Fire Safety Assessment of Epoxy Composites Reinforced by Carbon Fibre and Graphene

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Abstract

This paper presents a coupled numerical investigation to assess the reaction to fire performance and fire resistance of various types of epoxy resin (ER) based composites. It examines the fire response of carbon fibre (CF) reinforced ER (CF/ER), ER with graphene nanoplatelets (GNP/ER) and CF reinforced GNP/ER (CF/GNP/ER). Thermal, physical and pyrolysis properties are presented to assist numerical modelling that is used to assess the material ability to pass the regulatory vertical burn test for new aircraft structures and estimate in-fire and post-fire residual strength properties.

Except for the CF/GNP/ER composite, all other material systems fail the vertical burn test due to continuous burning after removal of the fire source. Carbon fibres are non-combustible and therefore reduce heat release rate of the ER composite. By combining this property with the beneficial barrier effects of graphene platelets, the CF/GNP/ER composite with 1.5 wt% GNP and 50 wt% CF self-extinguishes within 15 s after removal of the burner with a relatively small burn length. Graphene drastically slows down heat conduction and migration of decomposed volatiles to the surface by creating improved char structures. Thus, graphene is allowing the CF/GNP/ER composite panel to pass the regulatory vertical burn test.

Due to low heat conduction and reduced heat release rate, the maximum temperatures in the CF/GNP/ER composite are low so the composite material retains very high in-fire and post-fire mechanical properties, maintaining structural integrity. In contrast, temperatures in the CF/ER composite are much higher. At a maximum temperature of 86 °C, the residual in-fire tensile and compressive mechanical strengths of CF/GNP/ER are about 87% and 59% respectively of the ambient temperature values, compared to 70% and 21% respectively for the CF/ER composite that has a temperature of 140 °C at the same time (but the CF/ER temperature will be higher due to continuing burning). Converting mass losses of the composites into char depth, the post-fire mechanical properties of the CF/GNP/ER composite are about 75% of the ambient condition compared to about 68% for the CF/ER composite.

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1 Introduction

Precautions for fire safety are traditionally divided into two general considerations: reaction to fire performance that measures the ability of material to spread fire, and fire resistance, which is concerned with containment of fire by the structure. Reaction to fire typically deals with the early growth stage of fire behaviour when temperatures are relatively low while fire resistance is critical when the fire has reached the fully developed stage with very high temperatures. To achieve adequate fire resistance, the performance of structures should meet three requirements so as to prevent fire spread from the structure: loadbearing capacity (no structural failure), insulation (no excessive temperature rise on the unexposed side to cause further ignition) and integrity (no burning through of the structure by fire). For structures made of non-combustible materials such as steel and concrete, because the loadbearing structure is non-combustible and also structural loadbearing capacity is affected only when the structural materials reach much higher temperatures (>400 °C) than those involved in assessing material reaction to fire performance (<300 °C), considerations for reaction to fire and fire resistance performances are decoupled. This mean that there is no consideration of reaction to fire performance of materials when dealing with structural fire resistance [1] and vice versa. Furthermore, when calculating structural loadbearing capacity in fire, basic heat transfer calculations are performed to obtain structural temperatures. In such heat transfer calculations, it is assumed that there is no internal combustion and no heat generation in the structure, there is no phase change of materials and material thermal properties (thermal conductivity, specific heat and density) are temperature dependent but not affected by chemical reactions.

However, the fire safety problem becomes coupled when combustible materials are used in structures as is the case in aircraft where polymer composites are extensively used. Not only polymer composites lose their mechanical properties at lower temperatures thus causing composite structures to lose their loadbearing capacity at early stages of fire exposure, composite materials are also combustible [2–5]. Combustion involves decomposition and additional heat generation, coupled heat and mass transfer and material phase change (from virgin material to char), which all have important influences on temperatures attained in the composite structure. Therefore, the simplistic approach of evaluating heat transfer in non-combustible structures is no longer applicable to polymer composites. In order to accurately predict temperature changes, it becomes important to understand and model the combustion behaviour of composite materials and also obtain reliable material input properties, which is the aim of this paper.

Composite materials used in aircraft are reinforced with carbon fibre (CF). Because CF is non-combustible, the binding polymer matrix has the most critical influence on fire performance [6]. It is the polymer resin that decomposes, and its combustion dominates the softening process thereby causing the composite material to lose its stiffness and strength leading to possible structural failure, especially under compressive loading. Good reaction to fire performance (low flammability) of the polymer matrix is therefore crucial for the composite structure to maintain structure integrity in fire. Therefore, when selecting composite materials for structural loadbearing applications where fire safety is a critical consideration, a balance has to be stricken so that the material can fulfil the requirements of both reaction to fire and fire resistance performance, while ensuring easy large scale processing. Because of these demands, epoxy resin (ER) satisfies many of these demands, hence it is most commonly used in aircraft construction [7, 8].

However, ER has relatively high flammability and there are concerns about its safety in aircraft fire accidents [9]. When ER is reinforced with CF, it is important to account for the contributions of CF in the fire analysis, since they improve fire resistance. CF will not only mechanically reinforce ER, the introduction of a large amount of non-combustible material (CF) into ER will reduce the flammability of ER. For example, it is reported that when adding 70% of CF into ER, both the peak heat release rate (PHRR) and total heat release rate (THRR) of CF/ER is reduced to be below 30% compared to pure ER [10]. However, it is difficult to further improve the reaction to fire performance of CF/ER composite by adding more CF, because further decreasing the content of ER will result in not having sufficient binding power for the composite and thus damaging its mechanical properties.

To overcome fire safety problems caused by high flammability of ER, it is possible to modify ER using nanoparticles [11, 12]. A number of researchers have reported experimental results of reduced peak rate of heat release by incorporating graphene nanoplatelets (GNPs) [13–15]. The beneficial effects of GNPs are attributed to their gas and thermal barriers: GNPs cause the mass transfer routes inside ER to become tortuous [16] and GNPs most importantly improve ER char structure, thereby having low thermal conductivity. The authors have successfully modelled these processes [14]. For example, adding a small amount of GNPs (e.g. 3 wt%) into ER, the PHRR is reduced by 47%. Because the presence of a small amount (below 5 wt%) [17]) of nano fillers does not affect the processability of ER blends, it is possible to replace pure ER in CF/ER composite with GNP/ER to serve as the matrix to make GNP and CF co-reinforced ER composite (CF/GNP/ER). This hybrid composite with a hierarchy of structural scales has the potential to achieve the all-round performance requirements for reaction to fire and fire resistance performance in aircraft applications. This paper will present the results of a numerical modelling study to assess this potential.

Previous research studies on fire resistance of composite structures have focused on obtaining mechanical properties of composite materials and composite structural load carrying capacities at given elevated temperatures [2, 3, 18]. The crucial topic of how to accurately obtain temperatures attained in composite structures is not adequately addressed other than simplistic heat transfer modelling. This paper examines how to obtain results of temperatures in composites during a vertical burn test. In particular, it will present necessary input properties of composites for reliable calculations of composite temperatures that can be used to evaluate structural integrity when exposed to fire.

Therefore, the objectives of this study are to:

1. Propose reliable material property data that can be used to model the complex coupled physical, chemical reaction and heat transfer phenomena of different types of ER composites during different stages in fire.
2. Provide a method of simulating combustion behaviour of different types of ER composites containing CF and GNP, including its validation.
3. Assess whether the required reaction to fire performance for aircraft can be achieved by using CF and GNP co-reinforced ER, through comparison of modelling results with requirements of the regulatory vertical burn fire test.
4. Present an assessment of the effects of CF and GNP in reducing temperatures attained in ER so as to evaluate the in-fire and post-fire residual load carrying capacities of composite structures.

2 Material Properties to Simulate the Combustion of ER Composites

Accurately simulating the combustion behaviour of ER composites requires reliable input data for material thermal physical properties of all components including the reaction products. Many of these properties are hard to measure. However, by understanding mechanisms of combustion of ER composites, it is possible to construct theoretical models to evaluate these material properties.

The authors have carried out extensive research to quantify the required thermal physical properties of ER and GNP/ER composites [14], and for completeness their main findings are summarised in this section. These properties are necessary to model thermal degradation of the resin, gas migration through the material, and heat transport through porous char.

2.1 Effects of Char Layer during Combustion

After burning of ER composites, a char layer is formed that can offer a protection cover to inhibit further fire damage and protect the unburnt material underneath (Fig. 1). The thermal barrier effect can be explained using a defined ratio of the actual heat flux ($\dot{q}_{net}''$) at the interface of the char layer and the unburnt material to the external incoming heat flux on the surface ($\dot{q}_{ext}''$).

$$R = \dot{q}_{net}'' / \dot{q}_{ext}'' \qquad (1)$$

The $\dot{q}_{net}''$ determines the quantity of conduction heat into the unburnt material and the mass loss rate, as expressed by Eq. (2).

$$\dot{q}_{net}'' = -k\frac{\partial T}{\partial x} + \dot{m}'' L \qquad (2)$$

where $\dot{m}''$ is the mass loss rate at the interface, k is the thermal conductivity of the virgin material and L is the latent heat of pyrolysis.

When $\dot{q}_{net}''$ decreases to a critical value that the pyrolysis reaction fails to provide sufficient amount of combustible gases to sustain the surface fire, the fire will self-extinguish. It is revealed that $\dot{q}_{net}''$ decreases with increase of the char depth and/or decrease in thermal conductivity of the char layer [19]. This means that to effectively protect the underlying material, the char layer has to be either thick or has very low thermal conductivity or both. Without any intumescent fire protection on ER composite, the increased char depth comes
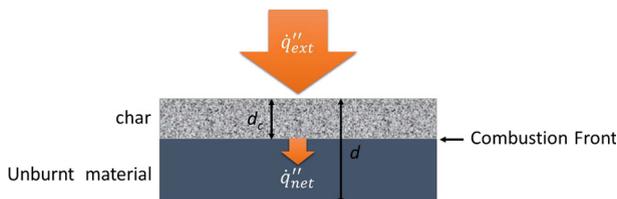
Fig. 1 Schematic view of heat transfer during pyrolysis of composites with a surface char layer

from growth in burning the virgin material, which leads to the undesirable situation of reduced mechanical resistance. Therefore, reducing the thermal conductivity of the char layer is the preferred solution for non-expanding composites such as CF/ER.

Low thermal conductivity of the char layer reduces temperature increase of the virgin material thereby reducing the rate of decomposition of the material, lowering the mass loss rate value in Eq. (2). Furthermore, because combustion only happens at the surface, if movement of the combustible volatiles from inside the material to the surface can be slowed down, combustion is slowed. The quantity that controls mass movement is gas permeability. The authors' previous research [14] suggests that with GNP, the thermal conductivity and gas permeability of ER can be reduced by an order of magnitude. The following section presents a theoretical model and a summary of these critical material property data.

2.2 Thermal Properties of ER Composites with CF and GNP Reinforcement

Figure 2 illustrates the state of CF/ER and CF/GNP/ER composites after combustion with fire exposure from one side. CF is considered non-combustible. Thermal oxidation of CF is also not considered because this only happens at very high temperatures (over 600 °C) long after losing their strength [20]. With the addition of GNP in ER, the char becomes more compact and less porous.

The decomposing ER composite and its char (with or without CF/GNP reinforcement) is generally a porous material. Their thermal conductivity can be considered to consist of two parts: that of the solid (K_s) material due to pure conduction and that due to radiant heat transfer (K_r) in the pores, as follows [21]:

$$K\,(T) = K_s(T) + K_r(T) \tag{3}$$

$$K_r(T) = \gamma\,\sigma\,T^3 \tag{4}$$

where σ is the Stefan-Boltzmann constant; γ is the coefficient for radiant conductivity, determined by [22]:

$$\gamma = \frac{13.5}{\varepsilon\,\psi}D \tag{5}$$
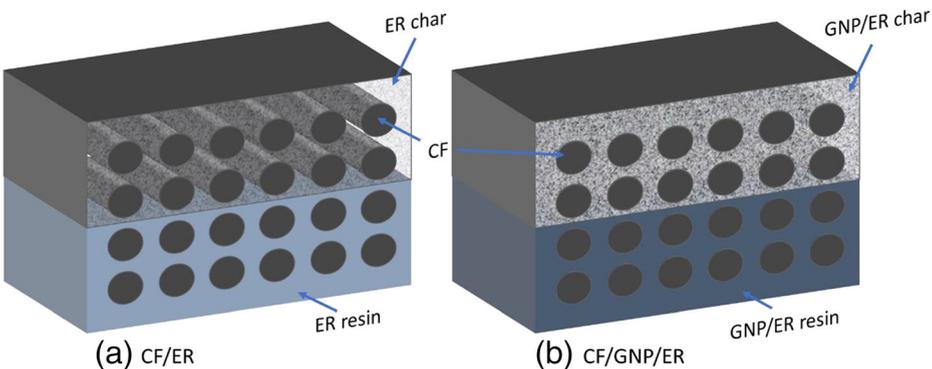
Fig. 2 Illustration of char layer for **a** CF/ER and **b** CF/GNP/ER composites

in which ε and ψ are emissivity and porosity, respectively; D is the characteristic dimension of pores (diameter for spherical pores or maximum length for slots in the direction of heat transfer).

For porous char of ER composites, radiant heat transfer across pores is the dominant mode of heat transfer at high temperatures instead of solid conduction, as it varies with the third power of temperature. The authors' previous work [14] has identified a pore characteristic dimension of 2.5 mm for the pure ER char, and a pore size of 0.5 mm for the GNP/ER char for 3 wt% GNP loading.

When CF is used, the solid component of thermal conductivity of ER composites is increased due to higher thermal conductivity of carbon than ER. However, since heat conduction in CF/ER composites in the thickness direction is usually more important for fire protection and the through thickness thermal conductivity of CF is 10–20 times lower than the in-plane value [20], the solid component of thermal conductivity of ER composites may be considered to be independent of CF. This simplistic underestimation of thermal conductivity due to CF may be considered to be compensated by neglecting the beneficial effects of CF in improving the ER char structure which would lead to reduced thermal conductivity due to CF. Further refinement of the thermal properties of ER composites due to CF are required, but this is not pursued in this research that is focusing on comparative performance of different composites.

Before reaching the surface for combustion, the combustible gases generated from the decomposing ER will need to transport through the char layer. The delay of this gas movement process will reduce combustion rate, and this can be achieved when the char layer has lower gas permeability. The existence of GNPs in the porous ER char is found to be able to improve the char structure to make the gas movement route more tortuous. The gas permeability of GNP/ER char is estimated to be one order of magnitude lower than pure ER char [23]. If CFs are added, its gas permeability will be even lower because the porosity is further reduced, but as mentioned earlier, such a refinement is not considered in this research.

Based on the above explanations, Table 1 presents thermal conductivity and gas permeability values for various ER composites [14].

During combustion, ER will convert to char when the temperature is over 350 °C [14]. The thermal conductivity and specific heat capacity of ER are considered to be constant because it is the char layer that plays a critical role at high temperature during combustion process and the thermal conductivity of char varies with the third power of temperature as listed in Table 1. All thermal properties of ER and char needed for the simulation are concluded in Table 2.

The thermal conductivity and gas permeability of the material at intermediate stage of reaction between virgin resin and complete char are calculated based on volume fractions of resin ($\varnothing_{ER}$) and char ($\varnothing_{char}$) using the rule of mixture. For example, the effective thermal conductivity is calculated as:

Table 1 Key properties of various types of ER char layer [12]

	Gas permeability (m^2)	Effective thermal conductivity (W/m-K)
ER char	4E-17	$0.219 + 0.04*\sigma\ T^3$
ER/GNP char	3.8E-18	$0.219 + 0.008*\sigma\ T^3$
ER/CF char	4E-17	$0.219 + 0.04*\sigma\ T^3$
ER/CF/GNP char	3.8E-18	$0.219 + 0.008*\sigma\ T^3$

Table 2 Thermal properties of virgin ER and char [14]

Properties	Unit	Value
ER Thermal conductivity	W/m-K	0.335
ER Specific heat capacity	J/kg-K	1748
ER Emissivity	–	0.95
ER Absorption coefficient	m^{-1}	2700
ER Gas permeability	m^2	1.36E-21
Char Specific heat capacity	J/kg-K	1294
Char Emissivity	–	0.95
Char Absorption coefficient	m^{-1}	2700

$$K_{eff} = K_{ER}*\varnothing_{ER} + K_{char}*\varnothing_{char} \tag{6}$$

As previously explained, reaction to fire and fire resistance performances are coupled for ER composite structures. Therefore, when evaluating temperatures in ER structures, it is necessary to include the combustion process. For this, reliable data on pyrolysis properties are necessary. Based on the authors' previous study [14], these pyrolysis data required in the Arrhenius equation to calculate the pyrolysis reaction rate (r) are listed in Table 3.

$$r = A \, exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{7}$$

It should be pointed out that instead of explicitly simulating carbon fibre reinforced composite structure in combustion, composite materials are assumed to be homogeneous and the effective properties are calculated based on the properties of the sub-components using the rule of mixture. Therefore, the combustible mass of CF/ER composite should be proportionally reduced because CFs are non-combustible. The pyrolysis of ER is simulated using the kinetics properties in Table 3. CF is set to be non-reactive and is assumed to have the same properties as carbonaceous char.

2.3 Equivalent Pyrolysis Kinetics for FDS Simulation

The thermal, physical and pyrolysis data in the previous section are needed in numerical modelling of fire performance of ER composites if mass transfer (migration of combustible volatiles) is explicitly considered. This is the case with the simulation model using Gpyro [24]. Such simulations were carried out by the authors [17] who validated the material properties in the previous section by comparison of simulation results with their cone calorimeter tests. However, Gpyro can only simulate solid phase. For realistic applications, the Fire Dynamics Simulator (FDS) software developed by NIST is most commonly used by fire protection

Table 3 Thermal properties of pure epoxy resin [14]

Heat of combustion	MJ/kg	30
A (pre-exponential factor)	s^{-1}	1.81E15
E (activation energy)	kJ/mol	240
n (reaction order)	–	2

engineers and researchers [25]. FDS does not explicitly simulate gas transport in solid, which effectively means that all pyrolysed gases are released immediately to the burning surface for combustion. This assumption is invalid for GNP/ER composites because of their very low gas permeability [14]. One method of overcoming this problem is to use Gpyro to establish an equivalent set of pyrolysis properties so that the amount of decomposed material in FDS simulation is the same as the amount of pyrolysed gases that have migrated to the burning surface in Gpyro. Without such a process, using the original data for pyrolysis in the previous section in FDS simulation would result in increased peak rate of heat release and shortened combustion duration, as illustrated in Fig. 3. In this figure and later in this paper, Mass loss rate (MLR) refers to that at the burning surface which directly converts to heat release rate (HRR).

To identify an optimal set of equivalent pyrolysis data, simulations were carried out to examine how MLR in FDS changes with variations in any of the three parameters of Arrhenius equation and Fig. 4 compares results for changing one of these parameters while keeping the other two unchanged. The results indicate that increasing the reaction order (value n) in FDS simulation suppresses the peak mass loss rate (PMLR), resulting in lower PHRR (Fig. 4a). This is similar to the effects of reduced gas permeability observed in Gpyro simulation (Fig. 3). Changing the other two values of pyrolysis (A and E in Eq. 7) significantly changes the time at PMLR (Fig. 4b, c), however, this is not observed in Gpyro simulations (Fig. 3). Therefore, to establish an equivalent pyrolysis model, only the reaction order n is changed (increased). For ER composite with 3 wt% GNP, an equivalent reaction order is determined to be 6, compared to a value of 2 in the previous section.

Figure 5 compares the FDS and Gpyro simulation results of MLR at the burning surface for GNP/ER with 3 wt% GNP weighting and also against the cone test results of [14]. The agreement is considered acceptable, indicating that the equivalent pyrolysis model is appropriate for use in FDS.

3 Numerical Model for Fire Performance of ER Composites and Validation

Due to lack of fire test data when using CF/ER or CF/GNP/ER composites, validation of the authors' FDS simulation is based on comparison against a Single Burning Item (SBI) test of Polyvinyl chloride (PVC). The SBI test is a standardized fire test method for determining the reaction to fire behaviour of materials when exposed to a thermal attack. Figure 6 shows the model setup. In this arrangement, the corner specimen consists of two wings: (i) short wing

Fig. 3 Simulated mass loss rates of 3 wt% GNP/ER composites in FDS and Gpyro with the same input data for pyrolysis
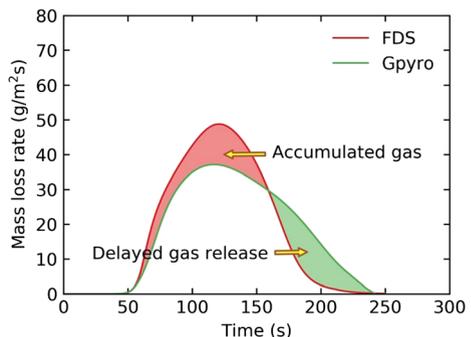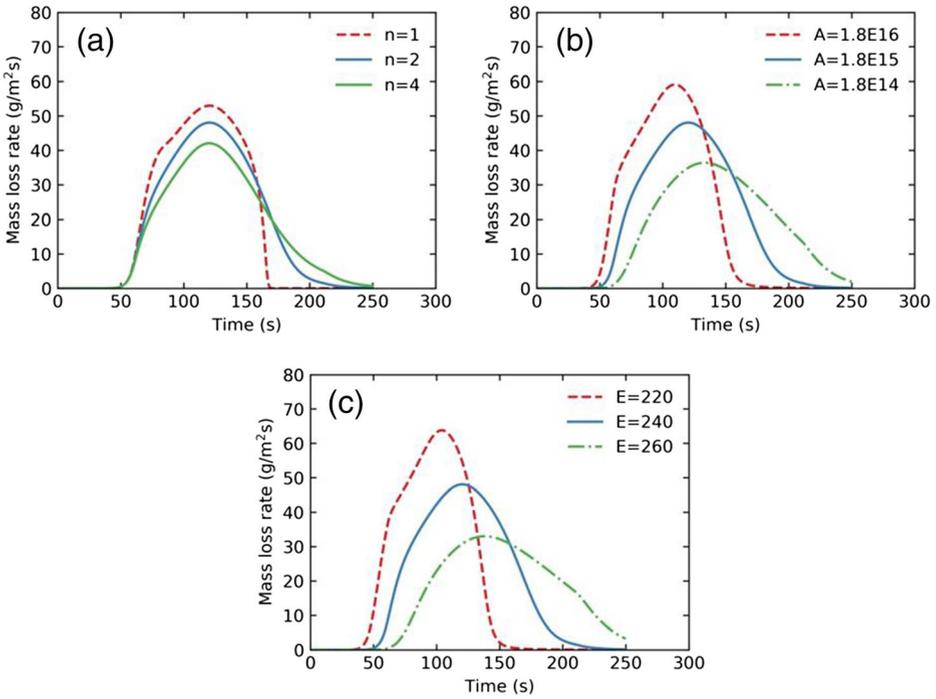
Fig. 4 Results of sensitivity study on predicted mass loss rate to pyrolysis kinetics (**a** reaction order; **b** pre-exponential factor; **c** activation energy) for 3 wt% GNP/ER composites in FDS

(495 ± 5) mm × (1500 ± 5) mm; (ii) long wing (1000 ± 5) mm × (1500 ± 5) mm. The specimen is exposed to fire from a sand-box burner supplied with propane. The panel material is ignited and the flame spreads upward from the corner along the panel surfaces. The SBI test is selected because it is an internationally accepted standard test for investigating reaction to fire
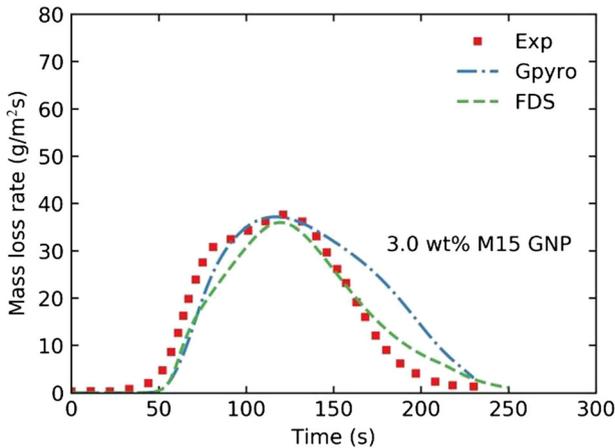
Fig. 5 Comparison of simulated MLR of GNP/ER composites by Gpyro ($n = 2$) and FDS ($n = 6$) against to the experimental result [14]
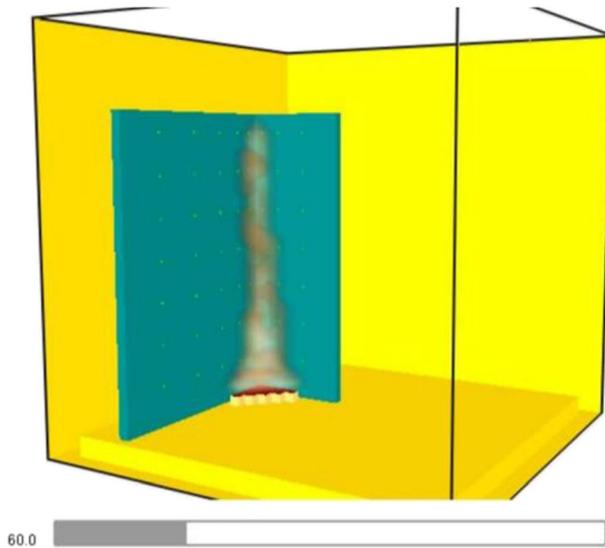
Fig. 6 Simulated SBI tests of PVC panels after 60s using FDS

performance of materials and it can be used to demonstrate the capability of FDS to accurately simulate burning behaviour of combustible materials.

Tsantaridis and Oestman [26] carried out SBI tests of PVC panels according to EN 13823 [27], and fire performance properties such as heat release rate were reported. The input parameters for PVC are also obtained and listed in Table 4 according to [28, 29]. The simulation domain is $2 \times 2 \times 2$ m and the grid size is 0.05 m. These values are according to Zhang et al. [30].

Figure 7 compares the simulation results of heat release rate (HRR) history with measured data and indicates good agreement with each other, giving confidence in the analysis and assumptions made. PVC is selected for this validation because there are well defined material property data and corresponding SBI test data in literatures [28, 29]. However, the capability of FDS in modelling burning behaviour is generic as long as accurate and reliable material properties are available. Therefore, this validation exercise based on a SBI test of PVC

Table 4 Input data for FDS simulation of a SBI test of PVC panel [28, 29]

Property	Units	Value
PVC density	kg/m³	1250
PVC thermal conductivity	W/m/K	0.16
PVC specific heat capacity	kJ/kg/K	1.7
PVC emissivity		0.9
PVC absorption coefficient	m⁻¹	2145
Char density	kg/m³	120
Char thermal conductivity	W/m/K	0.05
Char specific heat capacity	kJ/kg/K	1.5
Char emissivity		0.85
Char absorption coefficient	m⁻¹	2453
REFERENCE_TEMPERATURE	ºC	280
REFERENCE_RATE	s⁻¹	0.005
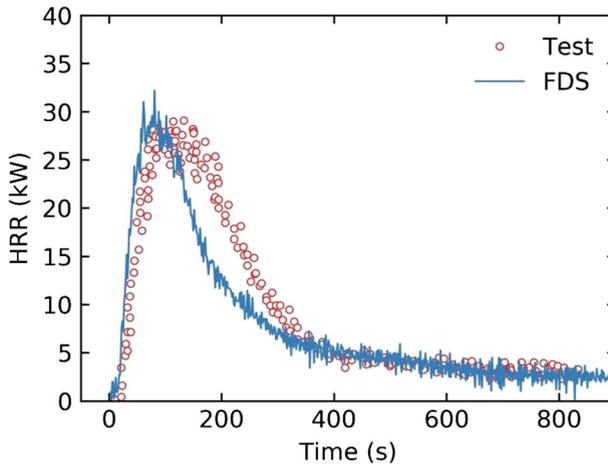
Fig. 7 Comparison between test and FDS simulation results of heat release rate – time relations for a SBI test of PVC

demonstrates the ability of using FDS to accurately simulate the reaction to fire performance of polymer composites. For ER composites, the corresponding data are not available. Therefore, as will be presented in the following sections, the authors use ER composite properties extracted based on a detailed investigation of Cone tests to evaluate their reaction to fire performance.

4 Assessment of Reaction to Fire Performance of Different Types of ER Composite Panels

4.1 Vertical Flame Spread Test Model

Polymer composite materials used in the modern aircraft construction are required to pass a specific certification test: the standard vertical flame spread test (or alternatively referred to as the vertical burn test) [31]. Figure 8 shows the authors' simulation model for this test. Similar to the SBI test, a propane burner is placed beneath the polymer panel. The size of the ER composite panel is $0.305 \times 0.05 \times 0.002$ m. A burner with a nominal size of 0.95 cm is set to give a flame height of 3.8 cm. The minimum flame temperature in the centre of the flame is over 1277 °C (1550 °F). The lower edge of the specimen is 1.9 cm above the top edge of the burner. The flame is applied to the centre line of the lower edge of the specimen for 60 s and then removed.

According to CFR 25.855 [31], after the removal of the burner, the performance requirements for passing the vertical flame spread test for aerospace applications are: the average burn length should not exceed 15 cm and the average flame time after removal of the flame source should not exceed 15 s.

4.2 Model Details

Once the FDS model is validated by the SBI test, it gives confidence to apply the model to simulate the vertical burn test of ER composites. For the virtual vertical burn test, the

Fig. 8 A schematic of the standard vertical flame spread test for aerospace applications
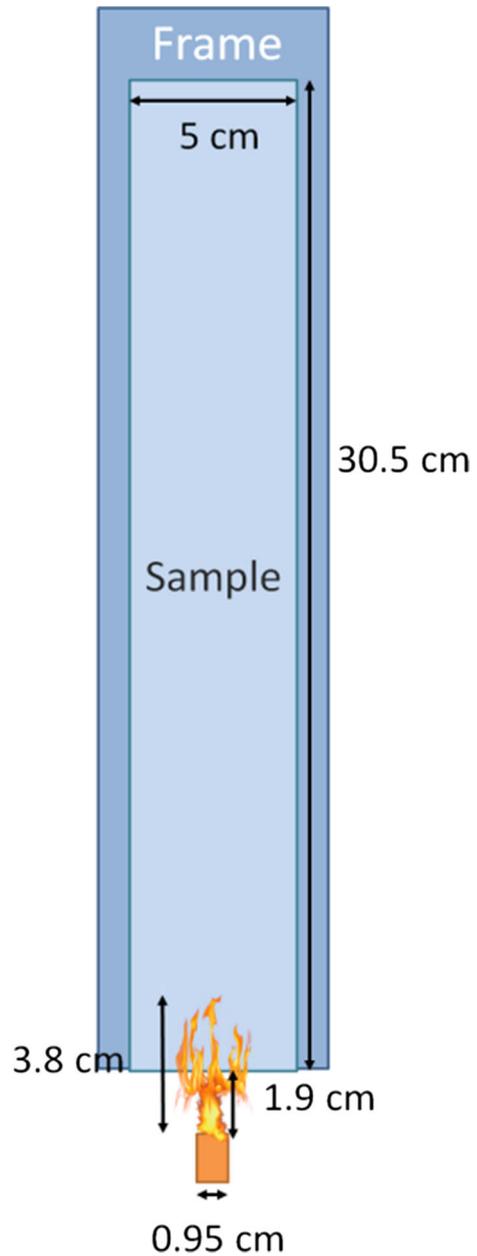
simulation domain is 0.1 m × 0.05 m × 0.4 m and the simulation grid size is obtained using the following equation [25]:

$$D^* = \left(\frac{\dot{Q}}{\rho_\infty C_p T_\infty \sqrt{g}} \right)^{2/5} \tag{8}$$

where D^* is the characteristic fire diameter; $\dot{Q}$ is the heat release rate of the fire. D^* is found to be 0.04 m for a heat release rate up to 0.6 kW of ER composites (Fig. 10a). The mesh size is optimised to be 0.0025 m ($D^*/16$).

Various ER composites in Table 5, with and without CF & GNP reinforcement, are considered to be homogeneous. The base properties in Table 2 and Table 3 are used to obtain the material properties and reaction kinetics for the ER composites, which are the input data in FDS simulations.

In the vertical flame spread test, the burn length is the distance from the original edge to the farthest location with evidence of damage due to flame impingement. In FDS modelling, the burning (fire damage) area is defined as when pyrolysis of the solid phase has started, specifically when the burning rate of the solid phase is over 0.001 g m^{-2} s^{-1}.

4.3 Reaction to Fire Performance Assessment of ER Composites

Figure 9 compares images of ER, CF/ER and GNP/CF/ER composites at different times of the vertical flame spread test. They indicate that ER and CF/ER panels do not self-extinguish after removal of the burner at 60s, and sustain fire spread by continuous burning, even though the CF/ER panel has reduced burning compared to the ER panel. In contrast, the CF/GNP/ER panel self-extinguishes at 75 s.

Figure 10 compares HRR, burn length and flame spread rate between pure ER, GNP/ER, CF/ER and CF/GNP/ER panels. As expected, ER panel has high values of HRR, burn length and flame spread rate. Although CF reinforced ER reduces these values, the CF/ER panel does not self-extinguish after removing the fire source at 60s and burning continues afterwards. Therefore, the CF/ER panel does not pass the vertical flame spread test.

The flame spread rate and HRR of GNP/ER panel are significantly lower than those of ER panel, which correlates with the findings of [32] when using polypropylene resin with GNP. However, the GNP/ER panel still fails to pass the test. However, the CF/GNP/ER panel self-extinguishes after removal of the burner at 60s, as indicated by Fig. 10, where HRR is returning to zero with no further increase in burn length. The maximum burn length is about 0.02 m. This suggests that the CF/GNP/ER composite panel would pass the reaction to fire test for aircraft applications.

The ability of CF/GNP/ER composite to pass the vertical burn test is very promising. In fact, the fibre content is usually higher than 50% volume fraction assumed for fibre reinforced polymers, which means that even better fire retardancy can be achieved.

Table 5 ER Composite formulations

	ER (wt%)	CF (wt%)	GNP (wt%)
ER	100	0	0
GNP/ER	97	0	3
CF/ER	50	50	0
CF/GNP/ER	48.5	50	1.5
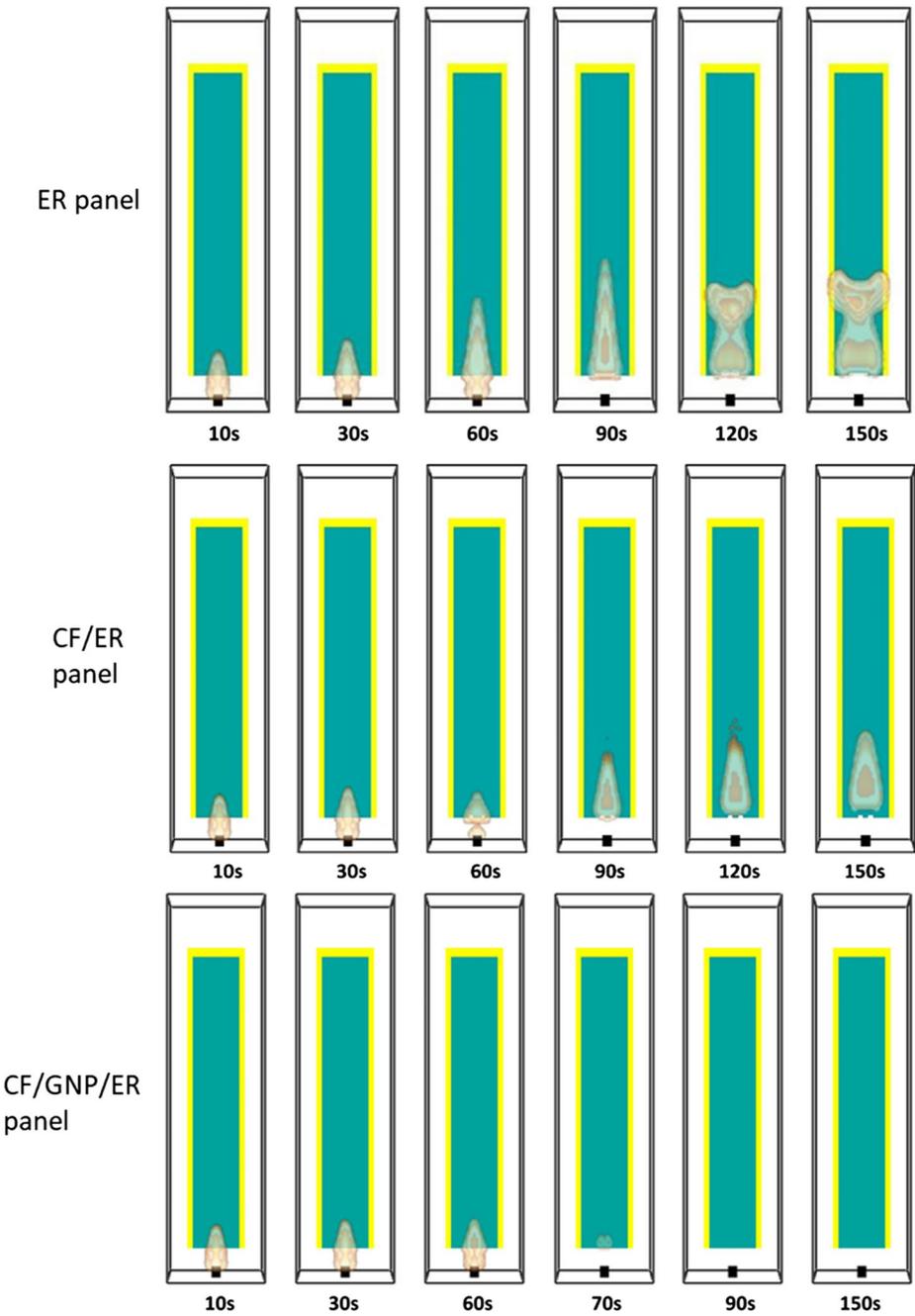
Fig. 9 FDS simulation results of vertical burn test for ER, CF/ER and GNP/CF/ER composite panels at increasing time intervals
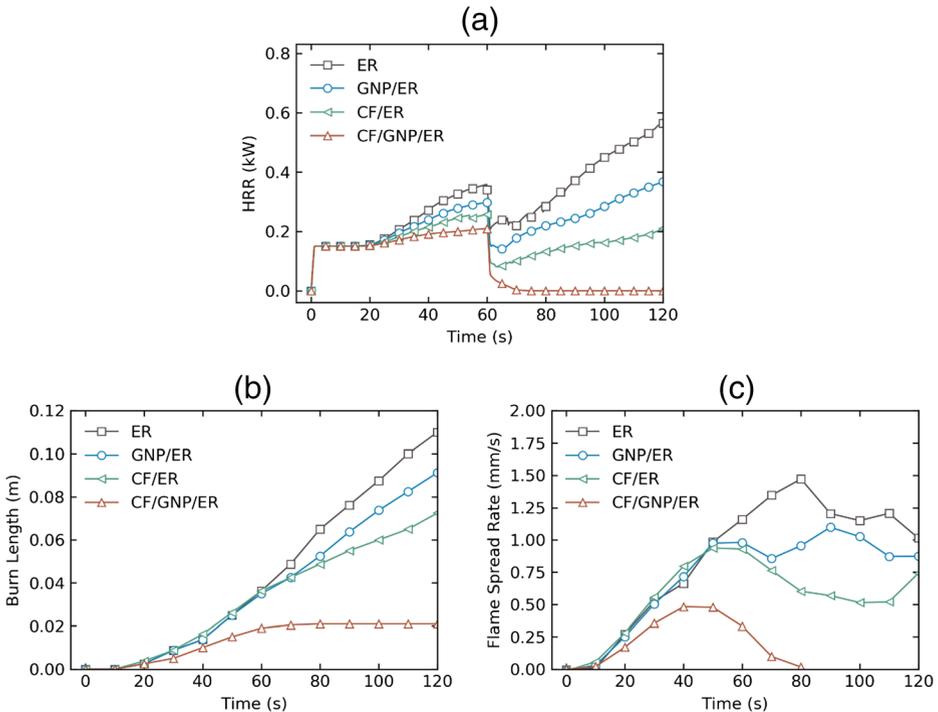
Fig. 10 Comparison of FDS simulation results for different types of ER panels (Pure ER, GNP/ER, CF/ER and CF/GNP/ER) in vertical burn test: **a** HRR, **b** burn length and **c** flame spread rate

5 Assessment of Fire Resistance and Post-Fire Performance of Different Types of ER Composite Structures

Complete assessment of fire resistance requires structural analysis of composite structures at elevated temperatures. Nevertheless, it is possible to demonstrate structural integrity of CF and GNP reinforced ER composite structures by examining the retention of mechanical properties of the materials.

For the simulated panels in the previous section, composite material temperatures are extracted at the position of the maximum temperature where structural damage is at the maximum, which is 1 cm from the lower edge of the panel, in the centre of the burner as shown in Fig. 8. The composite material temperature is taken at the centre of the polymer panel, i.e. at a depth of 1 mm (0.001 m) from the surface for a polymer panel thickness of 2 mm thickness.

Figure 11 compares temperature-time developments for the four types of ER composites considered in this study (pure ER, GNP/ER, CF/ER, CF/GNP/ER). They show vast differences in temperatures due to their different thermal properties (mainly, thermal conductivity), and heat release rates. Because the CF/GNP/ER composite has low thermal conductivity in the char and low heat release rate, temperatures are much lower than those in the other three systems. This allows CF/GNP/ER composite structures to remain structurally safe in fire, while other ER composite structures may lose their structural integrity; this can be demonstrated below.
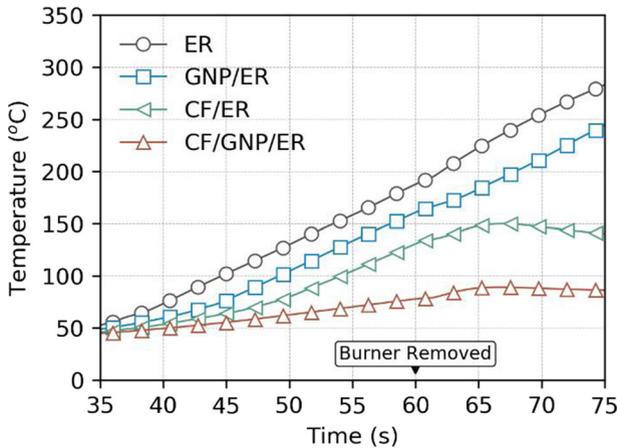
Fig. 11 Comparison of temperature profiles of different ER composites at a depth of 0.001 m and a height of 0.01 m

It has been shown that the CF/GNP/ER composite panel self-extinguishes at 75 s after removing the burner at 60s, whilst other composite panels continue burning. Therefore, a comparison of the residual mechanical properties of various types of ER composites at 75 s is most unfavourable to the CF/GNP/ER composite but favourable to other ER composites. At 75 s, the composite material temperatures are 283, 244, 140, and 86 °C for pure ER, GNP/ER, CF/ER, and CF/GNP/ER panels, respectively.

After obtaining the composite material temperatures, the residual tensile and compressive strengths of these composites are calculated using the reported temperature correlated material strength data from experimental results of Wang et al. [4] for tension and [5] for compression. Figure 12a, b compare the calculated results.

The ER panel temperature of 283 °C is much above its glass transition temperature [33], therefore, it will have very little strength left, if any. Furthermore, even though GNP/ER composite has relatively good reaction to fire performance, it would not be usable as a loadbearing material, since resin rich. Therefore, they are not included in further comparisons.
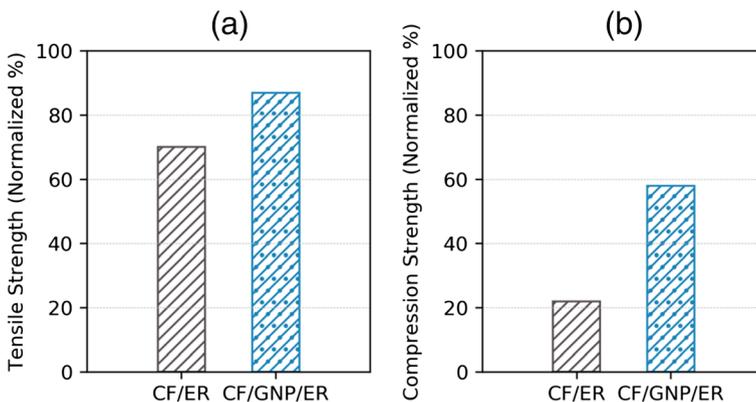
Fig. 12 Estimated tensile and compressive strengths (normalized to the ambient temperature value) of different ER composites after 75 s

It should be pointed out that although the ER formula and fibre type used in Wang et al. [4, 5] may be different from those of this research, this is considered acceptable because this research is to compare relative performance of different ER polymer composites.

Under tension, the retention of tensile mechanical properties of composites at temperatures below 400 °C is high due to contribution of non-combustible CF. Nevertheless, because CF/ER composite has much higher temperatures than CF/GNP/ER composite, it suffers substantial loss of mechanical properties (30% reduction in tension strength) while CF/GNP/ER composite retains 87% of its full tensile strength. Under compression, softening of the ER matrix plays a more critical role then under tension for both CF/ER and CF/GNP/ER composites, which leads to vastly different results due to their different temperatures. As indicated in Fig. 12b, the CF/ER composite loses nearly 80% of its compressive strength, whilst the CF/GNP/ER composite still maintains 59% of its original value, which typically is sufficient due to decreased applied mechanical loads in fire situations.

In addition to considering in-fire performance, it is sometimes also useful to assess post-fire residual loadbearing capacities of aircraft structures, especially in an emergency evacuation. The post-fire mechanical performance of polymer composites may be assessed by analysing their char depth [34]. If a fire damaged composite material can be divided into two distinctive layers, one virgin and one char layer, then the mechanical property S_t of the burnt composite could be estimated using the following simple linear expression [34]:

$$S_t = \left(\frac{d-d_c}{d}\right)S_o + \frac{d_c}{d}S_c \qquad (9)$$

where d_c is the char thickness, d is the original thickness of the composite, and S_c and S_o are the mechanical properties of the char and unburnt (original) material, respectively.

Mechanical property tests performed on fully charred composites by Mouritz and Mathys [35] revealed that fully composite chars have negligible (typically less than 10%) mechanical properties compared to the original material for most composites. Therefore, the proportion of char depth can be used as a direct measure of the loss of mechanical properties (strength and stiffness) of burnt composites. For post-fire assessment, the effect of temperature degradation on the mechanical properties of composites is assumed to produce a char layer that has negligible mechanical properties. This assumption may not be exact. However, since this study is to compare relative post-fire performance of different composites, this assumption is considered acceptable.

Figure 13 compares total mass loss histories of the four types of ER composite panels obtained by the present FDS simulation. Calculating the char depth based on the total mass loss for an average fire damage height of 2 cm, Fig. 14a compares char layer proportions for CF/ER and CF/GNP/ER composites after 75 s fire exposure and Fig. 14b compares the residual post-fire strengths of these composites. The CF/GNP/ER composite can retain about 75% of its ambient temperature strength value. At best, the CF/ER composite retains 68% of its ambient temperature mechanical property, because this comparison is made at 75 s and the CF/ER composite continues burning afterwards.

From the above analyses, it can be concluded that CF/GNP/ER composite can not only self-extinguish in the vertical flame spread test, thus passing the regulatory reaction to fire test for aircraft structures, it can also retain a high proportion of its tensile and compressive strengths.
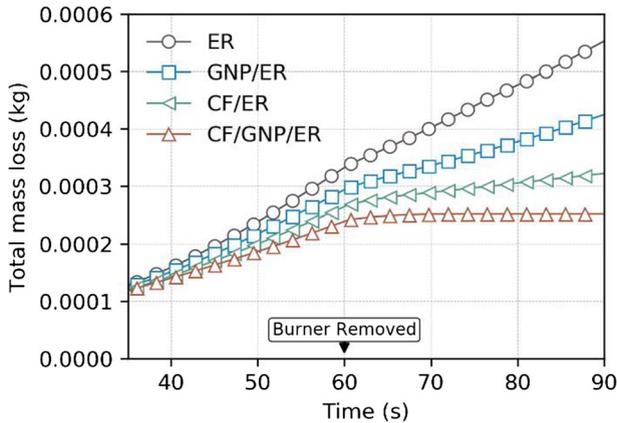
Fig. 13 Total mass loss of different ER composites when exposed to fire

This is true for the in fire as well as post-fire strength properties, due to low structural temperatures experienced by the unburned material as a result of the low thermal conductivity of the char layer and low heat release rate.

6 Concluding Remarks

This paper has presented a coupled FDS model [29] to simulate reaction to fire and temperatures developed in polymer composite panels. The composite materials are epoxy resin (ER) based and include pure ER, carbon fibre (CF) reinforced ER (CF/ER), ER with graphene nanoplatelets (GNP/ER) and CF reinforced GNP/ER (CF/GNP/ER). The aim is to assess their ability to pass the vertical burn test for new aircraft structures and to evaluate their in-fire and
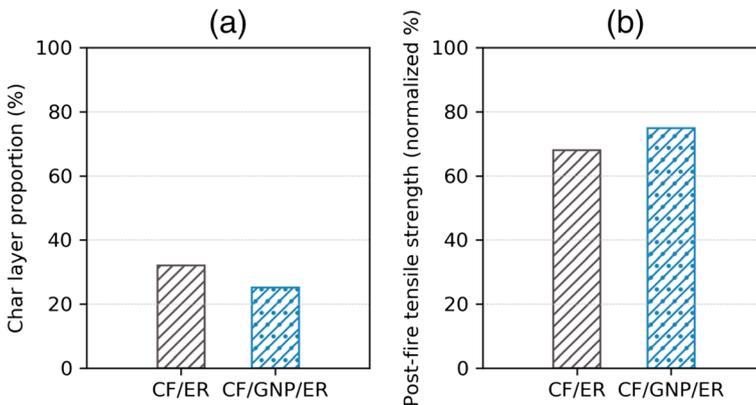
Fig. 14 Comparison of post-fire properties between CF/ER and CF/GNP/ER composites: **a** proportion of char layer depth and **b** ratio of residual mechanical property

post-fire strength properties that can be used in structural integrity evaluation. To assist accurate fire performance analysis, models of thermal, physical and pyrolysis properties of these composites are required and were presented. The following conclusions can be drawn:

1. Graphene nanoplatelets can drastically improve the reaction to fire performance of ER, by reducing thermal conductivity and gas permeability of the char layer.
2. Based on FDS simulations of the standard vertical burn test, ER, CF/ER and GNP/ER composites fail to pass the fire test, due to continuous burning after removal of the fire source and high burn duration. The CF/GNP/ER composite with 1.5%wt% GNP and 50 wt% CF self-extinguishes within 15 s after removal of the burner, and the burn length is low, thus allowing this panel to pass the vertical burn test.
3. The maximum temperature experienced by the CF/GNP/ER composite is much lower than that of the CF/ER system, thus allowing the CF/GNP/ER panel to maintain high in-fire tensile and compressive strengths, being 87% and 59% of the ambient temperature values, respectively. In contrast, these values are reduced to 70% and 21%, respectively, for the CF/ER panel. The in-fire mechanical properties of the CF/ER composite could be even lower because of the continuing burning of the polymer.
4. Similarly, the post-fire mechanical property of the CF/GNP/ER composite is much higher than that of the CF/ER composite due to less mass loss.

It should be appreciated that this paper is based on numerical simulation results of CF/GNP/ER composite that has not been manufactured. Nevertheless, this paper indicates the potential of this material system to pass the vertical burn test and to possess sufficient mechanical properties to ensure structural safety of aircraft structures in fire. Further simulations and experiments are necessary to increase the confidence level of simplifications and assumptions made, but this study has provided fundamental material properties as well as a validated simulation method that could be very useful in near future research work.

Compliance with Ethical Standards

Conflicts of Interest/Competing Interests   Not applicable.

References

1. Wang, Y., Burgess, I., Wald, F., Gillie, M.: Performance-based fire engineering of structures. Perform-Based Fire Eng Struct. 1–363 (2013)
2. Wong, P.M.H., Wang, Y.C.: An experimental study of pultruded glass fibre reinforced plastics channel columns at elevated temperatures. Compos Struct. **81**(1), 84–95 (2007). https://doi.org/10.1016/j.compstruct.2006.08.001
3. Wang, Y.C., Wong, P.M.H., Kodur, V.: An experimental study of the mechanical properties of fibre reinforced polymer (FRP) and steel reinforcing bars at elevated temperatures. Compos Struct. **80**(1), 131–140 (2007). https://doi.org/10.1016/j.compstruct.2006.04.069
4. Wang, Y.C., Kodur, V.: Variation of strength and stiffness of fibre reinforced polymer reinforcing bars with temperature. Cem Concr Compos. **27**(9–10), 864–874 (2005). https://doi.org/10.1016/j.cemconcomp.2005.03.012
5. Wong, P.M.H., Davies, J.M., Wang, Y.C.: An experimental and numerical study of the behaviour of glass fibre reinforced plastics (GRP) short columns at elevated temperatures. Compos Struct. **63**(1), 33–43 (2004). https://doi.org/10.1016/S0263-8223(03)00122-3
6. Soutis, C., Turkmen, D.: Moisture and temperature effects of the compressive failure of CFRP unidirectional laminates. J Compos Mater. **31**(8), 832–849 (1997). https://doi.org/10.1177/002199839703100805
7. Beaumont, P.W., Soutis, C., and Hodzic, A. The structural integrity of carbon fiber composites: fifty years of progress and achievement of the science, development, and applications. Springer (2016)
8. Soutis, C.: Fibre reinforced composites in aircraft construction. Prog Aerosp Sci. **41**(2), 143–151 (2005). https://doi.org/10.1016/j.paerosci.2005.02.004
9. Branch, A.A.I. Report on the serious incident to Boeing B787-8, ET-AOP London Heathrow Airport on 12 July 2013. 2015, Air Accidents Investigation Branch
10. Perret, B., Schartel, B., Stoss, K., Ciesielski, M., Diederichs, J., Doring, M., Kramer, J., Altstadt, V.: Novel DOPO-based flame retardants in high-performance carbon fibre epoxy composites for aviation. Eur Polym J. **47**(5), 1081–1089 (2011). https://doi.org/10.1016/j.eurpolymj.2011.02.008
11. Wang, D., Zhang, Q.J., Zhou, K.Q., Yang, W., Hu, Y., Gong, X.L.: The influence of manganese-cobalt oxide/graphene on reducing fire hazards of poly(butylene terephthalate). J Hazard Mater. **278**, 391–400 (2014). https://doi.org/10.1016/j.jhazmat.2014.05.072
12. Jumahat, A., Soutis, C., Abdullah, S.A., and Bahsan, R. Dimensional and thermal stabilities of nanomodified-epoxy systems. In Appl. Mech. Mater. 2013. Trans Tech Publ
13. Yu, B., Shi, Y.Q., Yuan, B.H., Qiu, S.L., Xing, W.Y., Hu, W.Z., Song, L., Lo, S.M., Hu, Y.: Enhanced thermal and flame retardant properties of flame-retardant-wrapped graphene/epoxy resin nanocomposites. J Mater Chem A. **3**(15), 8034–8044 (2015). https://doi.org/10.1039/c4ta06613h
14. Zhang, Q.J., Wang, Y.C., Bailey, C.G., Yuen, R.K.K., Parkin, J., Yang, W., Valles, C.: Quantifying effects of graphene nanoplatelets on slowing down combustion of epoxy composites. Compos Part B. **146**, 76–87 (2018). https://doi.org/10.1016/j.compositesb.2018.03.049
15. Wang, X., Song, L., Pornwannchai, W., Hu, Y., Kandola, B.: The effect of graphene presence in flame retarded epoxy resin matrix on the mechanical and flammability properties of glass fiber-reinforced composites. Compos Part A – Appl Sci Manuf. **53**, 88–96 (2013). https://doi.org/10.1016/j.compositesa.2013.05.017
16. Zhang, Q.J., Wang, Y.C., Bailey, C.G., Istrate, O.M., Li, Z.L., Kinloch, I.A., Budd, P.M.: Quantification of gas permeability of epoxy resin composites with graphene nanoplatelets. Compos Sci Technol. **184**, (2019). https://doi.org/10.1016/j.compscitech.2019.107875
17. Rallini, M., Natali, M., Monti, M., Kenny, J.M., Torre, L.: Effect of alumina nanoparticles on the thermal properties of carbon fibre-reinforced composites. Fire Mater. **38**(3), 339–355 (2014). https://doi.org/10.1002/fam.2184
18. Zhou, Z.Q., Liu, X.L., Chiu, W.K.: In-plane mechanical properties of a carbon-epoxy composite laminate at elevated temperatures. *Polym Polym Compos*. **15**(3), 207–216 (2007). https://doi.org/10.1177/096739110701500305
19. Zhang, J.P., Delichatsios, M.A., Fateh, T., Suzanne, M., Ukleja, S.: Characterization of flammability and fire resistance of carbon fibre reinforced thermoset and thermoplastic composite materials. J Loss Prev Process Ind. **50**, 275–282 (2017). https://doi.org/10.1016/j.jlp.2017.10.004
20. Tranchard, P., Samyn, F., Duquesne, S., Estebe, B., Bourbigot, S.: Modelling behaviour of a carbon epoxy composite exposed to fire: Part I-characterisation of thermophysical properties. Materials. **10**(5), (2017). https://doi.org/10.3390/ma10050494
21. Lautenberger, C. A generalized pyrolysis model for combustible solids, in Mechanical Engineering. Doctoral Dissertation, University of California, Berkeley (2007)

22. Di Blasi, C., Branca, C.: Mathematical model for the nonsteady decomposition of intumescent coatings. *AICHE J.* **47**(10), 2359–2370 (2001). https://doi.org/10.1002/aic.690471020
23. Zhang, Q. Fire performance of graphene/epoxy composites and feasibility for aerospace applications. University of Manchester (2019)
24. Lautenberger, C., Fernandez-Pello, C.: Generalized pyrolysis model for combustible solids. Fire Saf J. **44**(6), 819–839 (2009). https://doi.org/10.1016/j.firesaf.2009.03.011
25. McGrattan, K., Hostikka, S., McDermott, R., Floyd, J., Weinschenk, C., and Overholt, K. Fire dynamics simulator user's guide. (2013)
26. Tsantaridis, L. and Oestman, B. Mass Loss, Heat and Smoke Release for the SBI RR Products: Poster Paper Presented at Interflam '99, Edinburgh, June–July 1999: (Proceedings Page 1409–1414). (1999)
27. BSI BS EN 13823:2010+A1:2014 Reaction to fire tests for building products. Building products excluding floorings exposed to the thermal attack by a single burning item. BSI (2010)
28. Hietaniemi, J., Hostikka, S., and Vaari, J. FDS simulation of fire spread œ comparison of model results with experimental data. (2004)
29. Stoliarov, S.I., Crowley, S., Walters, R.N., Lyon, R.E.: Prediction of the burning rates of charring polymers. Combustion and Flame. **157**(11), 2024–2034 (2010). https://doi.org/10.1016/j.combustflame.2010.03.011
30. Zhang, J., Delichatsios, M., Colobert, M.: Assessment of fire dynamics simulator for heat flux and Flame Heights predictions from fires in SBI tests. Fire Technol. **46**(2), 291–306 (2010). https://doi.org/10.1007/s10694-008-0072-6
31. Code of Federal Regulations 14 CFR Part 25.858 Cargo or baggage compartment smoke or fire detection systems. Federal Aviation Administration (2015)
32. Papageorgiou, D.G., Terzopoulou, Z., Fina, A., Cuttica, F., Papageorgiou, G.Z., Bikiaris, D.N., Chrissafis, K., Young, R.J., Kinloch, I.A.: Enhanced thermal and fire retardancy properties of polypropylene reinforced with a hybrid graphene/glass-fibre filler. Compos Sci Technol. **156**, 95–102 (2018). https://doi.org/10.1016/j.compscitech.2017.12.019
33. Poutrel, Q.A., Wang, Z.X., Wang, D.Y., Soutis, C., Gresil, M.: Effect of pre and post-dispersion on electro-thermo-mechanical properties of a Graphene enhanced epoxy. Appl Compos Mater. **24**(2), 313–336 (2017). https://doi.org/10.1007/s10443-016-9541-0
34. Mouritz, A.P., Mathys, Z., Gardiner, C.P.: Thermomechanical modelling the fire properties of fibre-polymer composites. Compos Part B – Eng. **35**(6–8), 467–474 (2004). https://doi.org/10.1016/j.compositesb.2003.09.005
35. Mouritz, A.P., Mathys, Z.: Post-fire mechanical properties of marine polymer composites. Compos Struct. **47**(1-4), 643–653 (1999). https://doi.org/10.1016/S0263-8223(00)00043-X

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