated in the case of the 0.5 mm thick gelcoats. The lowest pHRR (180 kW/m^2) was reached by the PER composite coated with the gelcoat containing 15 % P (SG715 15 %P APP), which is equivalent to a pHRR reduction of 49 % compared to the uncoated PER reference composite, and a 61 % reduction compared to the PER reference composite coated with a 1 mm thick non-FR gelcoat, respectively. The overall fire performance of PER composites coated with gelcoat containing 10 % P and 15 % P outperformed the composite coated with the commercial SGi128 FR gelcoat on the basis of the FRI values. Due to the double gelcoat thickness, the advantage of the 15 % P coating increased compared to the 10 % P coating.

The pHRR of the composites coated with 1.0 mm thick FR coating was reduced by only 3% on average, due to the incorporation of RDP in the composite matrix, i.e. the additional FR effect was even less than experienced in the case of the 0.5 mm thick coating. Nevertheless, with this slight amelioration, the pHRR of the composite coated with the gelcoat containing 10 % P APP outperformed the uncoated composite sheet (besides the commercial FR gelcoat (SGi 128) and the gelcoat containing 15 % P APP, which already led to lower pHRR values in 0.5
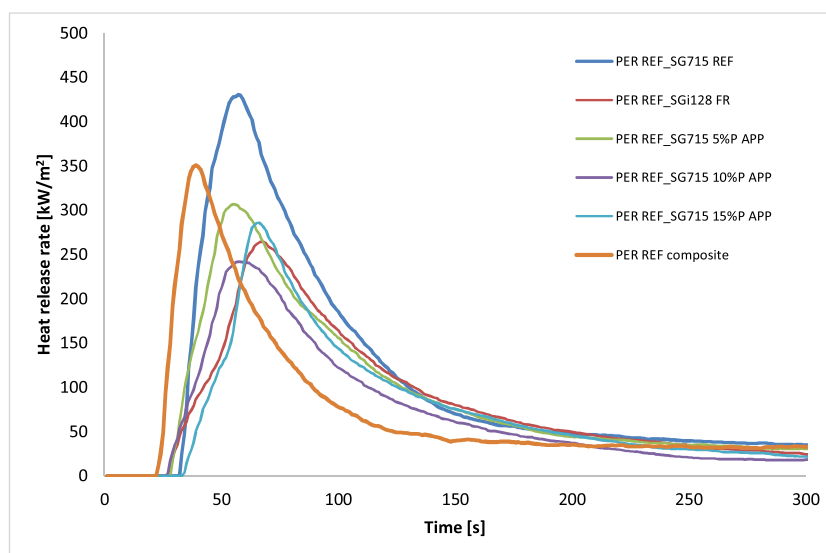

Fig. 5. Heat release rate of the coated reference composites with a 0.5 mm gelcoat thickness.
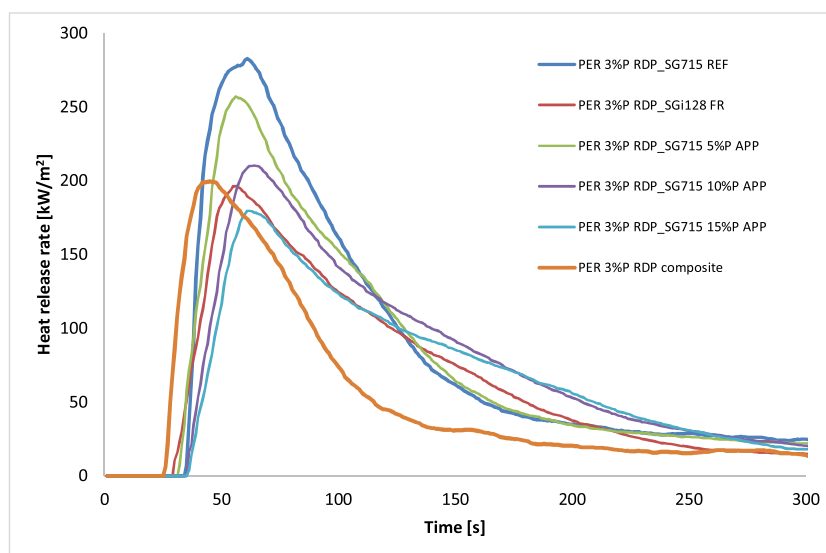
Fig. 6. Heat release rate of the coated FR composites with 0.5 mm gelcoat thickness.

Table 12
MLC results of the coated reference composites with 1.0 mm gelcoat thickness.

Sample	TTI [s]	pHRR [kW/m²]	Time to pHRR [s]	THR [MJ/m²]	Residue [%]	FRI [-]
PER REF composite	23	351	39	24.1	47.4	15.28
PER REF_SG715 REF	34	456	78	61.8	39.7	6.78
PER REF_SGi128 FR	30	164	122	43.1	42.7	23.86
PER REF_SG715 5 %P APP	29	274	83	43.5	45.8	13.68
PER REF_SG715 10 %P APP	35	191	108	39.3	51.5	26.21
PER REF_SG715 15 %P APP	34	164	107	35.8	53.9	32.55

TTI: time to ignition; pHRR: peak of heat release rate; THR: total heat release; FRI: flame retardancy index related to PER REF sample. Average standard deviation of the measured mass loss calorimeter values: TTI: ±3; pHRR: ±30; time to pHRR: ±5; residue: ±2.

Table 13
MLC results of the coated FR composites with 1.0 mm gelcoat thickness.

Sample	TTI [s]	pHRR [kW/m²]	Time to pHRR [s]	THR [MJ/m²]	Residue [%]	FRI [-]
PER 3%P RDP composite	26	200	45	15.8	56.2	46.25
PER 3%P RDP_SG715 REF	34	348	82	56.0	47.6	9.81
PER 3%P RDP_SGi128 FR	34	181	114	44.1	48.1	23.94
PER 3%P RDP_SG715 5 %P APP	35	251	89	43.9	49.0	17.85
PER 3%P RDP_SG715 10 %P APP	25	169	85	36.1	55.0	23.03
PER 3%P RDP_SG715 15 %P APP	35	149	96	35.8	59.4	36.88

TTI: time to ignition; pHRR: peak of heat release rate; THR: total heat release; FRI: flame retardancy index related to PER REF sample. Average standard deviation of the measured mass loss calorimeter values: TTI: ±3; pHRR: ±30; time to pHRR: ±5; residue: ±2.

mm thickness) (Table 13, Fig. 8). The lowest pHRR (149 kW/m²) was reached by the FR composite coated with the gelcoat containing 15 % P (SG715 15 %P APP), which is equivalent to a pHRR reduction of 58 % compared to the uncoated PER reference composite, and a reduction of 67 % compared to the PER reference composite coated with a 1 mm thick non-FR gelcoat, respectively. Although both the TTI and time to pHRR of the composite coated with the gelcoat containing 15 % P increased significantly, due to the increase in THR the overall fire performance based on FRI values decreased to some extent.

In general, the application of FR gelcoats increased the time of pHRR and led to a more elongated, but lower peak heat release, accompanied by significant char forming and foaming, especially in the case of 1 mm thick coatings.

In order to facilitate the comparison of the overall fire performance of the coated composite, the FRI values were summarized in Table 14. The results where the coated composite outperformed the reference composite base were highlighted with bold numbers.

By increasing the thickness of the gelcoat both the quantity of the flammable gelcoat matrix material and the quantity of the applied FR increases, thus for the improvement of the overall fire performance one should find the compositions where the effect of FR is larger than the

effect of the increased flammable gelcoat matrix material. Based on Table 14, in the case of the reference composite base at 0.5 mm thickness all FR gelcoats meet this requirement, while at 1.0 mm thickness 5% P content is not sufficient anymore to fulfil this criterion. From the point of industrial applicability, as the difference between the performance of the 0.5 mm and 1.0 mm thick coatings is minor, the application of 0.5 mm thick SG715 15 %P APP coating is more realistic. In the case of FR composite base it is even more challenging to further increase the overall fire performance of the composite: only the 0.5 mm thick 15 % P containing gelcoat fulfils this goal.

The fire retardant mechanism and results of the reference and FR composites coated with P-containing FR gelcoats are summarized in Fig. 9. In this depiction the height of the flames is proportional to the pHRR values, while the number of the flames is proportional to the THR values. As the TTI and residue values of the coated composites are similar, the overall fire performance is mainly characterized by the pHRR and THR values. By increasing the thickness of the coating the pHRR decreased due to the larger amount of P, but on the other hand the
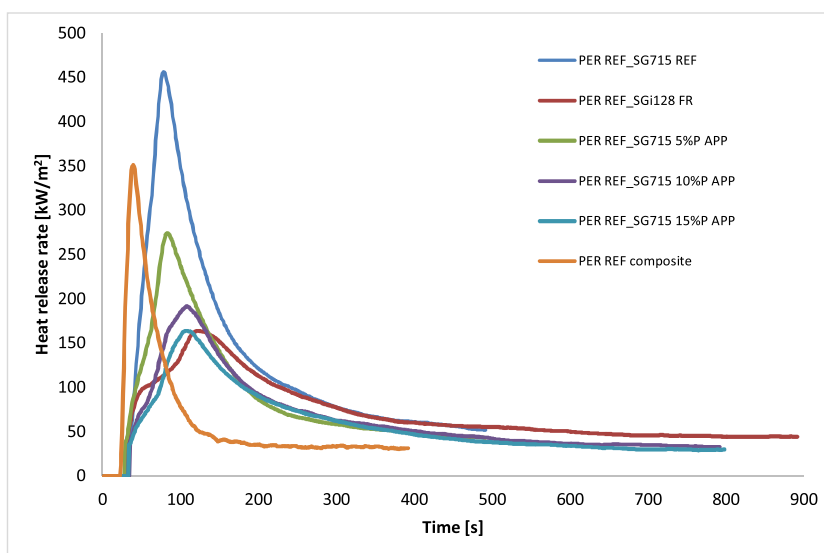
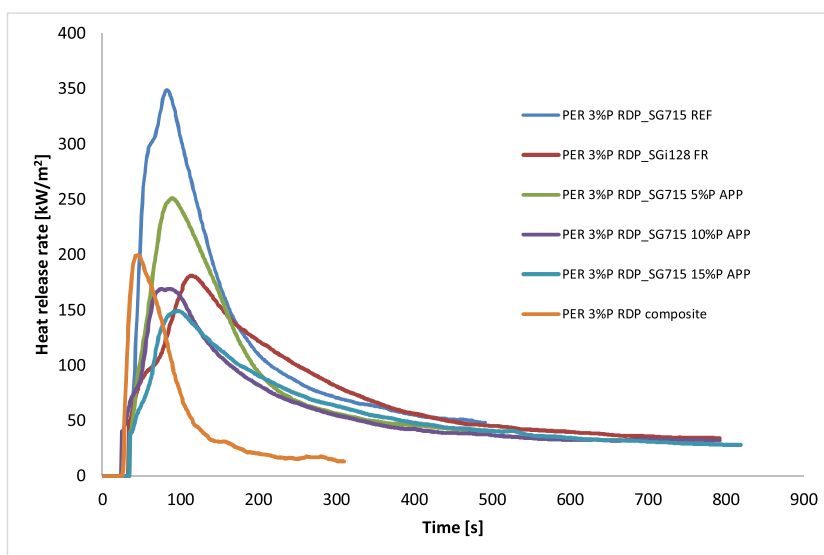**Fig. 7.** Heat release rate of the coated reference composites with 1.0 mm gelcoat thickness.

Fig. 8. Heat release rate of the coated FR composites with a gelcoat thickness of 1.0 mm.

Table 14
Overall fire performance of coated composites on the basis of FRI values.

coating type/thickness [mm]	REF composite base		FR composite base	
	0.5	1.0	0.5	1.0
–	15.28	15.28	46.25	46.25
SG715 REF	13.23	6.78	28.26	9.81
SGi128 FR	**23.85**	**23.86**	43.02	23.94
SG715 5 %P APP	19.81	13.68	30.43	17.85
SG715 10 %P APP	**29.58**	**26.21**	42.45	23.03
SG715 15 %P APP	**29.31**	**32.55**	**55.11**	36.88

THR increased as well due to the more flammable gelcoat material. Therefore, both in the case of reference and FR composites the application of 0.5 mm thick FR gelcoat is more reasonable.

4. Conclusions

We prepared carbon fibre reinforced reference and flame retarded epoxy resin composites by wet compression moulding, and investigated the effect of reference and flame retarded gelcoats in two applied thicknesses on their fire performance.

First, we prepared epoxy resin-based gelcoats with 5 %, 10 % and 15 % phosphorus (P) content using ammonium polyphosphate (APP), and compared their glass transition temperature (T_g), reaction enthalpy of crosslinking, thermal stability and fire performance to the reference epoxy resin-based gelcoat and a commercially available, flame retarded epoxy resin-based gelcoat containing titanium dioxide. The well-dispersed APP particles increased the T_g of the gelcoats, and the reaction enthalpy of crosslinking of the epoxy parts increased. All gelcoats containing APP outperformed the commercially available reference and FR gelcoat in terms of thermal stability. Increased APP content resulted in improved thermal stability and limiting oxygen index (LOI) of the gelcoats. All FR gelcoats reached the self-extinguishing, V-0 UL-94 classification. The 4 mm thick gelcoat specimens foamed into the cone during mass loss calorimetry (MLC) even at 25 kW/m², therefore we repeated the tests with 2 mm thick gelcoats. As for the heat release rates, 5% P APP content was not enough to outperform the commercial SGi128 FR gelcoat. The gelcoat with 10 % P APP behaved similarly, while the
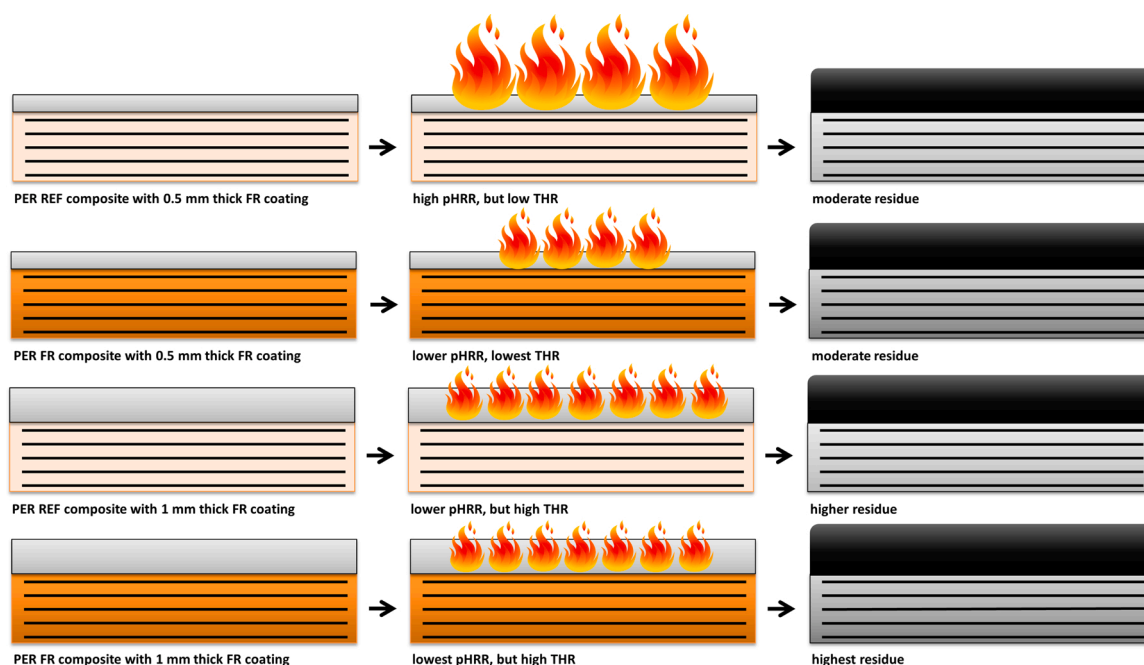
Fig. 9. The fire retardant mechanism and results of the reference and FR composites coated with P-containing FR gelcoats.

formulation with 15 % P APP outperformed the SGi128 FR gelcoat.

After the analysis of the gelcoat formulations, we carried out fire performance screening of the low-viscosity, tetrafunctional, pentaerythritol-based epoxy resin formulations selected for composite preparation. As we increased the resorcinol bis(diphenyl phosphate) (RDP)-content, the fire performance increased, but dynamic mechanical properties suddenly got worse over 3% P content due to the softening effect of RDP. Therefore, we prepared flame retarded carbon fibre reinforced composite substrates with a P content of 3% in the matrix. We coated the reference and flame retarded composite substrates in 0.5 and 1 mm thicknesses with the commercial reference and flame retarded gelcoats, as well as with the gelcoats containing APP. According to the mass loss calorimetry results, gelcoats containing no flame retardants significantly impaired the fire performance of the fibre reinforced composites, leading to high peak and total heat release rates, even when applied in 0.5 mm thickness. If a gelcoat layer is required on the surface of the composite part (e.g. to have appropriate surface properties), a significant increase in heat release must be taken into consideration, or a flame retarded multifunctional gelcoat should be applied. On average, the 0.5 mm thick FR gelcoats lowered the pHRR of the PER composite by 22 %, which was further decreased by 19 % with the addition of RDP to the composite matrix. Among the composites coated with a 0.5 mm thick gelcoat, the lowest pHRR (180 kW/m^2) was reached by the FR composite coated with the gelcoat containing 15 % P (SG715 15 %P APP).

The 1 mm thick FR gelcoats lowered the pHRR of the PER composite twice as much as the 0.5 mm thick coatings on average, but the additional FR effect of the RDP was decreased at the same time. The PER composite coated with a 1 mm thick gelcoat containing 15 % P (SG715 15 %P APP) without FR in the matrix had the same pHRR (180 kW/m^2) as the composite containing RDP in the matrix in combination with a 0.5 mm thick gelcoat containing 15 % P. Among all composites, the FR composite coated with a gelcoat containing 15 % P (SG715 15 %P APP) had the lowest pHRR (149 kW/m^2), which is equivalent to a pHRR reduction of 58 % compared to the uncoated PER reference composite, and a 67 % reduction compared to the PER reference composite coated with a 1 mm thick non-FR gelcoat, respectively.

The overall fire performance of the composites coated with FR gelcoats was evaluated by comparing the FRI values related to the PER reference epoxy resin matrix. Both from the point of overall fire

performance and industrial applicability, the 0.5 mm thick SG715 15 %P APP coating proved to be the most promising solution to improve the fire performance and the surface properties of the reference and flame retarded epoxy resin composites at the same time.

CRediT authorship contribution statement

Ákos Pomázi: Resources, Investigation, Validation, Formal analysis, Visualization, Writing - original draft, Writing - review & editing. **Andrea Toldy:** Conceptualization, Methodology, Supervision, Resources, Writing - review & editing, Visualization, Project administration.

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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