Development of advanced fire-retarded composite materials for engineering application

NKFIH K 120592 final report

01/12/2016 - 30/11/2020

1. Introduction

The importance of high-performance fibre reinforced polymer composites, in particular **carbon fibre reinforced epoxy resin composites** is significantly growing due to their beneficial properties. Epoxy resins are widely applied as adhesives, surface coatings, laminates, encapsulation material in electronic industry, matrix material in transport and aerospace industries due to their excellent characteristics. However, the **limited fire resistance of epoxy resins** reduces the application fields of composites made thereof. The aim of current research was the development of **high-performance flame retarded composites**, which could be used in special engineering fields including high-tech sectors as electronic, transport and aerospace industries.

Currently, the flame retardancy of epoxy resin composites by **solid-phase flame retardants** raises many issues, as solid additives **can be filtered out** during from matrix **during processing**, therefore the morphological and mechanical **properties will be inhomogeneous**. Therefore, in the present project application of solid and liquid flame retardants was investigated using **different composite processing technologies.** The influence of these additives on flame retardancy, as well as their **homogeneity** in polymer composites was investigated in order to **ensure consistent mechanical performance and fire resistance**. We aimed at determining the **optimal material compositions and manufacturing parameters** that allow for the **reproducible, scaled-up production** of these high-performance composite structures.

2. Results

2.1 Fire performance screening of epoxy resins and composites made thereof

First of all, a **literature review**, focusing on epoxy resin composites' processing technologies and industrial application areas as well as flame retardancy opportunities, was carried out. Then the necessary additive and reactive flame retardants, low viscosity epoxy resins and carbon fibre reinforcing materials were acquired, and finally, flame retarded epoxy resin matrix and composite specimens were prepared and extensively tested in order to **determine the optimal quantity of flame retardant additives**.

First, we investigated a **glycerol based epoxy resin** (**GER**; with an amine type hardener), which can be potentially produced from renewable resources as well. Two **phosphorus based flame retardants** were applied: ammonium polyphosphate (APP; solid particles) and resorcinol bis(diphenyl phosphate) (RDP; liquid). We produced neat reference and flame retarded samples with different phosphorus contents. First, the **viscosity** of the different resin systems was investigated with a rheometer. The chosen epoxy resin has an RTM compatible viscosity (100-

300 mPas) even with the addition of flame retardants. The **curing process** of the epoxy resins with and without additive flame retardants was examined using differential scanning calorimetry (DSC). According to the DSC results, both flame retardants decreased the glass transition temperature, as expected. From this point of view, the application of APP was more favourable, than of RDP, as due to its higher phosphorus-content less amount of APP is needed to reach the same ratio of phosphorus in the epoxy resin matrix. We investigated the **thermal stability** of these systems using thermogravimetric analysis (TGA). The GER-APP system had a relatively high, while the GER-RDP system a low maximum mass loss rate. A synergistic effect could be observed when both APP and RDP were applied. In the followings, the **flame retardancy** of the resin samples was investigated using limited oxygen index (LOI) and standard UL-94 measurements. The addition of the flame retardants increased the LOI, which is favourable in terms of flame retardancy, however it should be mentioned that only the mixed flame retardant system, containing both APP (acting in the solid phase) and RDP (acting mainly in the gas phase) could reach the self-extinguishing V-0 UL-94 classification. To describe the **complex properties of combustion** mass loss type cone calorimetry (MLC) measurements were carried out as well. We found that time to ignition (TTI) and peak heat release rate (pHRR) decreased with the addition of flame retardants, while the mass residue increased. Again, the **synergistic effect of the combination of flame retardants acting in gas and solid phase** was demonstrated. Based on the influence of fire retardants on fire performance and glass transition temperature the **optimal quantity of flame retardant additives was determined**.

After the experiments with the flame retarded epoxy resins matrices, reference and flame retarded **composites were prepared** using five layers of unidirectional (UD) carbon fibre reinforcement. These composites were prepared by hand lamination accomplished by hot-pressing method in order to reach high carbon fibre content (approximately 60%). The composites were investigated using the following techniques: LOI, UL-94, MLC, dynamic mechanical analysis (DMA), tensile test, three-point bending test, Charpy impact test. The **LOI and UL-94** measurements showed that the oxygen index of the flame retarded composites increased in comparison with the reference composite, furthermore the reference composite itself had higher LOI than the neat resin due to the incorporation of high amount of carbon fibre reinforcement (incombustible under the circumstances applied measurements). However, due to the high thermal conductivity of the carbon fibres, the composites reached only HB classification during the UL-94 test (this phenomenon is addressed as “candlewick effect”). According to the **cone calorimetry** test results, it can be stated that time to ignition was almost twice as much as in the case of resin samples in all composites. The peak heat release rate was much lower and the mass residue after the measurement was much higher in comparison with the resin systems. The explanation of this phenomenon is that there is proportionally less flammable material in the composite because of the high fibre content (approximately 60%). Comparing the peak heat release rate of the composite samples, it can be stated, that effect of flame retardants was less pronounced than in the case of the epoxy resin matrix samples. The reason for this is that the incorporated carbon fibres interfere in the mode of action of solid-phase flame retardants by hindering the formation of a protective charred layer (addressed as intumescent phenomenon). The **glass transition temperatures** of the composite samples were determined by **dynamic mechanical analysis**. The trend between glass transition temperatures was similar to the resin samples' glass transition temperatures, although it should be noted that glass transition temperatures from DSC and DMA measurements should not be compared because of the difference between the two methods. The lowest glass transition temperature could be observed in the case of the GER 4%P RDP sample (in both measurements), because the liquid RDP has a significant softening effect. This effect could be observed in the **mechanical properties** as well. The tensile modulus and the tensile strength of this sample were the lowest, while the Charpy impact strength was the highest accordingly. The three point-bending strength followed the same tendency. The suspected synergistic effect between the two phosphorus-containing flame retardants was investigated in the case of the mechanical properties as well.

We also investigated the flame retardancy of a **low viscosity tetrafunctional, pentaerythritol (PER)-based EP** as well, applying **ammonium polyphosphate (APP)**, acting in the solid phase, **resorcinol bis(diphenyl phosphate) (RDP)**, acting predominantly in the gas phase, and their combination. We expected better fire performance and mechanical properties applying the tetrafunctional epoxy resin. For **preliminary fire performance screening**, we prepared samples of gradually increasing phosphorus content (1%, 2%, 3%, 4%, and 5%) and mixed formulations with 2% P content from APP and 2% P content from RDP. Our results showed that at least 4% P content is necessary for a reasonable improvement in FR performance; the best overall results at this P content were achieved with GER 2% P APP 2% P RDP (limiting oxygen index (LOI) 28 V/V%, V-0 rate based on UL-94 standard), PER 4% P RDP (LOI 32 V/V%, V-0) and PER 2% P APP 2% P RDP (LOI 31 V/V%, V-0). Although the GER-based and the PER-based reference EP matrices have a similar initial limited oxygen index and horizontal burning rate, it is evident that with the same FR-content, **PER delivers better fire performance**. After the preliminary fire performance screening we analysed the compositions with 4% P content in detail. **Parallel plate rheology investigations** proved that all flame retarded systems are injectable at a temperature as low as 40 °C, except for the PER 4% P APP composition, which needs to be heated above 60 °C; this means that composites can be easily prepared by RTM and similar injection techniques. The **differential scanning calorimetry (DSC)** results of the EP matrices show that the plasticizing effect is more pronounced in the case of liquid RDP, and in the combined FR samples, APP slightly compensated for the softening effect of RDP. The reaction enthalpies related to the mass of the epoxy resin matrix indicated that the effects of APP and RDP are similar, and in mixed FR samples, the initiated decrease was slightly smaller than in the systems containing only one FR. The **thermogravimetric analysis (TGA)** results showed that RDP, acting mainly in the gas phase at the beginning of degradation, shifts the beginning of thermal degradation to lower temperatures. The initial maximum mass loss rate of GER is much higher than that of PER, which is consistent with the LOI results of these matrices. The FRs increase the amount of solid residues at 800 °C in the following order: 4% P APP < 4% P RDP < 2% P APP 2% P RDP, suggesting that the combination of these two FRs is advantageous in terms of thermal stability as well. The **mass loss calorimetry results** indicate that the trifunctional GER has approx. 1.5 times higher peak heat release rate (pHRR) than the tetrafunctional PER, which is in good agreement with the LOI results. In GER a clear synergistic effect was observed, in terms of pHRR and time to ignition (TTI) when APP and RDP were applied together, while in PER the

4% P APP sample had the lowest peak heat release rate followed closely by the mixed sample. Both in PER and GER the mixed FR systems had the lowest total heat release (THR) value.

2.2 Up-scaled composite production and testing

According to parallel plate rheology tests carried out the developed flame retarded epoxy resin systems are injectable only if the temperature is above room temperature (e.g.: 40-60 °C). Therefore, we designed and manufactured differently shaped**, temperable injection tools** with the mill machine purchased in the frame of the project.

The final version of the temperable mould is a sectionable tool with a glass upper part to follow the resin flow during injection. Pressure can be measured both before the inlet and after the outlet, so that we can determine the pressure difference occurring in the manufacturing process. There is also a possibility to measure and control the resin flow before the inlet (**Figure 1**).

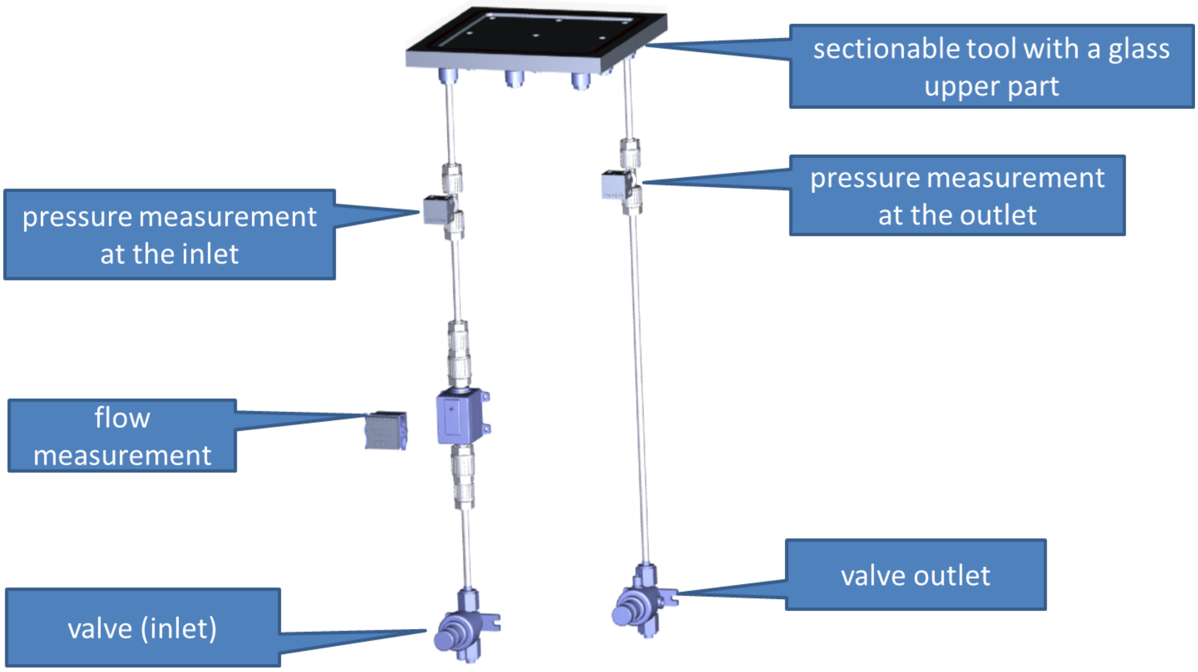
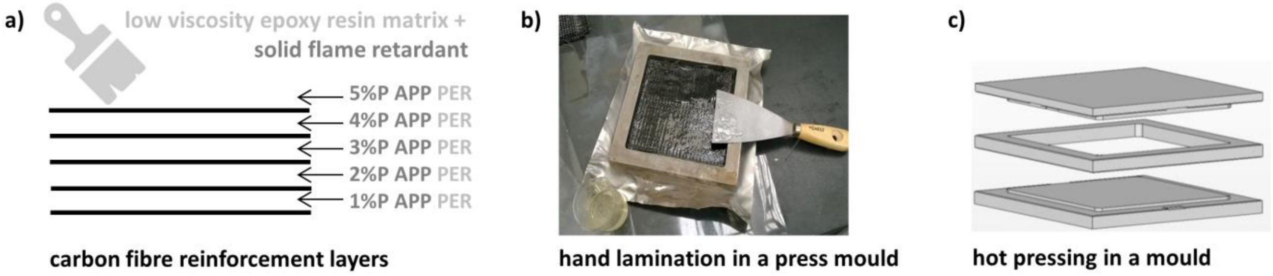


Figure 1. Temperable injection mould

In agreement with the research plan, **composite samples were manufactured with different processing technologies**. We prepared carbon fibre-reinforced reference and flame-retarded (FR) epoxy composite sheets by hand lamination followed by hot pressing (also known as **wet compression moulding**), and by **resin transfer moulding (RTM)**. Based on fire performance screening and mechanical testing carried out in the second year of the project, in all flame retarded composites the matrix had 3% total phosphorus (P) content from ammonium polyphosphate (APP). This APP concentration provided a good balance of reasonable fire performance and appropriate mechanical properties, furthermore, the same FR content facilitated the evaluation of the effect of processing technologies on the fire performance. We also prepared composite sheets containing different amount of P (1%, 2%, 3%, 4%, 5%) in each subsequent matrix layer by wet compression moulding in order to **model the particle filtration** of the flame retardant during liquid composite moulding techniques (**Figure 2.**). The fire performance of the composites was investigated by limited oxygen index (LOI), UL-94 and mass loss calorimetry (MLC) tests, while the extent of particle filtration was evaluated by scanning electron microscopy with energy dispersive spectrometry (SEM-EDS).



carbon fibre reinforcement layers

hand lamination in a press mould

hot pressing in a mould

Figure 2. The preparation of the model composite: (a) composition of the matrix layers in the model composite (b) hand lamination in a press mould (c) hot pressing in a mould

According to our results the composite **sample prepared by RTM had much lower peak heat release rate (pHRR)** and higher amount of residue than the sample made by wet compression moulding due to the filtration of APP particles in the upper layers of the 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 RTM), as increasing the ratio of carbon fibres reduces the amount of the highly burnable epoxy resin matrix. 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. The increased intumescence and the 24% more residue in the case of the flame-retarded composite produced by RTM suggest that the solid APP accumulated on the surface of the composite during RTM due to the so-called “deep filtration” mechanism.

2.3 Evaluation of particle filtration during composite processing

Liquid composite moulding (LCM) techniques (e.g. resin transfer moulding (RTM), vacuum infusion) are commonly used for the production of high-performance fibre-reinforced polymer composites. Its advantages over hand lamination (high productivity at a lower cost, increased fibre-to-resin ratio, controlled dimensional tolerances providing outstanding reproducibility) allow its use in the production of structural components for the automotive and aircraft industries. In numerous application areas, the addition of fillers is necessary to enhance some properties of the polymer matrix or provide it with additional properties, such as flame retardancy. As many of the applied additives are solid phase, the reinforcement layers may filter the solid phase additive particles during LCM, resulting in a non-uniform distribution and uneven performance. Consequently, the proper distribution of the solid phase additives in composites is of key importance. In order to facilitate the production of flame retarded structural composites by LCM in cases where the required fire performance can only be achieved with solid additives, the parameters influencing the particle distribution, along with the models describing it were reviewed. Analytical methods for determining the particle distribution in composites manufactured by LCM were summarized and the possible solutions to improve the particle distribution of solid-phase additives were outlined as well in the frame of a review article.

We prepared **carbon fibre reinforced reference and FR composite** sheets with hand lamination in a press mould (wet compression moulding) and vacuum infusion technique (**Figure 3.**). With these two preparation technique our aim was to **compare the possible particle filtration** in the samples.

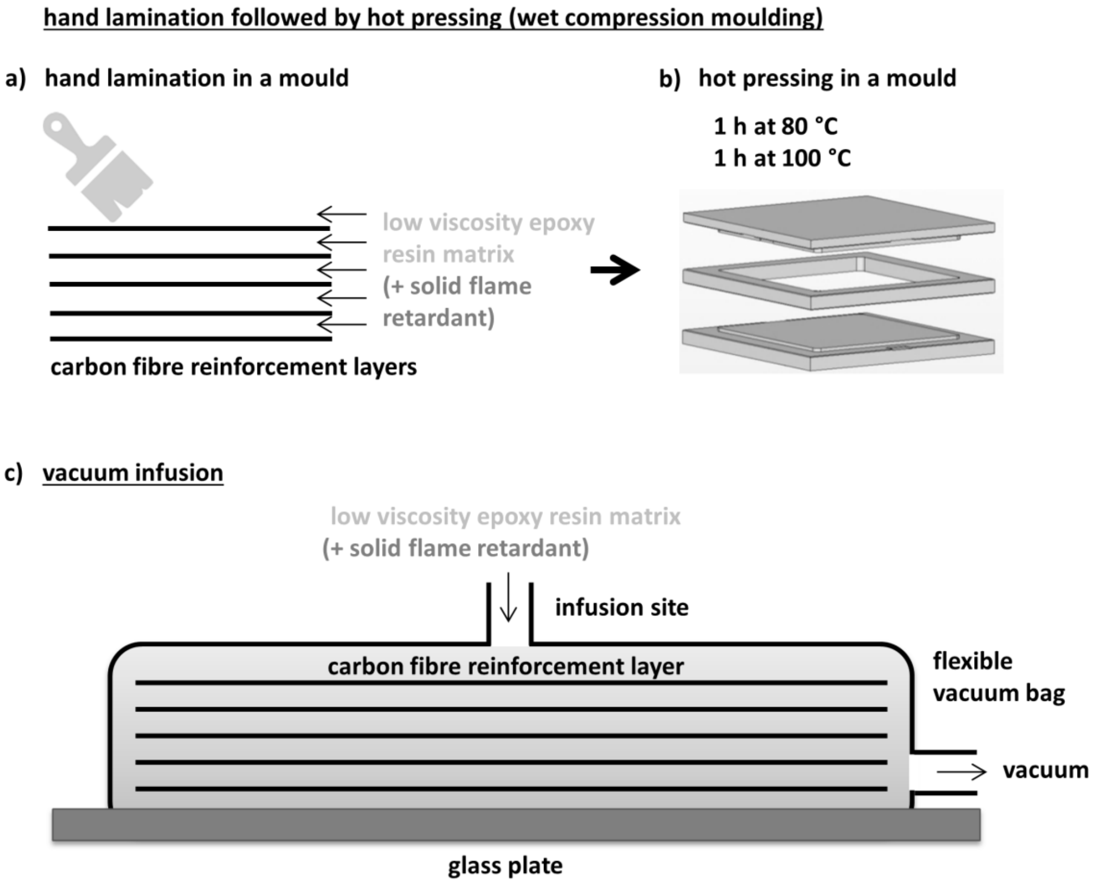
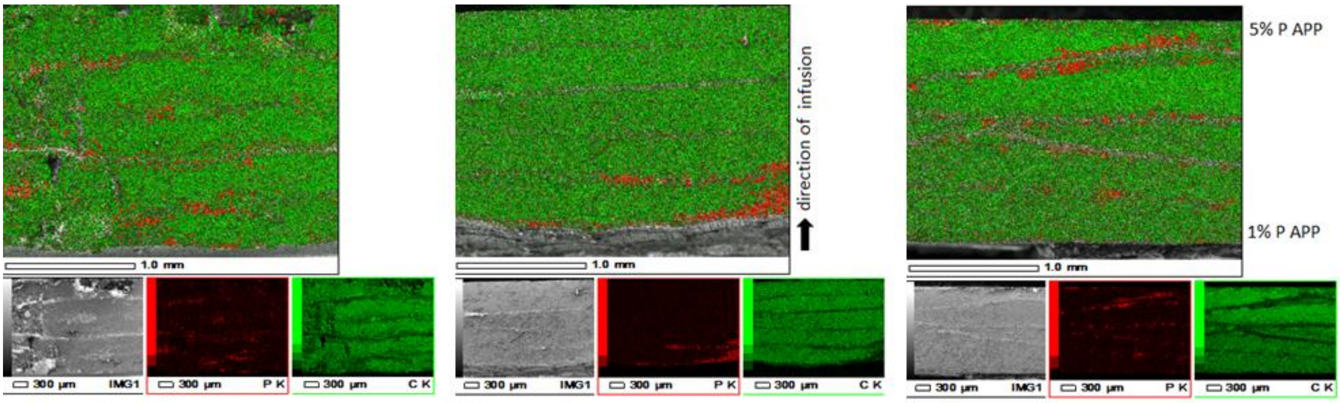


Figure 3. Composite processing methods: wet compression moulding (consisting of (a) hand lamination in a press mould and (b) hot pressing in a mould) and (c) vacuum infusion

Prior to testing, the **analytical methods for the determination of the extent of particle filtration** were reviewed in order to choose an appropriate method to characterize the filtration of flame retardants during resin transfer moulding of composite samples. Optical microscopy, transmission electron microscopy (TEM), and scanning electron microscopy (SEM) are usually used, often with a combination of wavelength dispersive spectrometry (WDS), energy dispersive spectrometry (EDS) or electron probe microanalysis (EPMA). With the above methods, both qualitative and quantitative analysis is possible. Fully cured composite parts can be investigated with other techniques as well, such as the so-called “burn-off” technique (which is an adaptation of the conventional matrix burn-off), confocal fluorescence microscopy, X-ray computed tomography (X-ray CT), or confocal Raman imaging (CRI). After the literature review, first we attempted to evaluate the filtration of the solid flame retardant by **Raman mapping method**. However, due to the fluorescence caused by the carbon fibres the obtained Raman spectra could not be evaluated. Therefore, in the followings, the **particle filtration was**

investigated by SEM-EDS on the cross section of carbon fibre reinforced epoxy resin composites flame retarded with phosphorus-containing solid ammonium polyphosphate (APP). The results showed a quasi-uniform particle distribution in the cross section of the flame retarded composites made by wet compression moulding; the APP particles occurred mainly in the resin-rich regions between the reinforcing layers. In case of the composite samples made by vacuum infusion, a non-uniform particle distribution could be observed: the particles were gathered at the inlet, and their concentration decreased with a higher filtration length. **We proved the suspected filtration of APP** in the infused flame-retarded composite with SEM-EDS analysis of the whole cross-section of the composite. Based on the SEM-EDS elemental maps, in the infused composite, APP accumulated in the first and second epoxy resin-rich layers from the injection site, while in the subsequent layers the presence of APP was negligible (**Figure 4.**). In the model composite with gradually increasing APP-content in each matrix layer the gradient of the P-content was also proven by this method.



(a) PER 3%P APP laminated

(b) PER 3%P APP infused

(c) PER 1-5% P APP

Figure 4. 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

This phenomenon is called "deep filtration" according to the literature (**Figure 5.**). To the extent of our knowledge, **this is the first time that SEM-EDS** combined method was successfully **applied to determine the filtration of solid flame retardants** in carbon fibre reinforced epoxy resin composites produced by liquid moulding processes.

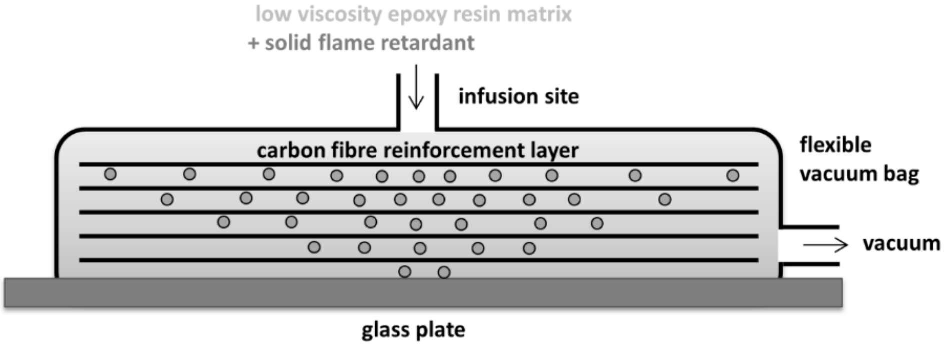


Figure 5. The suspected "deep filtration" scenario of solid flame retardants during vacuum infusion

2.4 Development of flame retarded gelcoats

Although there are attempts **to avoid filtration** (e.g. the application of a thermoplastic carrier for particles), the filtration of solid particles during composite preparation technologies based on injection presents a challenge to be solved, therefore we also overviewed the possibilities to **apply the flame retardants in a separate layer on the composite**. We focused on epoxy based and/or epoxy compatible reference and flame retardant (FR) gelcoats/topcoats and their application in the composite industry. Processing methods of gelcoats e.g. painting, brushing, rolling etc., besides other new methods - such as in-mould gelcoating (IMGC) or in-mould surfacing (IMS) – were reviewed as well.

During **liquid composite moulding processes**, a liquid resin is injected into a preform consisting of fibre reinforcement and then cured, therefore the phase of the additive and its effect on the viscosity of the matrix plays an important role. If the applied additive is solid-phased, it can be filtered by the reinforcement during the injection phase, which causes a **non-uniform particle distribution and an uneven performance**. To avoid this phenomenon, liquid-phase additives can be applied, as they can be more easily integrated into the injection process. In the case of flame retardants, besides particle filtration, the **fibre reinforcement layers also interfere in the solid phase action of the flame retardants by hindering the formation of an intumescent char** on the surface of the composite. Furthermore, even this hindered charring is sufficient to delaminate the composite layers, leading to a catastrophic loss of the post-fire mechanical properties. An obvious solution to overcome all these issues related to the application of additives in composites produced by liquid transfer moulding is either to **use liquid, non-intumescent flame retardant in the composite matrix**, acting mainly in the gas phase, such as resorcinol bis(diphenyl phosphate) (RDP), or to **apply the necessary additives in a separate layer on the surface of the composite**, although this would include an additional processing step. As in many application areas, gelcoats are used anyway to reach the required surface properties, a logical progression in the composite industry is the **development of multifunctional gelcoats**. We published a review article in an impact factor journal about the findings of this area.

We studied the possibilities of applying the flame retardants in a separate layer on the composite: we acquired a benchmark reference and flame retarded epoxy resin-based gelcoats, and developed our **own intumescent flame retarded gelcoat formulations** with 5, 10 and 15% P-content from APP. The crosslinking of the gelcoats was proved by DSC, while thermal stability was compared by TGA method. The fire performance of the gelcoats itself was compared by limiting oxygen index (LOI), UL-94 and mass loss calorimetry (MLC) tests. Based on the results, the additives did not affect the crosslinking process significantly. The thermal stability and fire performance of the own formulation with 10% P content were in the same range as in the case of the benchmark flame retardant gelcoat, while the developed new formulation with 15% P content overperformed the benchmark in most cases, therefore it is a **potentially patentable solution**.

We prepared, tested and compared the different FR and non-FR gelcoats both on reference and FR composite sheets prepared by wet compression moulding and RTM. **Figure 6** shows the preparation method of the coated composites made by **wet compression moulding**, while one of the composite sheets made by **RTM** can be seen on **Figure 7** (during demoulding from the RTM machine and before the coating process). The applied **RTM parameters** were based on the earlier **rheology and mould filling investigations**, while **material combinations** were based on previous fire retardancy and mechanical testing results. We applied the gelcoats on the surface by brushing with a thickness of 0.5 and 1.0 mm.

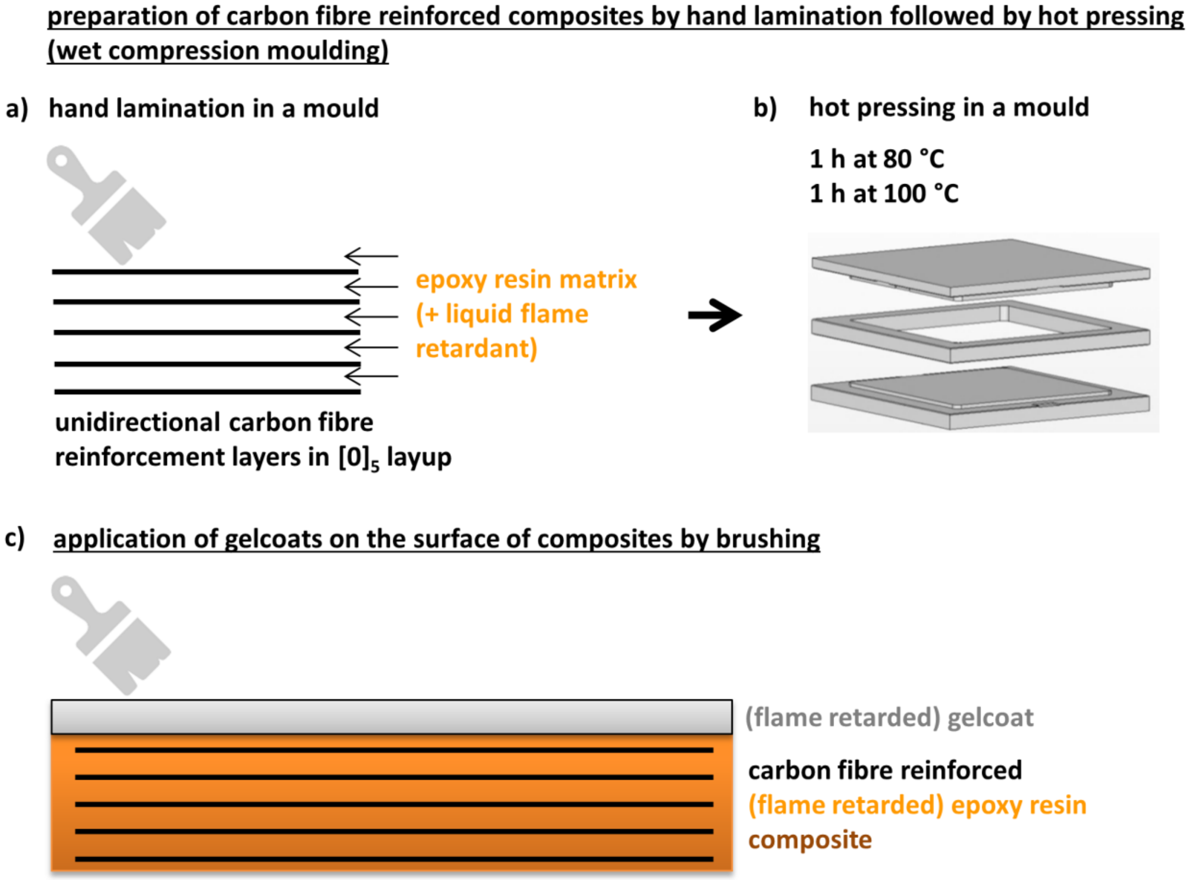


Figure 6. The preparation of coated composite samples by wet compression moulding (consisting of (a) hand lamination in a press mould and (b) hot pressing in a mould) and (c) application of gelcoats by brushing

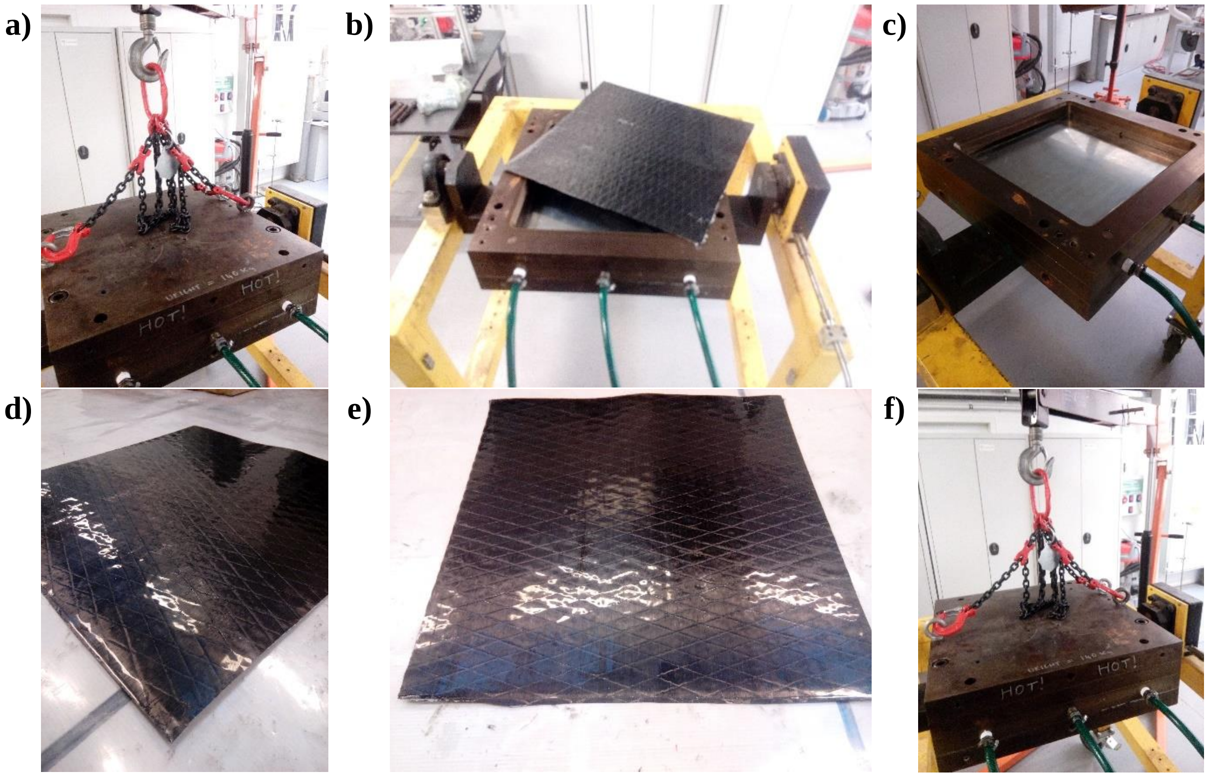


Figure 7. Demoulding process of fibre reinforced composite sheet made by RTM (a) mould opening; (b) removal of the composite sheet from the mould; (c) cleaning of the mould/preparing for the next cycle; (d) and (e) composite sheet made by RTM/deburring process (if necessary); (f) closed mould ready for the next production cycle

According to the **mass loss calorimetry** results of the coated samples made by wet compression moulding, 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, which was further decreased with the addition of RDP to the composite matrix. Among the composites coated with a 0.5 mm thick gelcoat, the **lowest pHRR** was reached by the **FR composite coated with the gelcoat containing 15% P APP**.

The 1.0 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 1.0 mm thick gelcoat containing 15% P APP without FR in the matrix had the same pHRR 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 APP had the lowest pHRR**, 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 1.0 mm thick non-FR gelcoat**, respectively.

We found that 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. With the application of liquid FR additives, the particle filtration can be avoided, although their use in the matrix is not always necessary.

3. Summary

The aim of this research was the development of **high-performance, carbon fibre reinforced flame retarded epoxy composites** for high-tech engineering applications (e.g. in the electronic, transport and aerospace industries). We determined the **optimal material compositions** and **processing parameters** in order to ensure the **reproducible, up-scaled manufacturing** of these composites. We eliminated the filtration of the applied solid-phase flame retardants by the reinforcement during these up-scaled composite manufacturing technologies (e.g. vacuum infusion, resin transfer moulding (RTM)) with a **liquid flame retardant in the matrix**, which provided consistent mechanical properties and fire performance. We also applied a gelcoat containing solid flame retardants on the surface of the composite, which at the same time provided appropriate surface quality. The composition of the developed **flame retardant gelcoat** is a potentially patentable result in the future.

4. Dissemination

The results related to the project were published in scientific journals and conferences, while the involvement of university students resulted in BSc, MSc and PhD theses.
Main achievements for the project duration (01/12/2016 - 30/11/2020) are summarized below:

- **number of conference proceedings: 8,**
- **number of scientific articles: 24,**
- **number of scientific articles with impact factor: 21,**
- **total impact factor: 84.28,**
- **number of PhD theses: 1 (2 in progress).**