

EFFECT OF FLAME RETARDANT FILTRATION ON THE FIRE PERFORMANCE OF CARBON FIBRE REINFORCED EPOXY COMPOSITES MADE BY RESIN TRANSFER MOULDING

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Keywords: Particle filtration, Phosphorus-containing additive flame retardants, Resin transfer moulding, Carbon fibre reinforced composites

ABSTRACT

The effect of flame retardant filtration on the fire performance was investigated in case of carbon fibre reinforced low-viscosity epoxy (a trifunctional glycerol based (GER) and a tetrafunctional pentaerythritol-based (PER)) composites made by liquid composite moulding techniques, such as resin transfer moulding (RTM). During preliminary tests, two phosphorus (P) containing flame retardants were used: resorcinol bis(diphenyl phosphate) (RDP), acting predominantly in the gas phase, ammonium polyphosphate (APP), acting in the solid phase, and their combination. First, thermal analysis (DSC, TGA), rheological investigations (parallel plate rheometry), flammability (LOI, UL-94) and dynamic mechanical analysis (DMA) were carried out. According to these results, PER epoxy resin with 3%P APP was chosen for further investigation of particle filtration. We examined the particle filtration phenomenon and particle distribution of solid flame retardant (APP) in the cross-section of the composites by scanning electron microscopy with energy dispersive spectrometry (SEM-EDS), while fire performance was evaluated by mass loss calorimetry (MLC) measurements. Flame retarded (FR) samples made by hand lamination followed by hot pressing, and by RTM were compared to each other, while a composite sheet containing different amount of P (1%, 2%, 3%, 4%, 5%) in each subsequent matrix layer was prepared to model the particle filtration.

1 INTRODUCTION

Due to their excellent mechanical properties, carbon fibre reinforced thermoset composites are emerging in high-tech engineering applications as an alternative to metallic structures. However, their main disadvantage, the flammability of the organic polymer matrix, has to be addressed especially in the aircraft and automotive industries, where strict safety requirements have to be met [1]. Because of these requirements, flame retardant (FR) properties of the composites have to be improved possibly by maintaining other important characteristics, such as high glass transition temperature and mechanical properties, given that flame retardants usually have a plasticizing effect [2].

Basically, two ways are available to provide FR properties: one is the application of reactive flame retardants (FRs), while the other is the use of additive FRs. Reactive type FRs can be chemically incorporated into the polymer structure via forming covalent bonds to polymer macromolecules. A huge advantage of these FRs is that they do not migrate to the matrix surface either during high temperature processing or application [3]. Although, reactive FRs have some advantages over additive FRs, industrial applications often prefer additive ones, because of the easier incorporation and manufacturing. Besides their high efficiency, the most used halogenated FRs are banned from the European market according to the directives of the European Parliament [4] because of the high health and environmental risk. To replace the halogenated FRs, developments are focusing e.g. on the application of phosphorus (P)-containing flame retardants. Phosphorus can act both in gas phase (predominantly in the beginning of the degradation) and solid phase (providing a thermal insulation porous char layer on the surface) depending on the chemical structure of the FR.

The fire retardancy of composites raises specific issues. First of all, the high thermal conductivity of the carbon fibres facilitates the ignition (this phenomenon is addressed as the candlewick effect). The application of flame retardants acting in the solid phase also raises other problems. On the one hand, carbon fibres interfere in their mode of action and hinder the intumescent behaviour. On the other hand, the charring of the flame retarded matrix delaminates the layers of the fibre reinforcement. These phenomena lead to decreased fire performance and loss of mechanical properties.

The applied flame retardants usually increase the viscosity of the polymer matrix, which is a key property during the production of high-tech composites by liquid composite moulding (LCM) technologies such as resin transfer moulding (RTM) or vacuum assisted resin transfer moulding (VARTM). These productive technologies are increasingly used for manufacturing structural aircraft and automotive components. To meet the relevant requirements, often different additives are required to improve some properties or to provide additional ones, such as adequate fire performance. These additives are often solid-phase, thus the particles can be filtered by fibre reinforcement during the injection phase of LCM processes, leading to a non-uniform particle distribution and decreased performance [5]. According to the literature, three type of filtration can occur [5,6]:

- No retention: Solid particles can flow freely through fibre reinforcement. A uniform particle distribution can be reached.
- Deep filtration: The particles are gathered at the inlet and the concentration decreases with a higher filtration length. Particle distribution is not uniform.
- Cake filtration: Particles cannot enter the fibre reinforcement; a cake of particles is formed outside the preform entry.

However, it should be stated that between these mechanisms there are no sharp borders. The particle filtration should be handled as a stochastic process and has to be always taken into account. There can be some solutions which can decrease the degree of filtration, but it cannot be completely eliminated.

2 MATERIALS, METHODS

2.1 Materials used

As matrix materials aliphatic trifunctional glycerol (GER; MR3012, IPOX Chemicals Ltd., Budapest, Hungary; main component: triglycidyl ether of glycerol, viscosity 0.16-0.2 Pas at 25 °C, density 1.22 g/cm³ at 25 °C, epoxy equivalent 140-150 g/eq) and a tetrafunctional pentaerythritol-based (PER; MR3016, IPOX Chemicals Ltd., Budapest, Hungary; main component: tetraglycidyl ether of pentaerythritol, viscosity 0.9-1.2 Pas at 25 °C, density 1.24 g/cm³ at 25 °C, epoxy equivalent 156-170 g/eq) epoxy resin (EP) were applied. A cycloaliphatic amine MH3122 was used as a hardener (supplier: IPOX Chemicals Ltd., Budapest, Hungary; main component: 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane, amine hydrogen equivalent 60 g/eq, viscosity 80-120 mPas at 25 °C, density 0.944 g/cm³ at 25 °C). These aliphatic EPs have low enough viscosity to be processed by liquid composite moulding techniques even at high FR loadings, which is important in terms of up-scaling and automatization of composite production. Furthermore, these epoxy resins can be possibly produced from renewable sources, although they are presently synthesized on a mineral oil base; glycerol is accessible from natural fatty acids, while pentaerythritol can be prepared from bio-based methanol.

As flame retardants, we applied ammonium polyphosphate (APP) (supplier: Nordmann Rassmann, Hamburg, Germany, trade name: NORD-MIN JLS APP, P-content: 31-32%, average particle size: 15 µm) and resorcinol bis(diphenyl phosphate) (RDP) (supplier: ICL Industrial Products, Beer Sheva, Israel, trade name: Fyrolflex RDP, P-content: 10.7%). APP acts in the solid phase, while liquid RDP acts predominantly in the gas phase. The combination of these two phosphorus-based FRs proved to be synergistic in terms of fire retardancy in previous studies of the authors [7,8].

PX35FBUD030 unidirectional carbon fibre (CF; Panex35 50 k rovings, areal weight: 300 g/m²; supplier: Zoltek Zrt, Nyergesújfalu, Hungary) fabric was used as the reinforcement with a [0]₅ layout.

The chemical structures of the EP monomers and FR additives used can be seen in Figure 1.

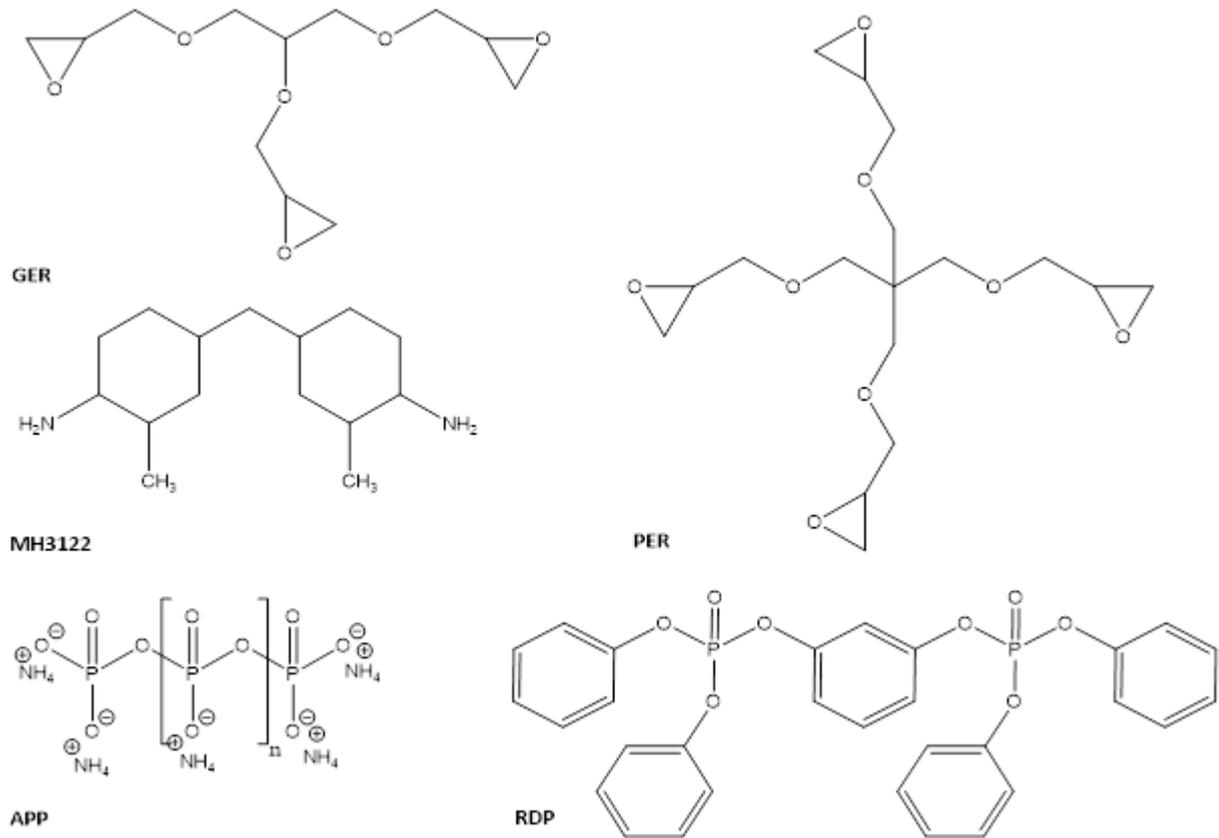


Figure 1: Chemical structures of the main components applied: triglycidyl ether of glycerol (GER), tetraglycidyl ether of pentaerythritol (PER), 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane (MH3122), ammonium polyphosphate (APP), resorcinol bis(diphenyl phosphate) (RDP)

2.2 Methods

2.2.1 Matrix sample preparation

During the preparation of the matrix specimens, the stoichiometric ratio (100:40) of the epoxy component and hardener was used both in case of GER and PER-based systems. We prepared EP samples with gradually increasing phosphorus (P) content (1%, 2%, 3%, 4%, 5%) from APP or from RDP in addition to mixed formulations with 2% P-content from APP and 2% P-content from RDP. Sample preparation started with the mixing of EP component and FR(s) (APP, RDP, or both). After that curing agent was added and they were mixed until the mixture was homogeneous. The samples were cured in appropriately sized silicon moulds. The curing procedure - based on DSC - consisted of two isothermal heat steps: 1 h at 80 °C, 1 h at 100 °C.

2.2.2 Composite sample preparation

Composite laminates were made both by hand lamination followed by hot pressing and by RTM. During hand lamination each carbon weave layer was separately impregnated. We compressed the prepared laminates with 200 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 (60±1 mass%). The heat treatment involved two heat steps: 1 h at 80 °C, followed by 1 h at 100 °C. During RTM method, flame retarded resin suspension (without hardener) was tempered at 60 °C for 15 minutes. After that, hardener was added to the resin suspension and homogenized. After the addition and homogenization of the hardener, resin

system was injected into the mould. Composite samples made by RTM were cured 24 h at room temperature. The fibre content of the composites made by RTM was 67 ± 1 mass%.

2.2.3 Rheology

The temperature dependence of the resin viscosity was determined by parallel plate rheometry with a TA Instruments AR2000 device (New Castle, DE, USA) in the range of 25-80 °C at 5 °C/min temperature ramp and at a shear rate of 0.1 1/s.

2.2.4 Differential Scanning Calorimetry (DSC)

The effect of FRs on the glass transition temperature (T_g) and crosslinking process was studied by differential scanning calorimetry in matrices with a TA Instruments Q2000 device (New Castle, DE, USA) in 50 mL/min nitrogen flow. The curing process of the samples was investigated with a three-step temperature program consisting of heat/cool/heat cycles. In the first cycle a linear ramp was used in the range of 25-250 °C with a heating rate of 3 °C/min. After that the sample was cooled down to 0 °C with a cooling rate of 50 °C/min, followed by a second linear heating ramp from 0-250 °C at a heating rate of 10 °C/min. Reaction enthalpy was determined from the first heating, while glass transition temperature values were determined from the second heating.

2.2.5 Thermogravimetric Analysis (TGA)

Thermal stability of the matrices was investigated with a TA Instruments Q500 device (New Castle, DE, USA) in 30 mL/min nitrogen flow. The samples were heated in the temperature range of 25-800 °C with a heating rate of 20 °C/min.

2.2.6 Characterization of fire behavior

Fire performance of the matrix and composite samples were investigated by limiting oxygen index (LOI) tests according to ASTM D2863. The LOI 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 x 15 mm x 2 mm in each case.

Standard UL-94 tests were carried out according to ASTM D3081 and ASTM D635 in order to classify the samples based on their flammability in horizontal and vertical test setups. The size of the samples was 120 mm x 15 mm x 2 mm. Increasing UL-94 values are the following: HB, V-2, V-1, V-0.

Mass loss type cone calorimetry (MLC) tests were performed with an instrument made by FTT Inc. (East Grinstead, UK) according to ISO 13927 standard. 100 mm x 100 mm x 2 mm samples were exposed to a constant heat flux of 50 kW/m² and ignited. Heat release values and mass reduction were recorded during burning.

2.2.7 Dynamic Mechanical Analysis (DMA)

DMA tests were performed in three-point bending setup with a TA Instruments TA Q800 device (New Castle, DE, USA) to investigate the dynamic mechanical properties and glass transition temperature of the composites. During measurements a temperature range of 25-200 °C with a heating rate of 3 °C/min was applied. The frequency was 1 Hz, while the amplitude was strain-controlled with 0.1% relative strain. The specimen size was 55 mm x 10 mm x 2 mm and the support span was 50 mm. The storage modulus (E') values at 25 °C and 75 °C and glass transition temperature from tan delta peaks were determined with the software of the instrument (TA Instruments Universal Analysis 2000 4.7A version).

2.2.8 Scanning Electron Microscopy-Energy Dispersive Spectrometry (SEM-EDS)

Composite samples were investigated under 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. We did a full mapping with energy dispersive spectrometry in 50x magnification. To avoid recharging, sample surfaces got a thin, conductive gold coating via sputtering.

3 RESULTS AND DISCUSSION

3.1 Preliminary screening of the flame retarded matrices based on LOI and UL-94 tests

To decide which FR epoxy matrix should be used for further investigation, EP samples of gradually increasing phosphorus content were prepared for preliminary screening of fire performance (Table 1).

<i>Matrix</i>	LOI (V/V%)	UL-94 (burning rate)	<i>Matrix</i>	LOI (V/V%)	UL-94 (burning rate)
GER	22	HB (27 mm/min)	PER	23	HB (32 mm/min)
GER 1%P APP	23	HB	PER 1%P APP	27	HB
GER 2%P APP	23	HB	PER 2%P APP	32	HB
GER 3%P APP	25	HB	PER 3%P APP	32	HB
GER 4%P APP	27	HB	PER 4%P APP	32	V-1
GER 5%P APP	28	HB	PER 5%P APP	32	V-0
GER 1%P RDP	24	HB (23 mm/min)	PER 1%P RDP	25	HB (15 mm/min)
GER 2%P RDP	26	HB	PER 2%P RDP	26	HB
GER 3%P RDP	26	HB	PER 3%P RDP	29	HB
GER 4%P RDP	29	V-1	PER 4%P RDP	32	V-0
GER 5%P RDP	30	V-0	PER 5%P RDP	32	V-0
GER 2%P APP 2%P RDP	28	V-0	PER 2%P APP 2%P RDP	31	V-0

Table 1: LOI values and UL-94 classification of reference and FR epoxy matrices

Both GER and PER reference epoxy resins had similar LOI and horizontal burning rate, but PER matrices reached better fire performance with the same FR-content. With increasing P-content, LOI values increased as well, as expected. Concerning the UL-94 classifications, increasing RDP-content led to significant improvement in both GER and PER epoxy resin matrices, while in case of APP only PER 5%P APP reached the self-extinguishing V-0 rate. Combined FR system (2%P APP 2%P RDP) reached the V-0 rate in both matrices as well. According to the results it can be stated that at least 4%P-content is necessary to reach appropriate flame retardancy in the matrix. 5% P-content resulted weak mechanical properties due to the softening effect of the large amount of FR incorporated. Because of the better fire performance, we used reference and flame retarded PER epoxy matrix in further investigations.

3.2 Viscosity of epoxy resins

Viscosity of epoxy resins and flame retarded epoxy systems is a reasonable property during liquid composite moulding technologies. According to the literature, the viscosity of these systems should be in the region of 100-300 mPas [9] even at high FR loadings to keep the resin system injectable. PER is a tetrafunctional epoxy resin contrary to the trifunctional GER, which means that PER has higher viscosity. Although these epoxy resins have lower glass transition temperature and mechanical performance in comparison to conventional epoxy resins for structural applications (e.g. diglycidyl ether of bisphenol A (DGEBA)), they might be injectable around room temperature according to our expectations (these systems are usually used as reactive diluents). FR loadings (especially in case of solid particles) may increase the viscosity of the resin system to that extent that this increased viscosity falls outside of the injectable viscosity region. To compensate this effect, resin or resin suspension temperature should be controlled: increasing temperature causes decreasing viscosity but shortens pot life as well. Viscosity of reference and flame retarded PER resin systems was investigated with

parallel plate rheology in the temperature range of 25-80 °C (from room temperature to the beginning of curing). Viscosities at different temperatures can be seen in Table 2.

<i>Matrix</i>	Viscosity [mPas]			
	25 °C	40 °C	60 °C	80 °C
PER	603	293	116	57
PER 4%P APP	1078	564	313	149
PER 4%P RDP	506	236	13	5
PER 2%P APP 2%P RDP	663	211	109	5

Table 2: Temperature dependence of the viscosity of PER matrix samples (viscosities suitable for LCM techniques are displayed with bold numbers)

Each resin system was injectable at 40 °C and above except PER 4%P APP (highest solid particle loading). Latter needs to be heated above 60 °C. These temperatures have a crucial importance in terms of up-scaling and automatization of composite structures production in the future.

3.3 Effect of FRs on the curing process and glass transition temperature of PER resins

Table 3 shows the temperature of exothermic peak, the reaction enthalpy and the glass transition temperature of the reference and flame retarded resin matrices in case of 4% P-content. To get a clear comparison of the effect of FR additives on the crosslinking process, reaction enthalpies related to the mass of epoxy resin matrix were compared. The results showed that the effect of both FRs is similar, and in case of combined FR system (both APP and RDP in the matrix) the decrease of relative reaction enthalpy was slightly smaller than in matrices containing only one FR. It can also be stated that FR additives had plasticizing effect which was more significant in case of liquid RDP. In mixed formulation, APP slightly compensated this effect resulting higher T_g than in case of 4%P RDP sample.

<i>Matrix</i>	$T_{ex,peak}$ [°C]	Reaction enthalpy		T_g [°C]
		J/g	J/g epoxy	
PER	93	378	378	114
PER 4%P APP	89	303	346	114
PER 4%P RDP	89	192	305	81
PER 2%P APP 2%P RDP	85	264	351	83

Table 3: Effect of FRs on the curing process and glass transition temperature of PER resins ($T_{ex,peak}$: temperature of exothermic peak; T_g : glass transition temperature)

3.4 Thermal stability of PER resins determined by TGA

RDP, acting mainly in the gas phase at the beginning of degradation, resulted in earlier thermal degradation and worse stability than in case of APP, acting in the solid phase at higher temperatures (Table 4). Mixed FR system had TGA results between the two samples containing only one FR. Besides, FR additives resulted in significant increase in char yield at 800 °C which is favourable in the aspect of thermal stability.

<i>Matrix</i>	T _{-5%} [°C]	T _{-50%} [°C]	dTG _{max} [%/°C]	T _{dTGmax} [°C]	Char yield at 800 °C [%]
PER	293	334	2.8	294	1.6
PER 4%P APP	288	342	1.0	314	12.5
PER 4%P RDP	273	328	1.0	296	13.8
PER 2%P APP 2%P RDP	280	333	1.0	292	15.0

Table 4: TGA results of reference and FR PER matrices (T_{-5%}: temperature at 5% mass loss; T_{-50%}: temperature at 50% mass loss; dTG_{max}: maximum mass loss rate; T_{dTGmax}: temperature belonging to maximum mass loss rate)

3.5 Dynamic mechanical properties of reference and flame retarded PER composites

As the previous chapters showed, the addition of FRs may influence the thermal properties and fire performance of epoxy resin matrices. Not surprisingly, composite structures made from these FR resin systems have different thermal and mechanical properties from the composites made using non-FR reference resins. However, the measurement methods are different; the glass transition temperature and dynamic mechanical properties (e.g. storage modulus) of composites can be determined by Dynamic Mechanical Analysis (DMA). Table 5 shows the T_g and storage modulus values (at 25 °C and 75 °C) of reference and flame retarded carbon fibre reinforced PER composites.

<i>Composite</i>	T _g [°C]	E'(25°C) [MPa]	E'(75°C) [MPa]
PER	69	85857	48002
PER 4%P APP	80	60935	39455
PER 4%P RDP	41	36146	7331
PER 2%P APP 2%P RDP	63	61416	21372

Table 5: Glass transition temperature (T_g) and storage modulus (E') values of reference and FR PER composites

The plasticizing effect of liquid RDP was underlined by the DMA results. This effect caused a significant decrease in glass transition temperature and storage modulus values as well (Table 5). The addition of APP to PER resin slightly increased the T_g and compensated the plasticizing effect of RDP in the composite made with both APP and RDP. However, it should be mentioned that PER reference composite has a T_g of 69 °C, hence it is not suitable for applications as structural elements anyway. These systems are more likely to find use as interior parts at this stage of the development.

3.6 Fire performance of PER composites

MLC results of 4%P-containing PER composites are listed in Table 6, while Fig. 2 shows the heat release rate of the composites. The reference PER sample had the lowest time to ignition (TTI) and residue after burning and the highest peak heat release rate (pHRR), total heat release (THR) and effective heat of combustion (EHC) as expected. The addition of 4%P FR decreased the pHRR and the THR, while the residues were higher than in case of the reference composite. The addition of RDP, acting predominantly in the gas phase, resulted in shorter TTI, because the gas phase action starts in the early phase of degradation, while PER 4%P APP sample ignited later. The combination of the two FRs had synergistic effect, leading to a further decrease in pHRR and THR than in case of PER composites containing only one FR.

<i>Composite</i>	TTI [s]	pHRR [kW/m ²]	Time to pHRR [s]	THR [MJ/m ²]	EHC [MJ/kg]	Residue [wt%]
PER reference	18	415	40	29.2	18.8	25.8
PER 4%P APP	24	272	45	20.5	13.4	32.6
PER 4%P RDP	20	235	46	19.3	13.6	34.8
PER 2%P APP 2%P RDP	23	218	45	18.2	10.8	31.0

Table 6: MLC results of 4%P-containing PER composites (TTI: time to ignition; pHRR: peak heat release rate; THR: total heat release; EHC: effective heat of combustion)

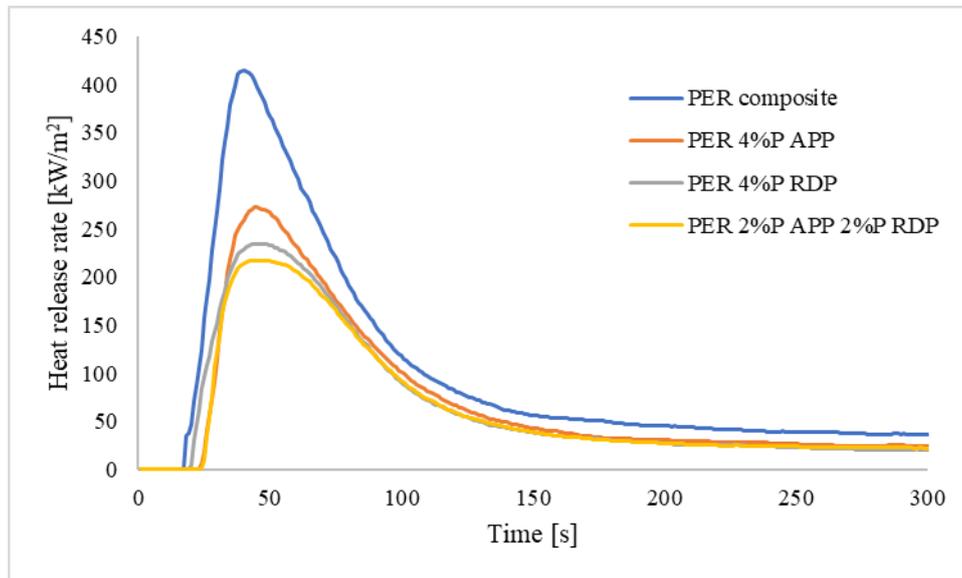


Figure 2: Heat release rate of 4%P-containing FR PER composites

3.7 Effect of particle filtration on the fire performance of PER composites

We also investigated the filtration of solid APP particles and the effect of their distribution on the fire performance of carbon fibre reinforced PER epoxy composites by mass loss calorimetry (MLC). For this purpose, composite specimens with overall 3% P-content in the matrix were made, as PER 3%P APP matrix had significant higher LOI (Table 1) and lower heat release (Fig. 3) than the PER reference and the other APP-containing compositions. At the same time, PER 3%P APP does not have such an overwhelmingly good fire performance (e.g. it has HB classification) which would make the evaluation of the effects caused by uneven APP particle distribution impossible.

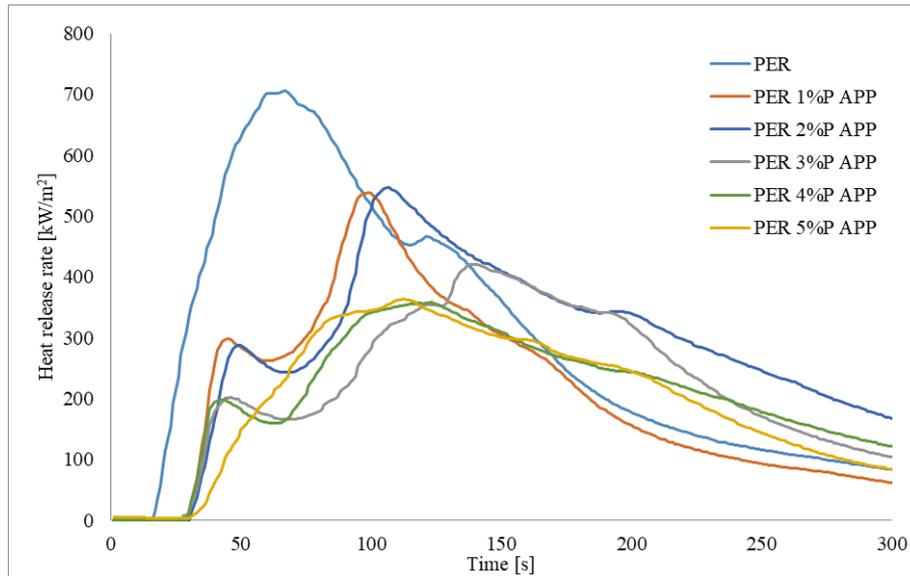


Figure 3: Heat release of APP containing PER epoxy matrices

Composite samples with 3% P-content were made both by hand lamination followed by hot pressing and by resin transfer moulding (RTM). A composite laminate containing different amount of phosphorus (1%, 2%, 3%, 4%, 5%) in each subsequent matrix layer was prepared by hand lamination followed by hot pressing to model particle filtration possibly occurring in the cross section of the composite during liquid composite moulding. The model composite sheets were measured from both side: one with the 1%P APP layer up, the other with the 5%P APP layer up (PER 1-5%P APP 1%P UP, and PER 1-5%P APP 5%P UP). The results are shown in Table 7 and on Fig. 4.

<i>Composite</i>	TTI [s]	pHRR [kW/m ²]	Time to pHRR [s]	THR [MJ/m ²]	EHC [MJ/kg]	Residue [wt%]
PER 3%P APP laminated	20	247	35	15.9	6.3	49.7
PER 3%P APP RTM	24	163	40	15.7	15.1	60.3
PER 1-5%P APP 1%P UP	22	221	41	18.9	13.8	41.1
PER 1-5%P APP 5%P UP	24	228	43	21.1	15.5	52.5

Table 7: Effect of particle filtration on the MLC results of flame retarded PER composites containing APP (TTI: time to ignition; pHRR: peak heat release rate; THR: total heat release; EHC: effective heat of combustion)

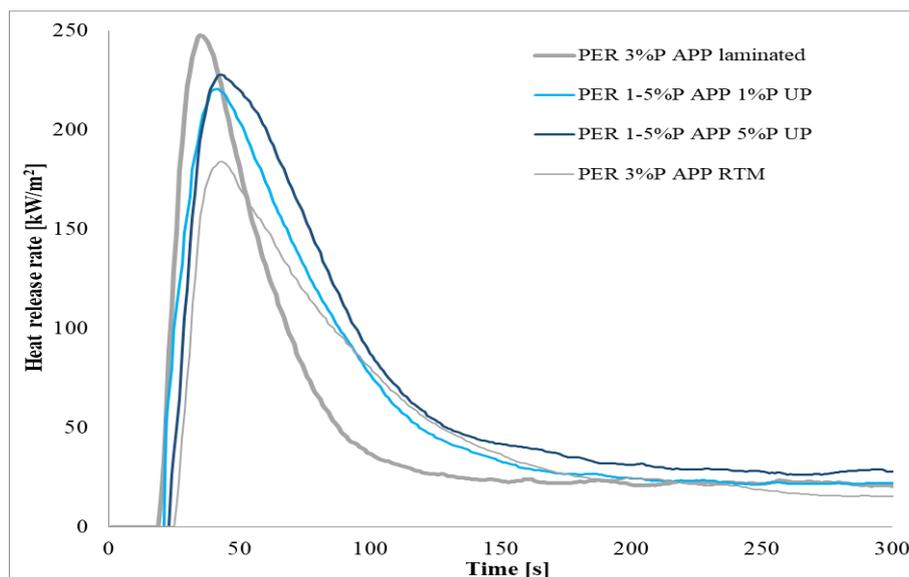


Figure 4: Effect of particle filtration on the fire performance of PER composites

When comparing the composites made by hand lamination followed by hot pressing and RTM, it is noticeable that the sample made by RTM had higher TTI and much lower peak heat release rate than the one made by hand lamination, though the time to pHRR remained the same. PHRR of the PER 3%P APP RTM sample decreased by ca. 35% comparing to the pHRR value of PER 3%P APP laminated, moreover its total heat release rate was also lower, and the residue reached ca. 60%.

As for the composite made with different amount of phosphorus in each subsequent layer, the results showed that it does not matter whether the composite laminate is ignited from the 1%P side or from the 5%P side. However, there was some difference in THR values and in the residue, these differences might come from the different sample mass.

In case of the laminated sample, there should be no particle filtration because of the manufacturing technology; an even particle distribution should be observed in the cross section. In case of PER 3%P APP sample made by RTM, particle filtration can occur (deep filtration is suspected), which leads to uneven distribution and fire performance as well. Fig 4 shows good agreement between theory and practice, however extensive conclusions cannot be drawn only based on MLC results. To prove the hypothesis, the particle distribution in the cross section of the composites was investigated by SEM-EDS method.

3.7 Investigation of particle filtration by SEM-EDS

To the extent of our knowledge, for the first time SEM-EDS method was successfully used to investigate the FR distribution in the cross section of carbon fibre reinforced epoxy composites. We did a full mapping in the cross section of the FR composites, searching for the most common elements in the matrices such as carbon (C), oxygen (O), nitrogen (N) and phosphorus (P). The SEM images and each map of the elements were merged into one image. Figure 5 shows the merged C- and P-maps.

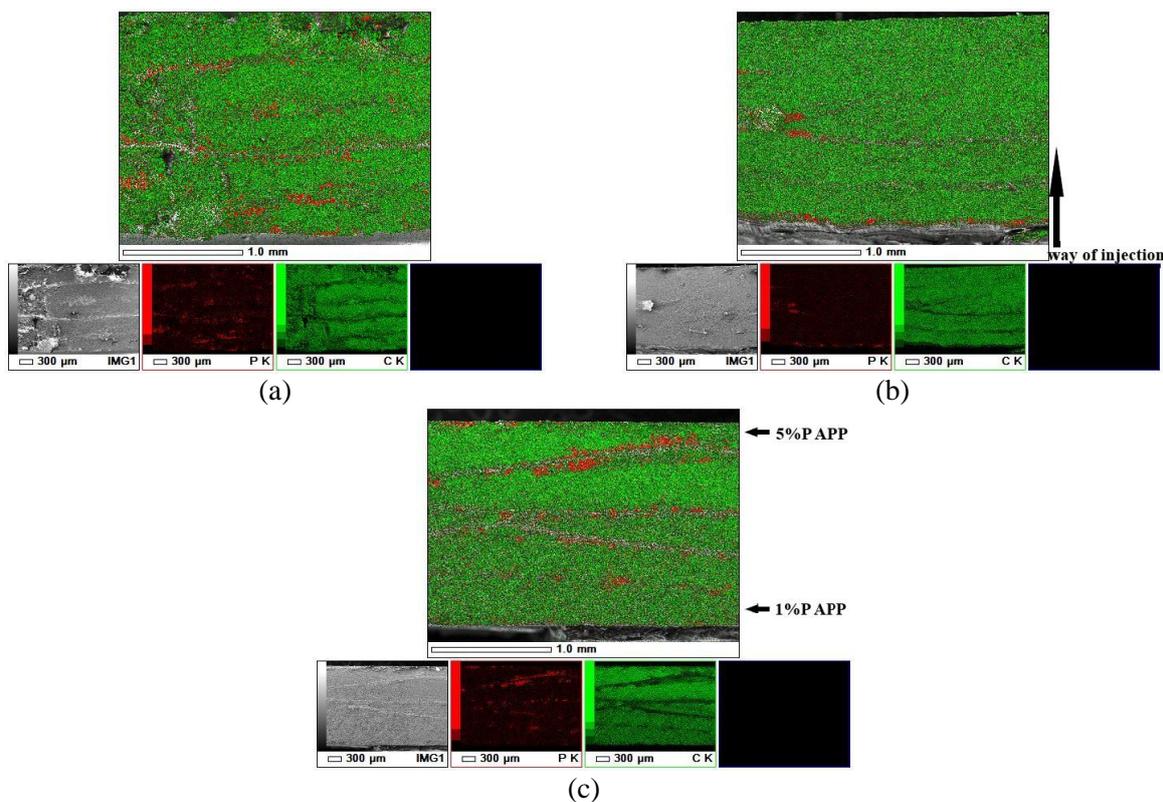


Figure 5: Distribution of phosphorus in the cross-section of the composites (red: P; green: C): (a) PER 3%P APP laminated, (b) PER 3%P APP RTM, (c) PER 1-5%P APP

In the SEM-EDS maps the detected signals of P (APP) are displayed in red, while signals of carbon (fibre reinforcement and epoxy) are displayed in green. The five UD carbon fibre layers can be easily observed in each map; as fibre reinforcement represents ca. 60% of the composites, green dots are in majority. In case of the sample made by hand lamination followed by hot pressing, C- and P-maps are complementary to each other; roughly equal number of APP particles is in each layer, no filtration occurred. In case of the sample made by RTM, an uneven distribution of P can be observed. Most of the P signals are gathered at the first layer of fibrous reinforcement and there are less and less particles with increasing filtration length. In PER 1-5%P APP, different amount of APP was laminated in each subsequent layer, which is easily observable on Fig. 5 (c). Although, the particle distribution was not the same in PER 3%P APP RTM and PER 1-5%P APP samples, the fire performance of the injected composite and of the one ignited from the 5%P side was close to each other. Presumably, in case of the sample made by RTM, the low heat release and high residue after burning can be explained by the high amount of APP on the surface caused by the filtration phenomenon, which was confirmed by SEM-EDS results.

4. CONCLUSIONS

We investigated the flame retardant particle distribution and its effect on the fire performance of carbon fibre reinforced epoxy resin composites made by liquid composite moulding techniques such as RTM. Fire performance was tested with mass loss calorimetry while the suspected solid particle filtration was proved by SEM-EDS method.

The preliminary flame retardancy results showed that although the inclusion of carbon fibres itself increased the limiting oxygen index (LOI) and peak heat release rate (pHRR), composite samples burned to the clamping during vertical UL-94 tests, probably due to the high thermal conductivity of the carbon fibres (candlewick effect). Comparing the two epoxy matrices (which are injectable and can be possibly produced from renewable sources, although they are presently synthesized on a mineral oil base), PER delivers better fire performance than GER with the same FR content. In both matrices the

combined solid and gas phase FR action proved to be favourable because of the synergistic effect of their application at the same time.

To the extent of our knowledge, for the first time SEM-EDS method was successfully used to investigate the filtration of solid flame retardants in the cross section of carbon fibre reinforced epoxy composites produced by liquid composite moulding. The composite sample prepared by RTM had much lower pHRR and higher amount of residue than the sample made by hand lamination followed by hot pressing due to the filtration of APP particles in the upper layers of the composite (Fig. 4). The fire performance of the composite made by RTM under MLC circumstances was closer to the performance of the model composite with the 5% P APP on the top, than the composite with the uniform APP distribution in the sample prepared by hand lamination followed by hot pressing.

When applying liquid composite moulding methods for the preparation of composites containing solid additives (e.g. flame retardants), particle filtration occurs, and it has to be taken into account as it affects the performance of the composite. If the solid additives contain heteroatom(s) different from ones present in the matrix, the extent of particle filtration in the cross section of fibre reinforced composites can be determined via SEM-EDS method, which makes the tailored design of these systems possible. If the particle filtration has to be eliminated, one possible solution is to use a liquid flame retardant in the matrix e.g. RDP, preferably acting mainly in the gas phase (to avoid delamination during combustion), and a flame retarded coating on the surface of the composite with a high phosphorus content FR, acting in solid phase e.g. APP (to form a highly porous intumescent char layer) to protect the composite part.

ACKNOWLEDGEMENTS

This research was supported by the Hungarian Scientific Research Fund (OTKA K 120592) and by the National Research, Development and Innovation Fund (2018-1.3.1-VKE-2018-00011). Á. Pomázi acknowledges the financial support received through the New National Excellence Program ÚNKP-18-3-I of the Ministry of Human Resources. A. Toldy acknowledges the financial support received through János Bolyai Scholarship of the Hungarian Academy of Sciences.

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