

## **FIRE RETARDANCY OF STRUCTURAL CARBON FIBER REINFORCED COMPOSITES USING THERMOPLASTIC INTERLAYERS**

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**Keywords:** CFRP, multi-layer laminate, flame retardancy, thermoplastic interlayers

### **Abstract**

*Carbon fiber reinforced composites have become more and more relevant in the aeronautic transportation sector because of their high specific mechanical properties. One drawback of this material is the behavior in case of fire. Most flame retardants reduce the mechanical properties, add additional weight or make the processing difficult. The aim of this study is the improvement of the Fire-Smoke-Toxicity Properties of structural carbon fiber reinforced epoxy composites using thermoplastic interleaves in multi-layered laminates without a decrease in the specific mechanical properties.*

### **1 Introduction**

The growing interest in carbon fiber reinforced polymers (CFRP) in light weight constructions is caused by their high specific mechanical properties which makes CFRPs an important construction material in the transportation industry, especially in the aeronautic sector.

Epoxy resins are one of the most common thermoset matrices in CFRPs in the aeronautic sector because of their specific mechanical properties, hot-wet properties, dimensional stability and chemical resistance [1,2]. The main problem of these CFRPs is their behavior during fire [3]. In addition to the use of alternative resins or modifying the chemical formulation of the epoxy resins, flame retardants are added to the resin to improve the Fire-Smoke-Toxicity (FST) properties of the composite.

However, many common flame retardants, which contain for example phosphorous flame retardants, release toxic decomposition products [4], which are undesired in transportation of passengers. Also effective halogenated flame retardants are not allowed since 2006 because of their toxic combustion products [5].

The modification of the matrix for example by inorganic fillers or hybrid materials can additionally increase the brittleness of the matrix, which leads to a drop in the mechanical properties. Modifying the matrix usually also increases the viscosity of the resin, which is sometimes intended for the fire retardancy mechanism [6], but mostly makes the processing

more difficult or impossible. Furthermore, there can be filtering effects by the carbon fibers, which lead to an inhomogeneous distribution and re-agglomeration.

Another approach in fire protection is an additional surface layer of the composite [4], which protects in case of fire the composite by expansion, intumescence or carbonization. However, this leads to additional, nonload-carrying weight. Furthermore such layers are sensible to damage, scratches and erosion.

Another disadvantage of many epoxy based CFRP is the brittle matrix and the low impact tolerance.

The idea presented in this article is that the thermoplastic interlayers act as load carrying layers which increase the toughness and impact tolerance on the one hand and act as barrier/expansion layers on the other hand which protect the bulk composite below the multi-layers in case of fire.

## 2 Experimental

### 2.1 Materials

Biaxial non-crimp fabrics (NCF) with a thickness of 250  $\mu\text{m}$  were used as reinforcement in a two component epoxy matrix.

Polyetherimide (PEI) was chosen as thermoplastic interlayer because of its high temperature properties and its processability. Former studies also showed a good compatibility of the PEI with the epoxy matrix. Another reason for PEI is the common use of PEI as toughness modifier for epoxy resins.

The thickness of the thermoplastic foils was 125  $\mu\text{m}$ .

### 2.2 Manufacturing of the composites

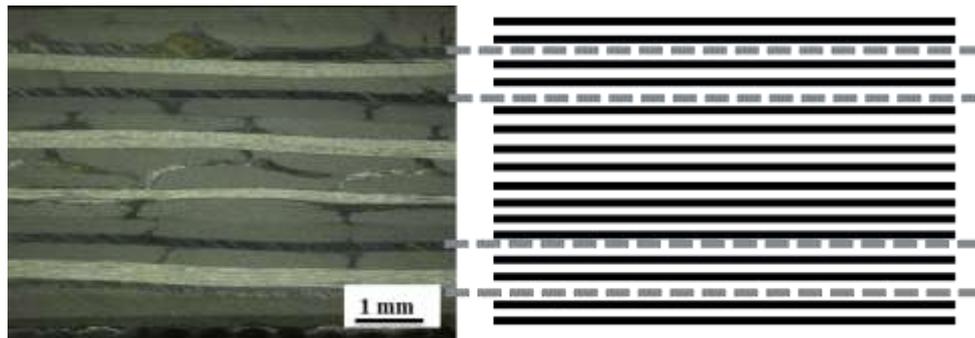
The composites were manufactured using Vacuum Assisted Processing.

For manufacturing of the reference specimens for cone calorimetry, eight biaxial NCFs were stacked to a quasi-isotropic, symmetric preform following  $[(+/-45)(90/0)]_2s$ . This results in a thickness of the final composite of 4 mm.

For manufacturing the multi-layered laminates (MLLs), the thermoplastic foils were perforated to allow the entire evacuation and infiltration of the preform during the infusion process and were placed between the first and the second and the second and the third biaxial NCF and symmetrical between the sixth, seventh and eighth biaxial NCF as showed in Equation 1 and illustrated in Figure 1 on the right.

$$[(+/-45)PEI(90/0)PEI(+/-45)(90/0)]_s \quad (1)$$

In Figure 1 on the left a cross section of a quasi-isotropic multi-layered laminate is shown. The overlap to the schematic lay-up of the preform on the right shows where the TP interlayers are located in the cross section.



**Figure 1.** Right: Cross section of a quasi-isotropic multi-layered laminate; right: schematic lay-up of the quasi-isotropic non-crimp fabrics (black continuous) with the thermoplastic interlayers (gray dashed).

For the interlaminar fracture toughness testing the lay-up was [(90/0)]3s and for interlaminar shear strength [(90/0)]2s. This results in a thickness of the specimens for the interlaminar fracture toughness testing of 3 mm and for the testing of the interlaminar shear strength of 2 mm.

The preform lay-up with the thermoplastic interlayers for the interlaminar fracture toughness testing is shown in Figure 2 on the left, the lay-up for interlaminar shear strength testing on the right.



**Figure 2.** Lay-up of the specimens for interlaminar shear strength and interlaminar fracture toughness testing.

The preforms were infused with a two component epoxy resin using Vacuum Assisted Processing [7]. Because of the observation of the partly solubility of the PEI in the epoxy resin far below its glass transition temperature of about 220°C at about 120°C, the infusion temperature of the resin was reduced to 100°C to avoid wash-out effects. After the infusion the resin was cured in its common curing cycle with its maximum temperature of 180°C.

### 2.3 Characterization methods

For determining the interlaminar properties, the interlaminar shear strength and the interlaminar fracture toughness mode I and mode II were tested according to the standards [8,9].

For evaluating the resistance against impact, the compression strength after impact was determined according to the standard [10].

For analyzing the behavior of the composites under heat impact, a cone calorimeter was used. The measurements in this article were made according to the standard [11] with a heat flux of 35 kW/m<sup>2</sup>.

## 3 Experimental results and discussion

### 3.1 Mechanical characterization

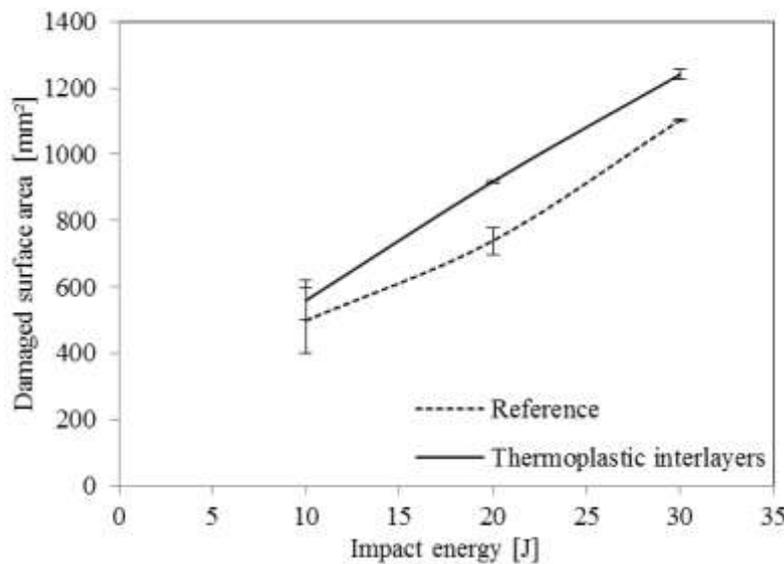
For the use as structural material, the mechanical properties of the modified composites shouldn't be lower than the properties of the reference material.

Critical mechanical properties of multi-layered laminates are the interlaminar properties. PEI was chosen as thermoplastic interlayer because of its compatibility to the epoxy matrix to avoid a decrease in mechanical properties by delamination. To analyze the interlaminar properties, the interlaminar shear strength and the interlaminar fracture toughness mode I and mode II were determined. The lay-up of the specimens for interlaminar fracture toughness and interlaminar shear strength are shown in Figure 2. The results of the interlaminar testing are shown in Table 1. It is obvious that the thermoplastic interlayers increase the interlaminar properties of the composite. The PEI has a strong connection to the epoxy resin caused by its partial solubility in the epoxy resin and also acts as toughener.

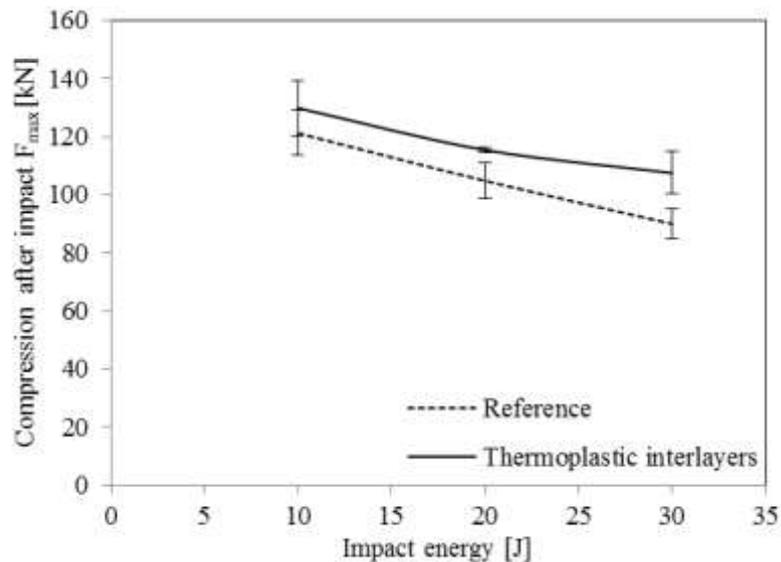
Sample	ILS [N/mm <sup>2</sup> ]	s (ILS)	G <sub>IC</sub> [J/m <sup>2</sup> ]	s(G <sub>IC</sub> )	G <sub>IIC</sub> [J/m <sup>2</sup> ]	s(G <sub>IIC</sub> )
Reference	41,1	2,1	368	22	1534	156
TP interlayers	57,3	8,7	1060	191	2292	396

**Table 1.** Interlaminar shear strength (ILS) and interlaminar fracture toughness mode I and mode II of the reference material and the multi-layered laminates with their standard deviations s.

Due to the low impact toughness of the composite caused by its brittle epoxy matrix, this study also investigated the influence of the thermoplastic interlayers on the impact tolerance. For this reason the compression strength after impact was determined. In Figure 3 the damaged surface area of impacted references and multi-layered laminate samples is plotted against the impact energy. It is visible that the damaged surface area of the samples with thermoplastic interlayers is higher than that of the references with the same impact energy. This, in combination with the higher compression strength after impact of the multi-layered laminates and the enlarging of the difference at higher impact energies (Figure 4), indicates a distribution of the impact energy along the thermoplastic interlayers which gives the material a higher remaining mechanical stability after an impact.



**Figure 3.** Comparison of damaged surface area after impact of 10, 20 and 30 J, determined with ultrasonic nondestructive testing.



**Figure 4.** Comparison of compression strength after impact testing of reference and modified samples which were impacted with 10, 20 and 30 J.

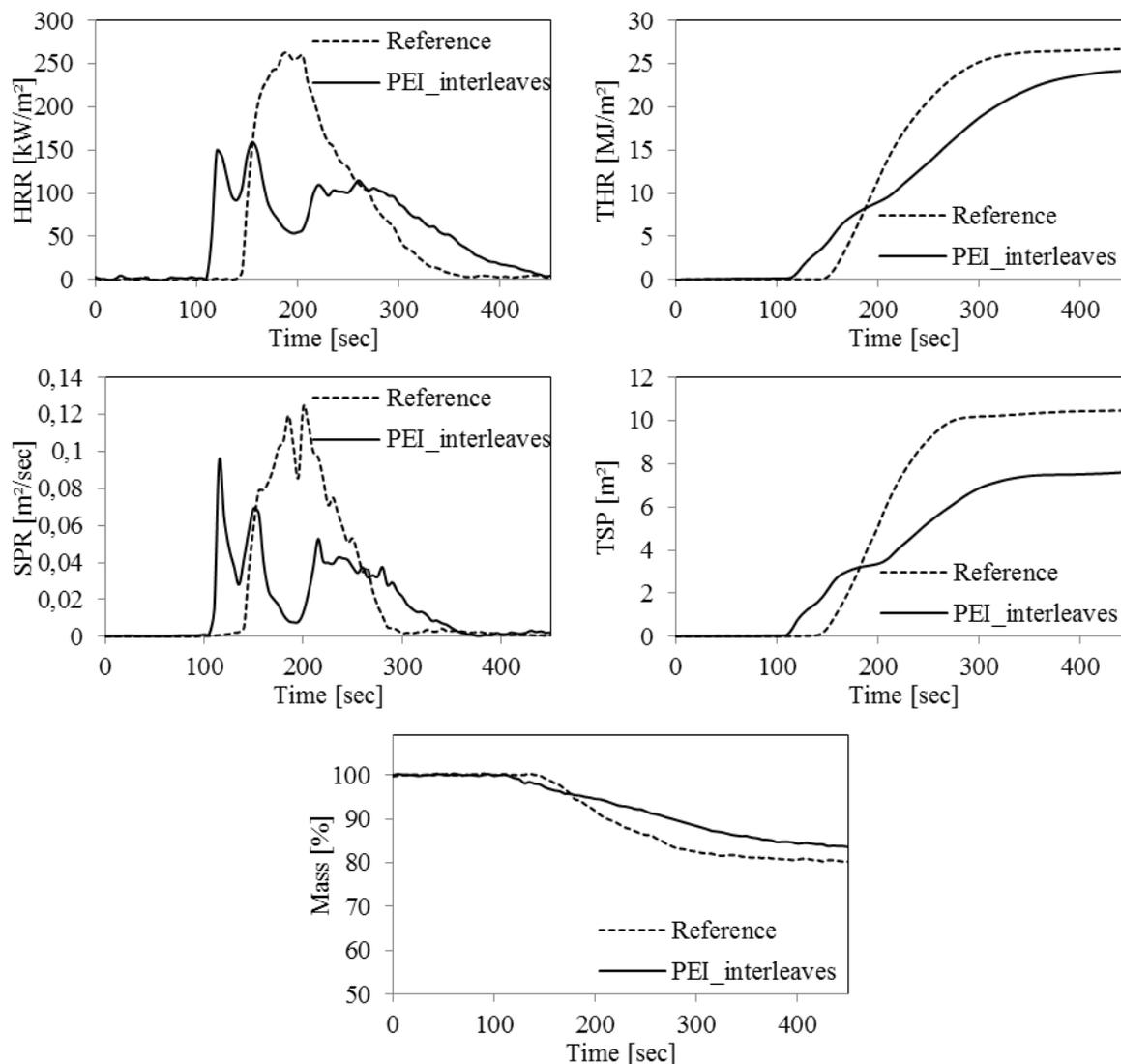
### 3.2 Characterization of the FST-properties

In Figure 5 typical results of cone calorimetry measurements of an unmodified reference sample and a multi-layered composite with thermoplastic (TP) interlayers are compared. The heat release rate (HRR), the total heat release (THR), the smoke production rate (SPR), the total smoke production (TSP) and the mass are plotted against the time during the heat impact with a heat flux of 35 kW/m<sup>2</sup>. The peak heat release rate (PHRR), the time to ignition (TTI), the total heat release (THR), the total smoke production (TSP) and the mass loss of the measurements are shown in Table 2.

Sample	PHRR [kW/m <sup>2</sup> ]	TTI [sec]	THR [kWmin/m <sup>2</sup> ]	TSP [m <sup>2</sup> ]	Mass Loss [%]
Reference	262	141	446	10,5	19,6
TP interleaves	159	109	413	7,8	16,3

**Table 2.** Peak heat release rate, time to ignition, total heat release, total smoke production and mass loss of a reference and a multi-layered laminate with TP interlayers (values from measurement plotted in Figure 5).

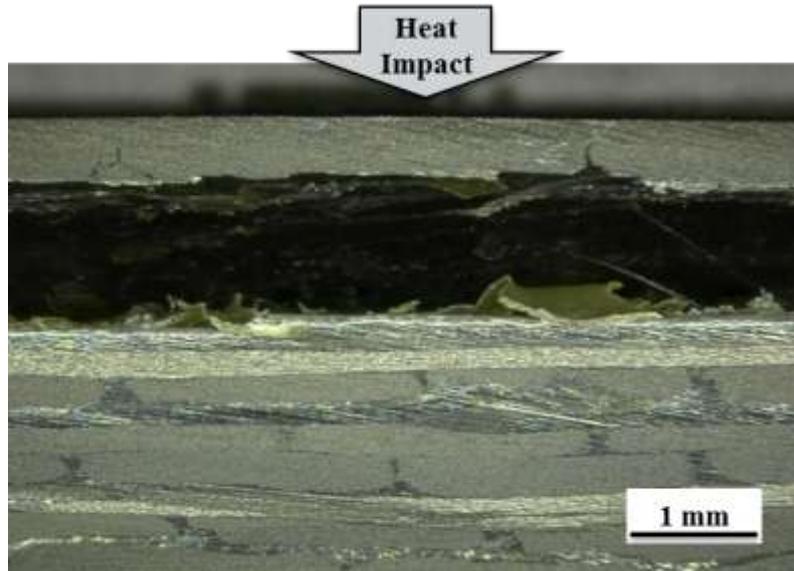
The HRR (above-left of Figure 5) of the multi-layered laminate (MLL) shows a drop in peak heat release rate (PHRR) of 40 % compared to the reference. Therefore also the time to ignition (TTI) decreases. The double peak after the ignition of the MLL indicates that both effects are related with the two thermoplastic interlayers below the surface of the sample. A possible explanation for the early ignition is the thermal insulation caused by the thermoplastic layers which leads to a faster heating and therefore combustion of the resin above these layers. The first dip after the peak at the ignition indicates that at this moment the resin above the TP layer is consumed and the TP layer protect the resin below the layer from the heat or does not allow the combustion gases to pass through. However, this could also be the typical peak after ignition caused by the high amount of combustion gases at the flashpoint. At the second increase, the first layer seems to lose its protective character which leads to further combustion of the resin between the TP layers. At the second dip the second TP layer loses its protective behavior and from then on the rest of the composite gets consumed.



**Figure 5.** Plotted results of cone calorimetry tests with reference composites (dashed) and samples with thermoplastic interleaves (continues); values plotted against the time axis: above-left: heat release rate [kW/m<sup>2</sup>], above-right: total heat release [MJ/m<sup>2</sup>], middle-left: smoke production rate [m<sup>2</sup>/sec], middle-right: total smoke production [m<sup>2</sup>], below: mass loss [%].

The THR during the measurement shows the earlier ignition of the MLL compared to the reference and the lower THR after the total consumption of the samples. The lower THR can be an evidence for a higher degree of carbonization of the resin caused by a confinement of the combustion gases in the sample.

The SPR (middle-left) shows the same characteristics as the HRR. The peak smoke production rate (PSPR) is reduced compared to that of the reference, but the shorter time to ignition also generates an earlier smoke production. The TSP (middle-right) shows a reduction of 26 % compared to the reference. This also suggests a confinement of combustion gases. The mass loss (ML) which can be seen in the plot of the mass against time (below-middle) shows also the earlier ignition. The reduction of the mass loss of about 17 % (3,3 wt-%) compared to the reference also suggests a higher degree of carbonization.



**Figure 6.** Cone calorimeter test interrupted before ignition.

In Figure 6 a MLL is shown which was exposed to a heat flux of 25 kW/m<sup>2</sup> in a cone calorimeter. The heat impact was interrupted before ignition of the sample. The figure shows an expansion of the upper TP layer of about 1000 % below the first biaxial NCF. A closer look shows that only the upper part of the TP layer is expanded, supposedly because the lower part has not yet reached its glass transition temperature, but the expansion process is definitely located in the thermoplastic layer which is shown by the remaining PEI attached to the upper NCF composite. Further measurements with dried samples at (10 days at 120°C) showed that the expansion of the TP is not caused by moisture, but probably by combustion gases which cannot escape because of the CFR resin layer on the top which seems to have not reached its softening/decomposition point yet.

#### **4 Conclusions**

Thermoplastic interleaves can be used as structural interlayers, which under heat impact act as expansion layers to protect the bulk composite below the multi-layered laminate. With these interleaves a decrease in peak heat release and total heat release could be observed. A decrease in peak smoke production rate, total smoke release and mass loss could be also observed. As effect of protecting the bulk material below the thermoplastic interlayers, the expansion of the thermoplastic layers could be determined. A disadvantage of the thermoplastic interlayers is the reduction of the time to ignition which is presumably caused by the higher surface temperature caused by the thermal insulation resulting from the expansion of the thermoplastic interlayers.

Furthermore it was shown that the thermoplastic interlayers also act as toughness modifiers and increase the impact tolerance of the composite.

### Acknowledgement

The authors would like to thank the European Commission for supporting the funding for the “Fire-Resist – Developing novel fire-resistant high performance composites” project (Seventh Framework Programme (FP7) Grant Agreement Number 246037).

The authors would also like to thank all of the participating project partners.

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