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The effect of manufacturing technologies on the flame retardancy of carbon fibre reinforced epoxy resin composites

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ABSTRACT

We prepared reference and flame-retarded carbon fibre reinforced composites both by liquid composite moulding, in particular vacuum infusion, and by hand lamination followed by hot pressing (wet compression moulding) in order to study the effect of carbon fibre reinforcement and particle distribution of solid flame retardants (FRs) on fire performance. The flame-retarded matrix had 3% total phosphorus (P) content from ammonium polyphosphate (APP). When the infusion site of the composite produced by vacuum infusion faced the conical heater during the mass loss type cone calorimeter tests, the peak of heat release rate (pHRR) was lower, the time of pHRR became longer and the intumescence increased in comparison to the laminated sample, which supported our hypothesis about the filtration of solid APP during the vacuum infusion process. In order to model the suspected filtration, we prepared a laminated composite sample with an increasing amount of APP equivalent to 1%, 2%, 3%, 4%, 5% P content in each subsequent layer.

The HRR curve of the composite produced by vacuum infusion with the infusion site facing the conical heater was basically identical with the curve of the model composite with the 5% P layer facing the conical heater in the early phase of the degradation, while in the main degradation phase, the lower burnable ratio of the composite prepared by vacuum infusion led to a further decrease in pHRR (184 kW/m^2) and THR (15.5 MJ/m^2), and the consequent best overall fire performance of the composite produced by vacuum infusion. The suspected accumulation of APP in the first layers of the composite caused by the carbon fibre reinforcement was proven by SEM-EDS elemental maps of the whole cross-section of the composite.

1. Introduction

Carbon fibre is considered a benchmark fibre reinforcement in many structural polymer composite applications, where its relatively higher price level is offset by technical benefits such as low density in combination with high strength, low moisture uptake, chemical resistance and high thermal stability. It is considered an inert material at least up to 600 °C [1,2]; consequently, simply by increasing the ratio of carbon fibre reinforcement in the composites, their flammability decreases due to the lower proportion of the highly flammable organic polymer matrix.

Productive liquid composite moulding (LCM) techniques, such as resin transfer moulding (RTM), vacuum assisted resin transfer moulding (VARTM) and vacuum infusion are increasingly used for the manufacturing of high-performance carbon fibre reinforced thermoset polymer composites, including structural automotive and aircraft components [3]. Although these technologies provide high and reproducible carbon fibre content, in many application areas, additional flame retardants (FRs) are required to fulfil the relevant industrial standards. For a tailored fire retardancy solution for these composites, it is necessary to clarify the possible effects of carbon fibre reinforcement on fire performance [4,5].

First of all, due to their high thermal conductivity, carbon fibres conduct the heat inside the composites in the case of a fire event, which is addressed as the candlewick effect [6]. This may lead to some increase in time to ignition as it takes longer to achieve the

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surface temperature necessary for ignition. Nevertheless once the composite is ignited, thermal degradation may be much more intense, as the heat is already effectively transferred inside the composite as well. This effect is particularly disadvantageous when FRs acting in the solid phase are incorporated into the epoxy resin matrix, as it facilitates the heat transfer before a protecting and insulating layer is formed on the surface of the composite. Furthermore, in the case of FRs acting in the solid phase, the carbon fibres interfere in their mode of action and hinder the intumescent behaviour as well, leading to decreased fire performance [7,8]. On the other hand, even this limited charring of the flame-retarded matrix layers delaminates the layers of fibre reinforcement, leading to intense gas and heat transfer, which facilitates the burning of the composites; and it also results in the loss of the mechanical properties of the composite [9,10].

Many of the applied FRs are solid-phase, thus the reinforcement layers may filter them during the LCM process, leading to non-uniform resin flow [11] and FR distribution, and consequent unpredictable fire performance. The authors recently reviewed the parameters influencing particle distribution in composites manufactured by LCM, the models describing particle distribution, the analytical methods capable of determining its extent and the possibilities to improve the particle distribution of solid phase additives [12]. Fundamentally, there are three possible filtration scenarios in particle-filled resin systems: (a) no retention (particles can flow freely through fibre reinforcement, uniform particle distribution is likely); (b) deep filtration (distribution is not uniform, the particles are accumulated at the inlet, and the concentration decreases with a higher filtration length); (c) cake filtration (particles cannot enter the fibre reinforcement and cake of particles is formed outside the preform entry) [12] (Fig. 1).

The dominant filtration mechanism is mostly determined by the ratio of particle size and the pore size of the fibrous media. Typically, above the diameter size of 4 μm the solid additives are likely to filter out to some extent by most fibre reinforcements [13].

Additionally, these solid additives usually increase the viscosity of the polymer matrix. Viscosity is a key property during the production of composites by productive LCM processing technologies. Consequently, either the application of an epoxy resin matrix with a lower initial viscosity should be considered, or hand lamination followed by hot pressing (wet compression moulding) can be applied instead of LCM to achieve similarly high fibre content.

In this paper, we investigate the effect of carbon fibre reinforcement and composite manufacturing technologies on the fire performance of epoxy resins, with special emphasis on the particle distribution of solid flame retardants. We prepared reference and flame-retarded carbon fibre reinforced composites from a low viscosity epoxy resin matrix, suitable for LCM, using ammonium polyphosphate (APP) as model solid-phase FR acting in the solid phase [14,15]. The fire performance of composites made by hand lamination followed by hot pressing (wet compression moulding) and by liquid composite moulding, in particular vacuum infusion method, was compared with respect to the particle distribution of solid FR, which was determined by the SEM-EDS method. Although there are some studies, which investigate the effect of fibre content of composites on their fire behaviour [16,17], to the best of our knowledge, neither the effect of processing technology and related fibre content, nor the effect of solid FR filtration on the fire performance of fibre reinforced composites prepared by LCM techniques has not been yet investigated in detail previously.

2. Materials and methods

2.1. Materials

We used a low-viscosity, tetrafunctional, pentaerythritol-based epoxy resin (EP) component PER (type: 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) with a cycloaliphatic amine hardener (type: MH 3122; supplier: Ipox Chemicals, Budapest, Hungary; main component: 3,3′-dimethyl-4,4′-diaminodicyclohexylmethane; amine hydrogen equivalent 60 g/eq; viscosity at 25 °C 80–120 mPas; density at 25 °C 0.944 g/cm^3).

We applied ammonium polyphosphate (APP) (type: NORD-MIN JLS APP; supplier: Nordmann Rassmann (Hamburg, Germany); P content: 31–32%, average particle size: 15 μm) as the flame retardant additive.

We used PX35FBUD030 type unidirectional carbon fibre (CF) fabric consisting of Panex 35 50k rovings (fibre diameter: 7.2 μm), with an areal weight of 300 g/m^2 (supplier: Zoltek Zrt., Nyergesújfalu, Hungary) as reinforcement.

The chemical structures of the EP monomer, hardener and FR additive used can be seen in Fig. 2.

2.2. Methods

2.2.1. Matrix sample preparation

During the preparation of the specimens, the stoichiometric ratio of the EP component and hardener (100:40) was used in all cases. We prepared EP samples of gradually increasing P content (1%, 2%, 3%, 4%, 5%) from APP. We added the curing agent to the EP component and mixed them at room temperature in a crystallizing dish until the mixture was homogeneous. The samples were cured in appropriately-sized silicon moulds. The curing procedure, determined on the basis of differential scanning calorimetry (DSC),

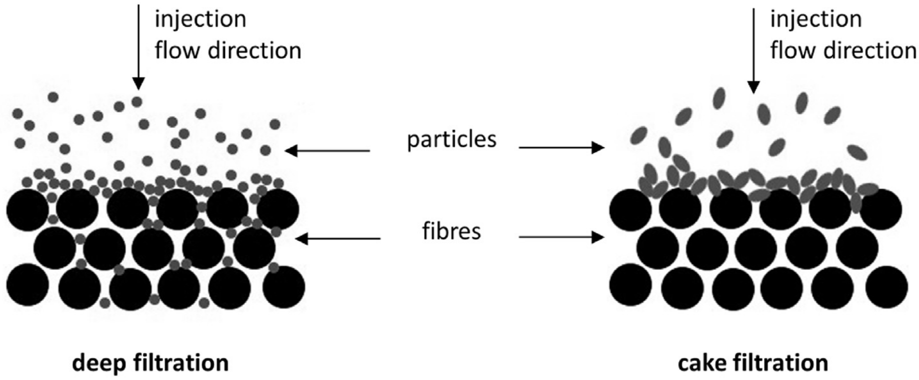


Fig. 1. Illustration of deep filtration and cake filtration mechanisms.

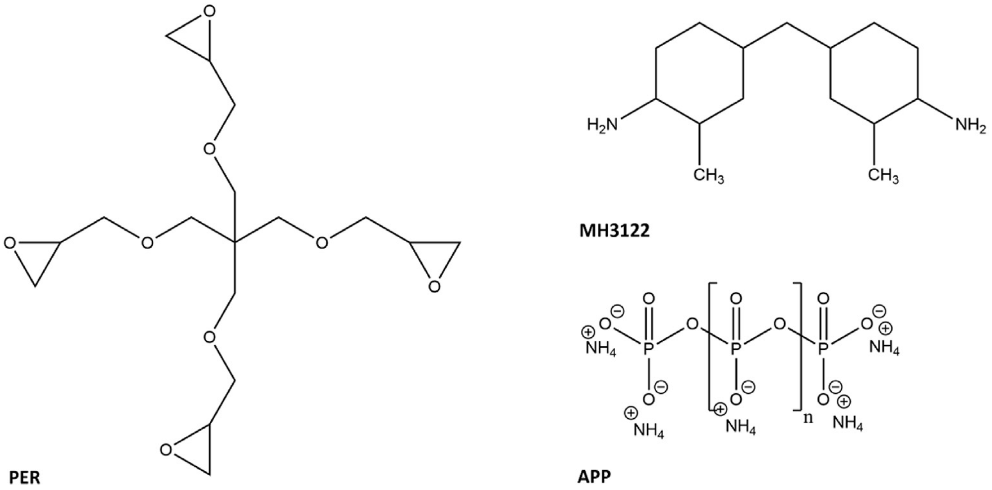


Fig. 2. The chemical structures of the EP monomer (PER), hardener (MH 3122) and FR additive (APP).

consisted of the following isothermal heat steps: 1 h at 80 °C and 1 h at 100 °C.

2.2.2. The preparation of composite samples

We prepared 2 mm thick EP composites in $[0]_5$ layup with 3% overall P content related to the matrix both by hand lamination followed by hot pressing and by vacuum infusion. In the case of hand lamination, each carbon weave layer was separately impregnated. We compressed the prepared laminates with 180 bar of hydraulic pressure (which equals to approx. 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. The heat treatment was the same as in the case of the matrices, and it was carried out during pressing. The fibre content of the composites was 60 ± 1 mass%. In the case of vacuum infusion, five 200 mm × 200 mm layers of unidirectional carbon reinforcement were stacked on a glass plate, which was previously treated with mould release agent. After that, peeling ply and distribution mesh were laid over the surface of the reinforcement, and the layers were sealed in a flexible vacuum bag. The resin inlet tube was placed inside the vacuum bag at the middle of the square sized sample and was connected to the epoxy components previously mixed for 15 min at 60 °C. The vacuum outlet tube was placed in the middle of the edge of the square sized sample and it was connected to a

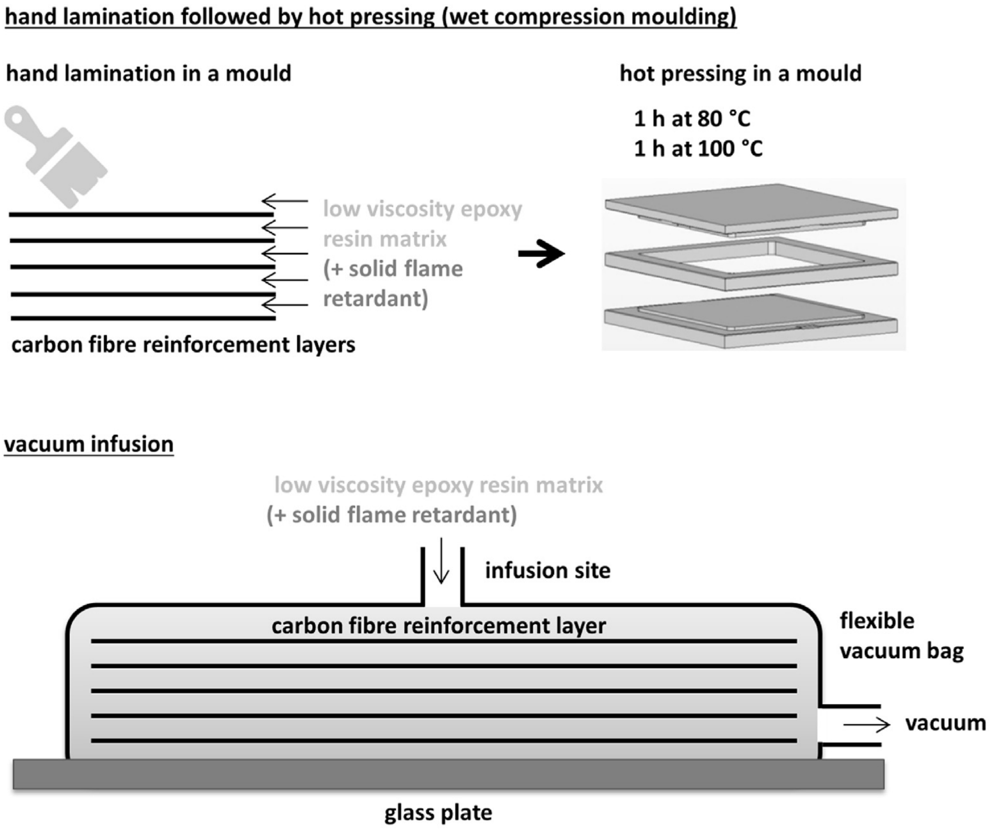


Fig. 3. Composite processing methods.

Table 1
The properties of prepared composite samples.

Composite	flame retardant	overall P-content [%]	layup	preparation method	heat treatment	fibre content [mass%]
PER reference laminated	–	–	$[0]_5$	hand lamination followed by hot pressing	1 h at 80 °C 1 h at 100 °C	60 ± 1
PER 3%P APP laminated	APP	3	$[0]_5$	hand lamination followed by hot pressing	1 h at 80 °C 1 h at 100 °C	60 ± 1
PER reference infused	–	–	$[0]_5$	vacuum infusion	24 h at room temperature	67 ± 1
PER 3%P APP infused	APP	3	$[0]_5$	vacuum infusion	24 h at room temperature	67 ± 1
PER 1–5%P APP laminated	APP	3	$[0]_5$	hand lamination followed by hot pressing	1 h at 80 °C 1 h at 100 °C	60 ± 1

*the exact preparation method of PER 1–5%P APP laminated model composite is described in detail in chapter 3.3 and Fig. 7.

Table 2
LOI, UL-94 and MLC results of the reference and flame-retarded PER matrix samples.

Matrix	LOI [V/V%]	UL-94[a]	TTI [s]	pHRR [kW/m^2]	pHRR time [s]	THR [MJ/m^2]	residue [%]
PER	23	HB (32 mm/min)	17	706	67	100.5	0
PER 1%P APP	27	HB	31	547	106	102.6	10
PER 2%P APP	32	HB	40	539	99	69.2	13
PER 3%P APP	32	HB	28	421	139	78.1	12
PER 4%P APP	32	V-1	30	358	123	74.9	17
PER 5%P APP	32	V-0	31	364	114	69.2	18

LOI: limiting oxygen index, TTI: time to ignition, pHRR: peak of heat release rate, THR: total heat release.
Average standard deviation of the measured mass loss calorimeter values: TTI: ±3, pHRR: ±30, time of pHRR: ±5, residue: ±2.
[a] In parenthesis the horizontal burning rate is showed in mm/min, where measurable.

vacuum pump. The premixed resin was vacuum infused into the stacked layers at room temperature under vacuum. The composite samples were cured for 24 h at room temperature under vacuum prior to demoulding. The fibre content of the composites made by vacuum infusion was 67 ± 1 mass%.

In order to model the suspected gradient of APP filtration in the case of vacuum infusion, we prepared a composite sample containing different amount of P (1%, 2%, 3%, 4%, 5% P) in each subsequent matrix layer by hand lamination followed by hot pressing. The overall P content of this sample was also 3% related to the matrix.

The applied composite processing methods are schematically depicted in Fig. 3.

The properties of prepared composite samples are summarized in Table 1.

2.2.3. Characterization of fire behaviour

We characterized the fire behaviour of the reference and flame-retarded composites 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

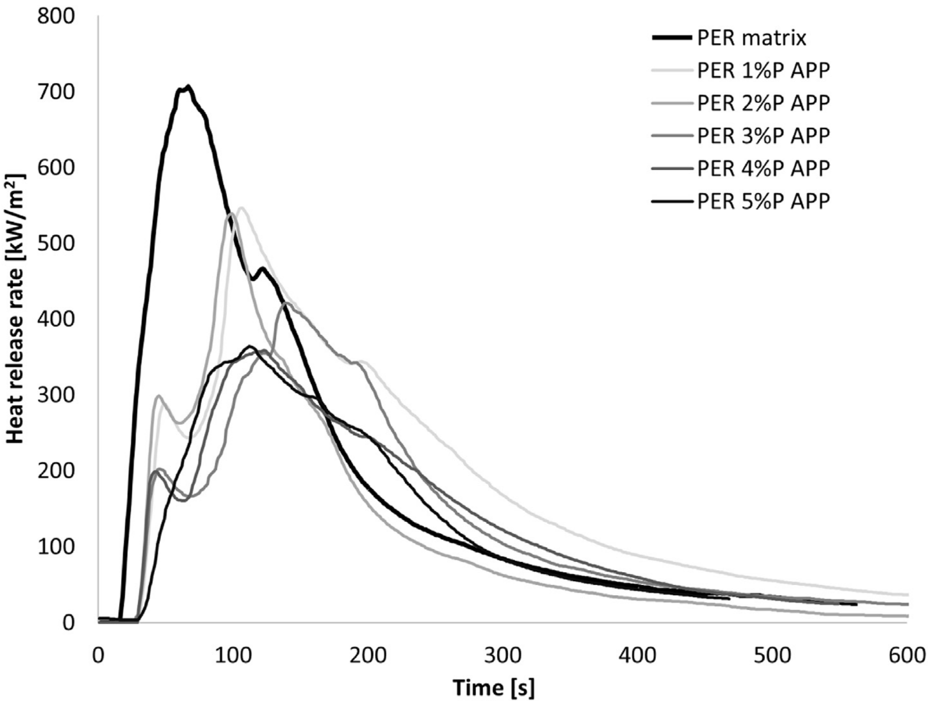


Fig. 4. The effect of gradually increasing APP content on the heat release rate of PER matrix samples.

Table 3
MLC results of reference and flame-retarded carbon fibre reinforced composites made by hand lamination followed by hot pressing or by vacuum infusion.

Composite	TTI [s]	pHRR [kW/m^2]	time of pHRR [s]	THR [MJ/m^2]	residue [%]
PER reference laminated	23	351	39	24.1	47
PER 3%P APP laminated	20	247	35	15.9	50
PER reference infused	29	242	51	19.5	59
PER 3%P APP infused	26	184	43	15.5	62

TTI: time to ignition, pHRR: peak of heat release rate, THR: total heat release.
Average standard deviation of the measured mass loss calorimeter values: TTI: ±3, pHRR: ±10, time of pHRR: ±3, residue: ±3.

supports flaming combustion of the material under specified test conditions. The sample size was 120 mm × 15 mm × 2 mm.

We performed standard UL-94 flammability tests (according to ASTM D3801 and ASTM D635) in order to classify the samples based on their flammability in horizontal and vertical test setups. The 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.

We carried out mass loss type cone calorimetry (MLC) tests with an instrument made by FTT Inc. (East Grinstead, UK) using the ISO 13927 standard method. Specimens (100 mm × 100 mm × 2 mm) were exposed to a constant heat flux of 50 kW/m^2 and ignited. Heat release values and mass reduction were continuously recorded during burning.

2.2.4. Raman mapping

Raman spectra were collected with a Horiba Jobin-Yvon LabRAM system (Villeneuve d'Ascq, France) coupled with an external 785 nm diode laser source and an Olympus BX-40 optical microscope. For Raman mapping, objective of 100 × magnification was used for optical imaging and spectrum acquisition. The spectrograph was set to provide a spectral range of 290–1540 cm^{-1} with a resolution of 1.25 cm^{-1}. The measured area was 20 μm × 20 μm in each case. A step size of 1 μm × 1 μm was chosen. The spectrum acquisition time was 10 s per spectrum.

2.2.5. SEM-EDS

We investigated the morphology of the composites with a JEOL JSM 6380LA type (Jeol Ltd., Tokyo, Japan) scanning electron microscopy (SEM). We determined the particle distribution in the cross-section of the composites by full mapping with energy dispersive spectrometry at a magnification of 50x. To avoid recharging, we coated the sample surfaces with a thin, conductive gold layer via sputtering.

3. Results

3.1. Preliminary screening of the flame-retarded PER matrix compositions based on LOI, UL-94 and MLC results

PER matrix samples of gradually increasing phosphorus (P) content (1%, 2%, 3%, 4%, 5%) were prepared with the use of APP for the preliminary screening of fire performance (Table 2, Fig. 4).

With the P content gradually increased, the LOI shows an increasing tendency up to 2% P content, where it reaches a plateau. All matrix samples of 2% P content and above have an LOI of 32 V/V%. Concerning the UL-94 results, 4% P content led to a V-1 rate, whereas 5% P content was necessary for a self-extinguishing V-0 rate.

The APP increased the TTI during the MLC test by approx. 15 s (Fig. 4). In samples with 1–4% P content, a small shoulder appeared before the main heat release peak, which was significantly lowered and shifted in time as well. At 5% P content, the shoulder

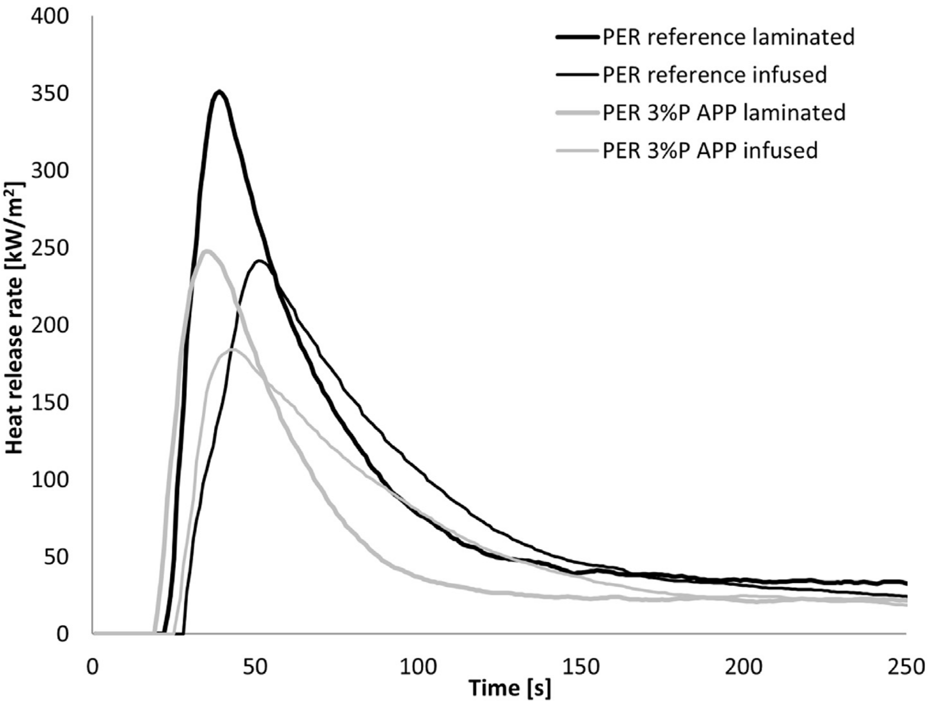


Fig. 5. Heat release rate of carbon fibre reinforced, reference and flame-retarded composites made by hand lamination followed by hot pressing or by vacuum infusion.

disappeared due to the large amount of APP incorporated, and the time to pHRR and pHRR values were similar to those of matrix samples containing 4% P.

Based on these results, we decided to prepare carbon fibre reinforced composites with 3% P content, as it provides a decent, yet not overwhelming fire performance, which still allows the detection of possible improvement due to the suspected accumulation of APP on the surface of the composites prepared by infusion. From practical point of view, this P content also allowed the easy modelling of APP filtration (the exact preparation method of PER 1–5% APP laminated model composite is described in detail in chapter 3.3 and Fig. 7.) and resulted in moderate viscosity increase (the matrix remained injfusible at room temperature).

3.2. The effect of processing technologies on the flame retardancy of composites

In order to examine the effect of processing technologies on the fire performance, we compared the MLC results of reference and flame-retarded carbon fibre reinforced composites, prepared either by hand lamination followed by hot pressing or by vacuum infusion (Table 3, Fig. 5). In all composites the matrix had 3% total P content from APP, it facilitated comparison.

As expected, the inclusion of APP reduced the pHRR values in both the PER composite prepared with lamination (by 30%) and the composite produced with vacuum infusion (by 24%), and slightly reduced the TTI (by 3 s in both cases). Less expectedly, changing the composite preparation method from hand lamination followed by hot pressing (also called wet compression moulding) to vacuum infusion reduced the pHRR values significantly (by 31% in the reference and by 26% in the flame-retarded composite). The time of pHRR also increased (by 12 s in the reference and by 8 s in the flame-retarded composite). One reason for this behaviour is the slightly different fibre content of the composites (60 mass% in composites made by hand lamination followed by hot pressing and 67 mass% in composites made by vacuum infusion), as increasing the ratio of carbon fibres reduces the amount of the highly burnable epoxy resin matrix. If we have a look at the side view of the MLC residues (all composites displayed in Fig. 9 in chapter 3.3), it becomes also obvious that the residue of the composites prepared by vacuum infusion remained more compact in all cases. The difference is the most spectacular in the case of the reference composites, where in the laminated one the matrix almost completely burned and the fibres in the rovings were separated from each other, while the infused one preserved its integrity. Also, the decreased delamination of the carbon fibre layers in the case of the flame-retarded composite produced by vacuum infusion suggests that the solid APP may accumulate on the surface of the composite during vacuum infusion. As the average diameter of APP particles is 15 μm, while the diameter of the carbon fibres is 7.2 μm, it is reasonable to suspect, that during the vacuum infusion the APP particles will be able to flow mainly between the rovings, and not

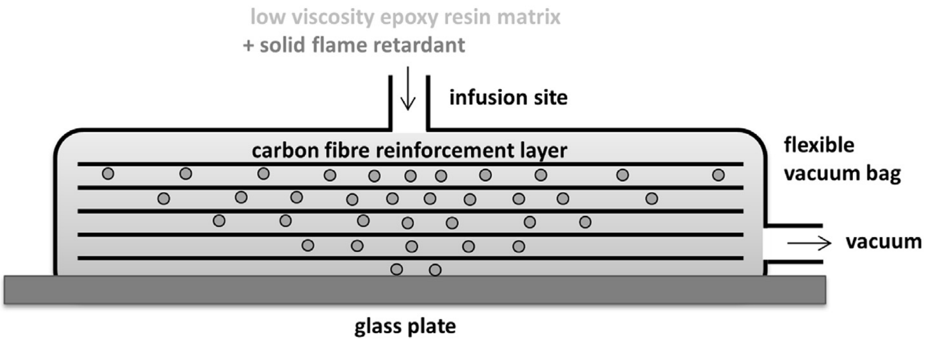


Fig. 6. The suspected "deep filtration" scenario of solid flame retardants during vacuum infusion.

Fig. 7. The preparation of the model composite.

Table 4
MLC results of flame-retarded carbon fibre reinforced composites made by hand lamination followed by hot pressing or by vacuum infusion.

Composite	TTI [s]	pHRR [kW/m^2]	time of pHRR [s]	THR [MJ/m^2]	residue [%]
PER 3%P APP laminated	20	247	35	15.9	50
PER 3%P APP infusion site UP	26	184	43	15.5	62
PER 3%P APP infusion site DOWN	24	208	47	17.2	62
PER 1–5%P APP 5%P UP	24	228	43	21.1	52
PER 1–5%P APP 1%P UP	22	221	41	18.9	41

TTI: time to ignition, pHRR: peak of heat release rate, THR: total heat release average standard deviation of the measured mass loss calorimeter values: TTI: ±3, pHRR: ±10, time of pHRR: ±3, residue: ±3.

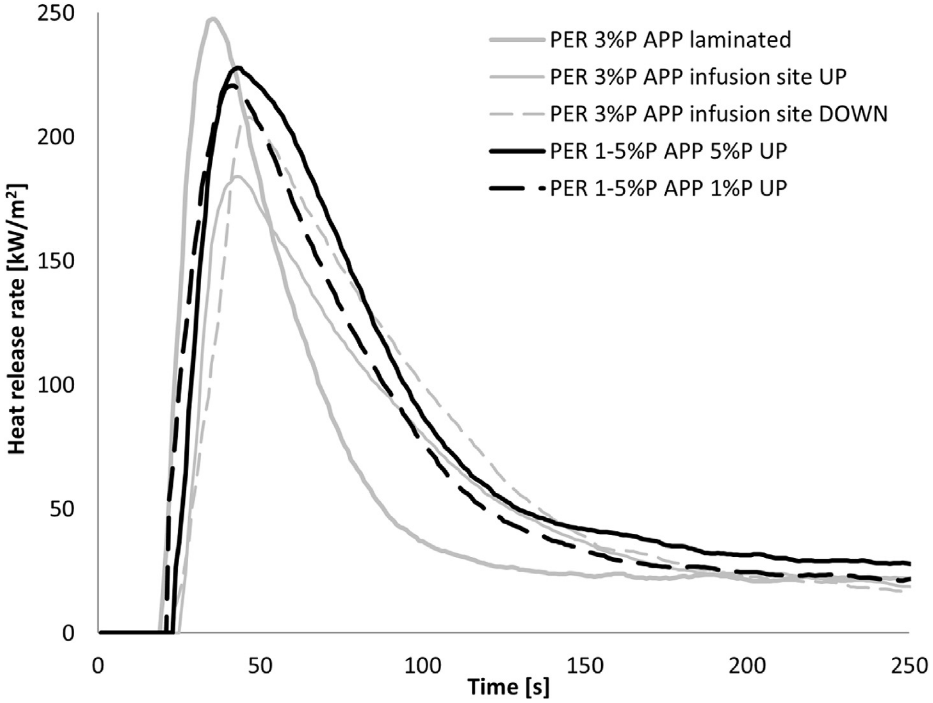


Fig. 8. Heat release rate of flame-retarded carbon fibre reinforced composites made by hand lamination followed by hot pressing or by vacuum infusion.

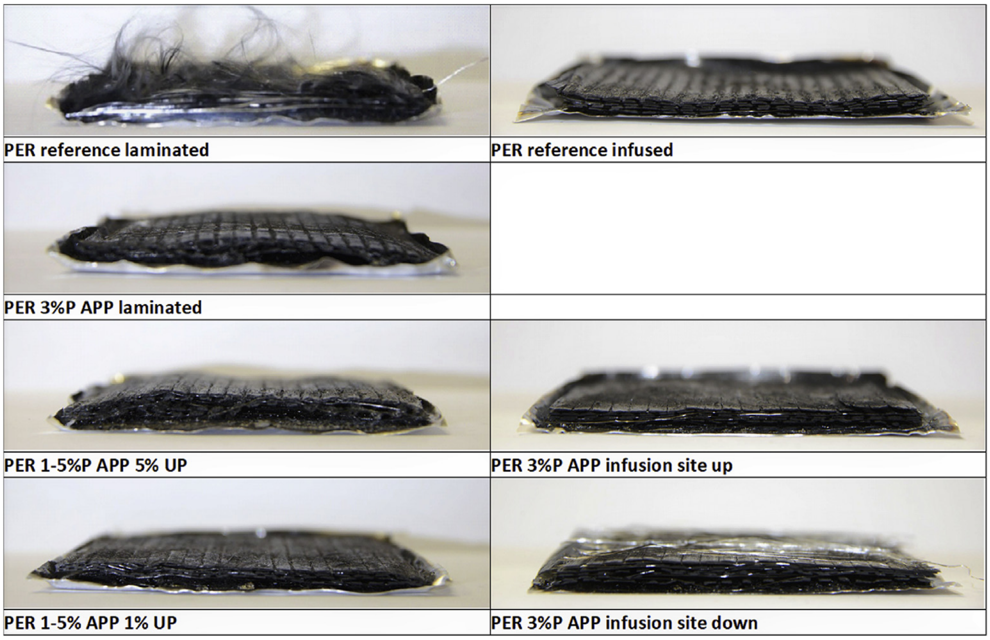


Fig. 9. MLC residues of the reference and flame-retarded carbon fibre reinforced composites made by hand lamination followed by hot pressing or by vacuum infusion.

inside the rovings. Ultimately, the gradual deposition of APP can narrow and clog the flow channels, but the supposed main filtration mechanism is the so called “deep filtration” (Fig. 6).

3.3. *The effect of particle filration during vacuum infusion on the flame retardancy of composites*

To model the suspected filtration mechanism, we prepared a composite by hand lamination followed by hot pressing, where each subsequent carbon fibre layer was impregnated with PER containing an increasing amount of APP equivalent to 1%, 2%, 3%, 4% and 5% P content. The preparation of this model composite is illustrated in Fig. 7. To facilitate comparison, we also set the overall P content of this sample to 3% related to the matrix.

We compared the MLC results of the model composite to flame-retarded carbon fibre reinforced composites made by hand lamination followed by hot pressing or by vacuum infusion (Table 4, Fig. 8). The residues of the MLC tests for all composites are displayed in Fig. 9. The model composite was tested in two different ways: either the 5% P layer (PER 1–5%P APP 5%P UP) or the 1% P layer (PER 1–5%P APP 1%P UP) side was subjected to the heat flux of the calorimeter. Similarly, the composite manufactured by vacuum infusion was also tested in two different ways: either the infusion site (PER 3%P APP infusion site UP), where the APP accumulation was suspected, or the opposite site was subjected to the heat flux of the calorimeter (PER 3%P APP infusion site DOWN).

The flame-retarded composite prepared by vacuum infusion has better overall fire performance if the infusion site is subjected to the heat flux: the TTI increased by 2 s, the pHRR decreased from 208 to 184 kW/m^2, and the THR decreased from 17.2 to 15.5 MJ/m^2. Although the amount of residue was 62% both when the infusion site was up and when it was down, it can be seen from Fig. 9, that in PER 3%P APP infusion site DOWN composite the intumescence occurred between the sample and the aluminium sample holder and did not serve essentially the protection of the composite surface subjected to heat flux as in the case of PER 3%P APP infusion site UP composite.

As for the model composite, independently of the side, TTI, pHRR and time of pHRR were in the same range. A high amount of APP on the surface caused intensive charring and led to more residue when the 5% side was up. Although the overall P content and the preparation method were the same in the case of PER 3%P APP laminated composite and the model composite, the latter outperformed the composite with the even P distribution. In the case of the PER 3%P APP laminated sample, intumescence was hindered by the carbon fibre reinforcement, yet it was enough to decrease the structural integrity of the composite by delamination, which obviously affects the fire performance as well. In the model composite, when the 5%P side was up, the accumulated P on the surface led to rapid and less hindered charring. When the 1%P side was up, although there was no significant charring, delamination was also less significant. This led to better overall fire performance than in the case of the laminated sample with even P distribution.

In the early phase of degradation, the HRR of PER 3%P APP infusion site UP composite is the closest to the HRR of the model sample with the 5%P side up; the HRR curves are practically identical in the first 35 s of the test. In the main degradation phase the lower ratio of highly burnable matrix and more compact structure results in lower pHRR in the case of the PER 3%P APP infusion site UP composite. Nevertheless, based also on its fire behaviour, the filtration of APP during vacuum infusion is highly probable.

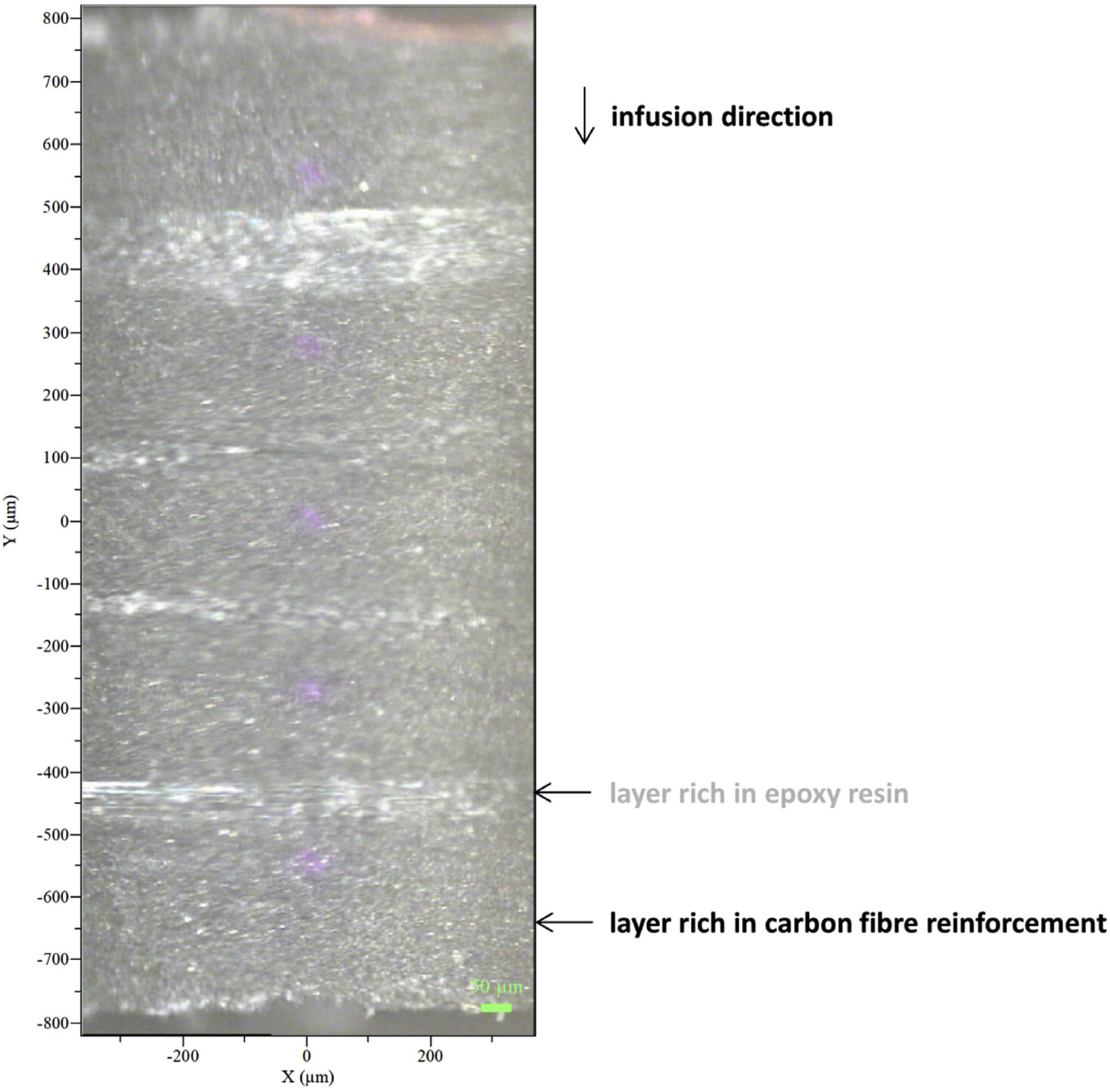
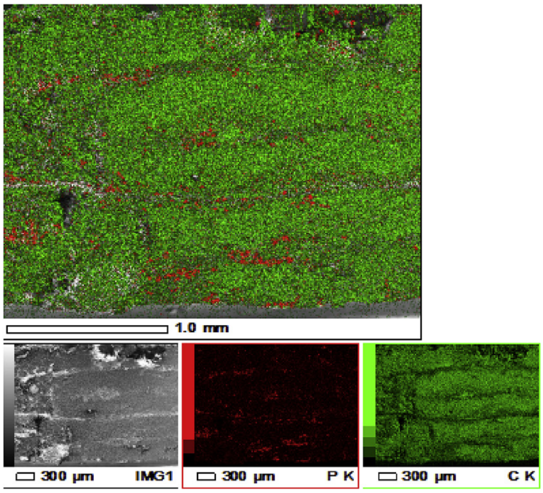
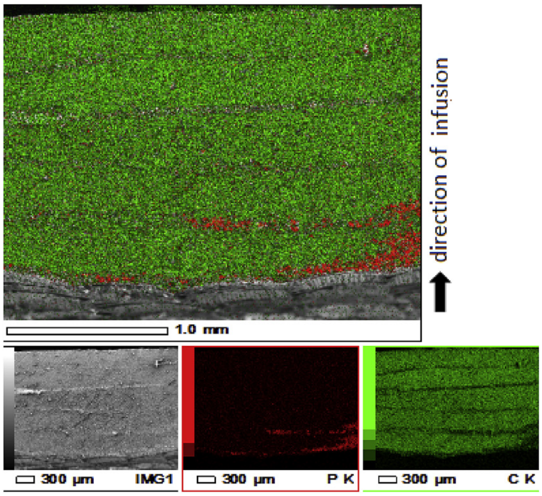


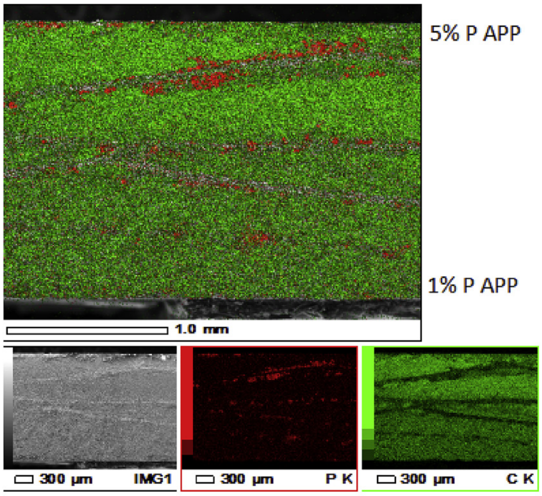
Fig. 10. Optical microscopy image of the cross-section of the PER 3%P APP infused composite.



(a) PER 3%P APP laminated



(b) PER 3%P APP infused



(c) PER 1-5% P APP

Fig. 11. SEM-EDS map of the cross-section of (a) the PER 3%P APP laminated, (b) the PER 3%P APP infused and (c) the PER 1–5%P APP model composite.

3.4. Characterization of particle filtration

In order to examine the suspected filtration of APP in the flame-retarded composite produced by vacuum infusion, we carried out a Raman-mapping in the cross-section of the composite. Due to the strong fluorescence of the carbon fibres, this method was not suitable for the chemical mapping of the cross-section of the composite; nevertheless, the carbon fibre layers and the epoxy resin-rich layers were clearly distinguishable on the optical microscopy image taken by the device (Fig. 10).

Then, we attempted to determine the distribution of the solid FR in the cross-section of the composites using the SEM-EDS method. To the best of our knowledge, this method has not yet been used in the literature for determining the distribution of solid FRs in fibre reinforced composites. Fig. 11 shows the SEM image, the distribution map of P (red) and C (green) atoms, along with the overlay distribution map of the cross-section of the PER 3%P APP laminated, the PER 3%P APP infused and the PER 1–5%P APP model composite.

In the PER 3%P APP laminated sample (Fig. 11 (a)), the signal of C and P is practically complementary. The SEM image and the C map clearly show the carbon fibre reinforcement layers, while the overlay image shows that P accumulates mainly in the resin-rich layers, although P is also observed in the reinforcement layers. Though the distribution of P is not uniform in the laminated sample, no significant accumulation was detected, contrary to the PER 3%P APP infused sample (Fig. 11 (b)), where there is a large gathering of P atoms, i.e. of FR particles in the first and second layer from the infusion site. In the subsequent layers, the detected P signal is minimal, therefore deep filtration can be clearly detected with this method.

In the PER 1–5%P APP model composite (Fig. 11 (c)), an increasing FR, i.e. P content can be detected from the 1% P layer to the 5% P layer, marked on the overlay image.

4. Conclusions

We investigated the fire performance of carbon fibre reinforced epoxy resin composites with special emphasis on the effect of the particle distribution of solid flame retardants influenced by composite manufacturing technologies.

Based on the preliminary fire performance screening of the selected low-viscosity, tetrafunctional, pentaerythritol-based epoxy resin, we prepared carbon fibre reinforced composites with a total of 3% phosphorus (P) in the matrix. Composites were prepared either by hand lamination followed by hot pressing (also called wet compression moulding) or by liquid composite moulding (LCM), in particular vacuum infusion. The lower peak heat release rate (pHRR), the longer time of pHRR and the less delaminated residual structure in the case of the composite prepared by vacuum infusion when its infusion site faced the conical heater led us to the presumption that the carbon fibre reinforcement may filter the applied solid APP FR. To model the suspected so called “deep filtration” mechanism, we laminated a composite, where each subsequent reinforcement layer was impregnated with PER containing increasing amount of APP equivalent to 1%, 2%, 3%, 4%, 5% P content. Independently of the side of the composite subjected to the conical heater of the calorimeter, TTI, pHRR and time of pHRR were in the same range in the case of this model composite. The higher APP content on the surface (when the 5% side was up) resulted only in rapid charring and a higher amount of residue, which can be explained by the fact that intumescence was less hindered here than in the case of PER 3%P APP laminated composite with even P distribution. The HRR curve of the PER 3%P APP infusion site UP composite is practically identical to the curve of the PER 1–5%P APP 5%P UP model composite in the early phase of degradation, which indicates APP filtration during the vacuum infusion process. In the main degradation phase, the effect of the lower burnable ratio in the composite prepared by vacuum infusion prevailed, resulting in lower pHRR and THR, and in the best overall fire performance of the PER 3%P APP infusion site UP composite as well. If we compare the HRR curves of the composites prepared by vacuum infusion with the same fibre content and consequently the same ratio of burnable materials, the lower pHRR and THR of the PER 3%P APP infusion site UP composite is obvious, which also supports the hypothesis of APP filtration. On the other hand, in the case of PER 3%P APP infusion site DOWN composite the intumescence occurring between the bottom of the composite and the sample holder is also a result of the APP filtration during infusion, however, it does not serve the fire protection of the sample. These results highlight the importance of determining the extent of particle filtration in flame-retarded composites made by LCM. Even if the filtration of solid additives cannot be avoided, the proper placement of the composite surface with increased solid flame retardant can serve the protection of the composite surface subjected to heat flux.

We determined the extent of suspected APP filtration in the flame-retarded composite produced by vacuum infusion with SEM-EDS analysis of the whole cross-section of the composite. Based on the SEM-EDS elemental maps, in the composite prepared by vacuum infusion APP accumulated in the first and second epoxy resin-rich layers from the infusion site, while in the subsequent layers the presence of APP was negligible.

It can be concluded that if the applied solid additives contain heteroatom(s) different from the ones present in the matrix, the extent of particle filtration in the cross-section of fibre reinforced composites produced by liquid composite moulding can be determined via the SEM-EDS method. Knowing the extent of particle filtration, engineers can tailor the design of flame-retarded fibre reinforced composites prepared by liquid composite moulding to specific needs.

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.

CRediT authorship contribution statement

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

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