EXPERIMENTAL STUDY OF THE BURNING BEHAVIOUR OF A COMMERCIAL CARBON FIBRE COMPOSITE MATERIAL USED IN HIGH PRESSURE VESSELS

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Abstract

This paper presents an analysis on the charring rate experienced by a commercial CFRP material used to construct composite pressure vessels for hydrogen storage and transport applications. An experimental programme using the Cone Calorimeter apparatus explored the effect of incident heat flux, sample thickness and rear face boundary condition on the charring rate, which is critical to the residual mechanical strength under fire conditions. Samples measured 100 mm by 100 mm, with thicknesses of 4.5 mm and 29 mm. Mass loss was determined for each thickness and at heat fluxes between 15 and 80 $kW{\cdot}m^{-2}$. Two back boundary conditions were used: ceramic insulation and an aluminium block, representing bounds on heat loss. A method to estimate the CFRP charring rate is proposed based on mass loss rate measurements and the assumption that the material does not shrink after pyrolysis. Characteristic times of surface oxidation are found to be much longer than those for charring and pyrolysis. Initial peak charring rates are found within the range of 1.5 – 2.3 $mm{\cdot}min^{-1}$ for heat fluxes up to 80 $kW{\cdot}m^{-2}$. Reasonably steady charring rates of below 0.5 $mm.min^{-1}$ only occur with back face heat losses, with a secondary peak for insulated cases.

1. Introduction

Carbon fibre reinforced polymers (CFRP) are novel materials increasingly used to fabricate composite pressure vessels for hydrogen storage and transport applications. Despite their highly desirable mechanical properties (e.g. high strength to weight ratio) [1], their combustible nature presents new fire risks in the storage of pressurised gas. Understanding the performance of the composite under severe conditions of heat exposure is therefore essential for the design of strategies to maintain the integrity of the vessels and the associated consequences should they be subject to a fire (when assuming the pressure relief valve has failed). This requires development of predictive models that can simulate the thermo-mechanical behaviour of the material. This work is specifically focussed on identifying methods that will allow prediction of the charred section from carbon fibre composite materials during the design stage, considering an arbitrary temporally and spatially varying fire boundary condition.

1.1. Thermal degradation and mechanical behaviour of CFRP

The behaviour of CFRP when exposed to severe conditions of heat exposure has been studied by several authors [2-7]. In particular, the composite assessed herein has been studied at material/sample scale within the context of the FireComp project (www.firecomp.info), so that the composite thermal decomposition reactions and mechanical behaviour could be understood [3-7]. Figure 1 shows the characteristic thermogravimetric behaviour of the composite under non-oxidative (Fig. 1a) and oxidative (Fig. 1b) conditions with a heating rate of 5 $°C{\cdot}min^{-1}$. Results provided in Fig. 1a correspond to the

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pyrolysis reaction using different sample preparations, i.e. as a solid piece extracted and as powder ground from the material. These results serve to assess the bounds of variability of the ratio residue – virgin material of the composite product.

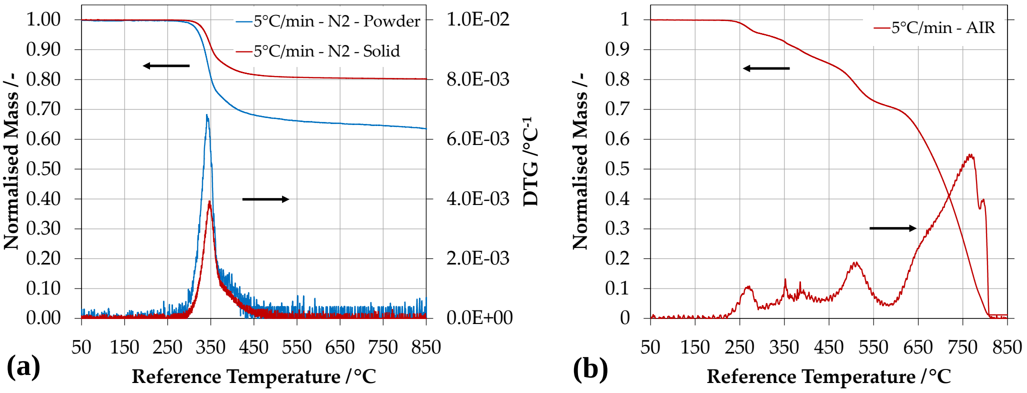

Figure 1. Normalised mass and mass loss rate (DTG) of the composite from thermogravimetric experiments under (a) a non-oxidative atmosphere and (b) air [6] with a heating rate of 5 °C·min^{-1}.

The main pyrolysis reaction corresponds to the polymer adhesive (epoxy) used to bond the carbon fibres, which pyrolyses in the temperature range 300 – 450 °C under a heating rate of 5 °C·min^{-1}. This range is consistent with the piloted ignition temperature range of 314 – 349 °C estimated by Hidalgo *et al.* [7]. Under non-oxidative conditions no further decomposition occurs, with an epoxy residue and carbon fibre left as residue as shown in Fig. 1a. The final mass ratio of char is within the range 65 – 80% of the original mass. Under oxidative conditions this residue proceeds to smoulder [6] in the temperature range 600 – 800 °C as shown in Fig. 1b, which suggests a good fire performance as the insulating char aids to reduce the heat flux delivered to the pyrolysis-reaction zone, therefore gradually reducing the progression rate of the charring front [8-9]. Using this data, an *a priori* assessment of the performance of CFRP subject to fire conditions indicates that a charring response will be observed, but that this will be somewhat simpler to analyse under non-oxidative conditions due to the oxidation reactions occurring at higher temperatures and larger mass residue (char).

Carbon fibre composites are characterised as showing outstanding mechanical properties such as tensile strength due to the remarkable stiffness and strength from the carbon fibres and the cohesion provided to the matrix by adhesive polymers [1]. Under conditions of severe heat exposure, the mechanical properties are reduced due to (1) the softening of the adhesive once the glass transition temperature is achieved (change from elastic to viscoelastic response), and (2) to the pyrolysis of the epoxy inducing a loss of bond between the fibres within the matrix. Alemany Mari *et al.* [4] experimentally demonstrated a proportional reduction of the flexural modulus of CFRP samples with respect to the energy density they absorbed under various heat exposures and times. Furthermore, Quach *et al.* [6] recently confirmed that there is a proportional relationship between the ultimate stress and the non-charred thickness. Therefore, predicting the evolution of the charred section becomes essential for direct assessment of the potential for mechanical failure of these composites under fire conditions.

1.2. Parameters for developing simplified predictive models

The prediction of the charred region propagation for composite materials can be undertaken using detailed pyrolysis models that can simulate the heat transfer and thermal degradation processes experienced by CFRP under various design conditions. Several pyrolysis models have recently been developed with prediction capabilities for charring materials. These include comprehensive treatment of the physics [10,11] and simplified approaches [5]. Despite the fact that solving the physical phenomena related to the evolution of the char layer is fundamentally the correct approach, there is significant uncertainty in the quantification of model and boundary condition parameters [12], which

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make their wider application at an engineering level difficult. Consequently a simpler tool would be of great value in aiding the design of CFRP vessels under wide range of possible fire conditions.

The charring behaviour of CFRP presents one of the main advantages regarding the fire performance of structural elements made of this composite. This behaviour is expected to be driven by the relatively high material density together with the low pyrolysed mass. This means that the char layer will quickly form and will help to protect the remaining material from the fire. Although the literature on the charring of CFRP is not well developed, the charring of timber has been studied in detail [13]. Recent work has identified that the charring rate is strongly dependent on parameters such as the incident heat flux and density of the sample [14]. This is also expected to be the case for CFRP, but since the form used in construction for pressure vessels tends to be thinner than used for common timber applications, the thickness and rear face boundary condition will also play a major role in determining the charring rate for the CFRP and ultimately the loss of mechanical properties.

Parameters such as incident heat flux, sample thickness, and heat losses at the unexposed surface are thus identified as primary factors that may affect the charring rate of the composite, since they strongly determine the thermal evolution under fire conditions. Ideally, simple tools will be based on pre-quantified charring rates as a function of these conditions, so constrained limits and predefined functions could be established for design purposes, without having to solve for the full heat and mass transfer phenomena. This paper aims to develop and verify the essence of such a methodology.

1.3. Aim

The aim of this work is to assess the charring rate (spread rate of the char front under) different heat transfer conditions for a commercial CFRP used for construction of pressure vessels. To investigate the dependence of the charring rate on these conditions, two different back face boundary conditions are explored: (1) an insulated condition with reduced heat losses and (2) a heat sink with significant heat losses. These represent practical limiting conditions within which real end-use behaviours may be encountered.

Characteristic times of the charred region propagation and surface regression are studied for each experimental condition by means of a methodology based on mass loss rate measurements from bench-scale testing. Mass loss rate and charring rate are linked by the change in density between the virgin and charred CFRP. This assessment is first used to evaluate assumptions often made for the design of charring materials in fire, e.g. semi-infinite solid thermal behaviour, steady charring rate and negligible surface oxidation rate, and secondly in determining the limits of applicability of this approach as a function of the heat exposure and the composite thickness.

2. Experimental programme

2.1. Experimental set-up

A series of experiments were performed using the Cone Calorimeter apparatus [15], and samples of 4.5 and 29 mm thickness. The nominal sample size was 100 mm x 100 mm, and two different backing materials are used for the CFRP sample: (1) a ceramic insulation and (2) an aluminium block (heat sink). The sample mass loss evolution was determined for each sample thickness and rear boundary condition for external heat fluxes between 15 and 80 kW·m^{-2}. Table 1 presents a summary of the test conditions.

Table 1. Sample and test conditions for the experimental programme.

Nominal Sample Thickness (mm)	Surface area (m^2)	Heat flux (kW·m^{-2})	Rear face boundary condition
4.5 – 29	0.010	15 – 80	Ceramic insulation (25 mm) – Aluminium block (~ 640 g)

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2.2. Summary of results

The experiments confirmed the hypothesis that CFRP behaves as a charring material, with a first peak of mass loss rate (MLR) followed by a decay due to the char which remains after the pyrolysis of the epoxy. The char consists of epoxy residue and carbon fibres. A secondary peak at the end of the burning phase could be observed for samples with an insulated back face. This is a result of the thermal feedback on the pyrolysis zone when this approaches the insulated boundary. When a thermal heat sink was applied, the secondary peak was not observed or was much attenuated, and the MLR displayed a long decay representative of an approximately constant progression rate of the pyrolysis front. Figure 2 shows a series of samples used for this experimental programme, both before exposure (a) and after being exposed to a heat flux of 80 and 40 kW·m^{-2} for one hour with an aluminium block at the rear face (b, c, respectively). Visually it can be assessed that the sample tested at 80 kW·m^{-2} did experience very minor surface oxidation (white filaments on the surface), but no shrinkage was apparent at the end of the test. The samples exposed to 40 kW·m^{-2} did not experience apparent oxidation, but it is completely charred after an exposure of one hour. It can thereby be concluded that the characteristic times of surface oxidation (smouldering) are significantly longer than those of pyrolysis and charring. In addition, shrinkage due to pyrolysis appears to be negligible.

Figure 2. 29mm thick samples: (a) before being exposed to heat, (b) residue after 80 kW·m^{-2} exposure for an hour (c) residue after 40 kW·m^{-2} exposure for an hour.

Figure 3 shows the mass loss under different external heat fluxes for 4.5 mm thick samples with insulation (Fig. 3a) and aluminium (Fig. 3b) at the back face. Two clear patterns in the mass loss can be identified in Fig. 3a, distinguished by a dotted lined. The first is a domain where pyrolysis gases are generated rapidly after flaming ignition, and the second a domain where virtually no further mass loss is obtained (15 – 40 kW·m^{-2}), or alternatively a significantly reduced rate of mass loss due to smouldering combustion at the surface (50 – 80 kW·m^{-2}). The latter only seems to become pronounced for higher heat fluxes, which confirms the oxidation behaviour shown by thermogravimetry at high temperatures (Fig. 1b) and observed at high heat fluxes (Fig. 2b), but with a minor rate and after flame out. As shown in Fig. 3b, the mass loss for samples tested with a heat sink proceeds at a slower rate, as the same mass consumption is obtained in longer durations. The two domains of mass loss are clearly evident for this testing condition, although a decay in mass loss rate for longer durations is clearly observed for most of the cases.

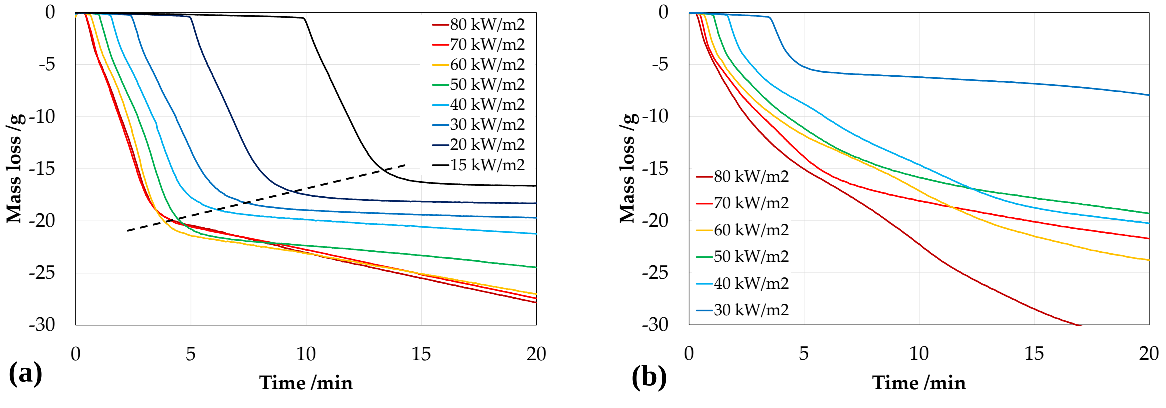

Figure 3. Mass loss curves for 4.5 mm thick samples with (a) a ceramic insulation and (b) an aluminium block at the back face, subject to various incident radiant heat fluxes.

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Figure 4, on different scales, shows the mass loss under different external heat fluxes for 29 mm thick samples with insulation (Fig. 4a) and aluminium (Fig. 4b) at the back face. Samples tested with insulation at the back (Fig. 4a) show two domains of mass loss, as for the thin specimens in Fig. 3a. The first domain experiences three clear stages of mass loss rate characterised by the change in slope. When samples are tested with a heat sink (Fig. 4b), the mass loss presents a more linear behaviour for most of the duration of the experiments, with steeper slopes only at the beginning.

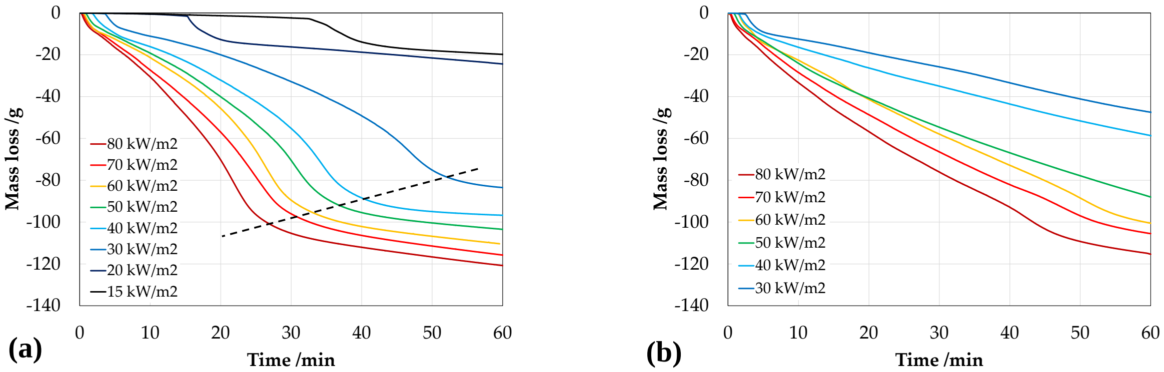

Figure 4. Mass loss curves for 29 mm thick samples with (a) a ceramic insulation and (b) an aluminium block at the back face, subject to various incident radiant heat fluxes.

2.3. Charring rate quantification

The recognised sufficient approach to quantify the charring rate consists in monitoring the temperature evolution within the sample, and identifying the temporal evolution of onset of pyrolysis isotherm [14]. This is, however, not an ideal set-up if mechanical testing is pursued, as the insertion of thermocouples may damage the specimen. Therefore, an approach based on the sample mass loss, similar to the one proposed by Mikkola for charring of wood [16] and represented in Fig. 5, is proposed for this work.

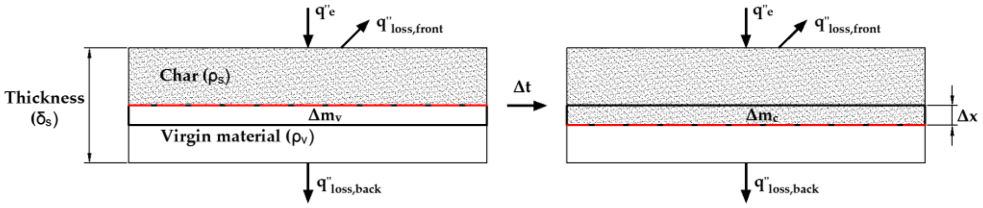

Figure 5. Ideal evolution of the char layer within a sample of thickness (δ_s) exposed to an external heat flux (q''_e) for a time step (Δt), assuming a thin reaction zone.

As shown in Fig. 5, this approach assumes that the pyrolysis reaction zone is sufficiently thin, and that there is no material shrinkage, thus no change in volume after the epoxy pyrolysis. This is in agreement with the experimental observations above. Then, the rate of progression of the char layer front through the depth of the sample, β (mm·min^{-1}), i.e. the region where the composite has completely pyrolysed, can be defined as a function of the section of thickness of material that is pyrolysed, Δx (mm), at each time step, Δt (min):

$$\beta = \Delta x / \Delta t \tag{1}$$

The rate of mass loss experienced by the CFRP sample $\dot{m}_{loss}$ (g·min^{-1}) can be expressed as a function of the propagation rate of the charred front β (mm·min^{-1}):

$$\dot{m}_{loss} = (\Delta m_v - \Delta m_c)/\Delta t = \beta \cdot S \cdot (\rho_v - \rho_c) \tag{2}$$

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where Δm_v (g) and ρ_v (kg·m^3) are the mass and density of the section Δx before charring (virgin material), Δm_c (g) and ρ_c (kg·m^3) are the mass residue and volume of the section Δx after complete pyrolysis (char), and S (m^2) is the sample surface area. Since there is no change in volume after pyrolysis, the char density can be defined as a function of the virgin density:

$$\rho_c = r_c \cdot \rho_v \tag{2}$$

where r_c is the mass ratio char versus virgin material obtained by thermogravimetry under non-oxidative conditions (Fig. 1a). Rearranging Eq. 2, the charring rate can effectively computed as:

$$\beta = \frac{\dot{m}_{loss}}{S \cdot \rho_v \cdot (1 - r_c)} \tag{3}$$

The parameters required for estimating the charring rates presented herein are presented in Table 2.

Table 2. Sample and material properties used for the estimation of charring rates.

	S (m^2)	ρ_v (kg·m^{-3})	r_c (-)
Nominal value	0.010	1360	0.30
Uncertainty	± 0.001	± 30	± 0.10

Figures 6 and 7 show the charring rates calculated using the method above for 4.5 and 29 mm thick samples, respectively, when exposed to various incident radiant heat fluxes. In order to simplify the interpretation of these curves, the timelines for each case have been normalised such that the peak mass loss rate coincides with t = 0 min. As shown in Fig. 6, the first charring rate peak for thin samples with insulated rear face is within the range 1.5 – 2.3 mm·min^{-1} with a weak dependence on heat flux. For samples with a heat sink, lower charring rates are observed for lower heat fluxes (< 50 kW·m^{-2}), but the same maximum value (below 2.3 mm·min^{-1}) is observed for high heat fluxes. An insulated boundary results in a decay of the first peak down to a minimum charring rate of about 1.0 mm·min^{-1} before increasing to second peak for heat fluxes larger than 30 kW·m^{-2}. On the contrary, a heat sink boundary induces a decay period following the peak resulting in a quasi-steady state charring rate below c. 0.5 mm·min^{-1}.

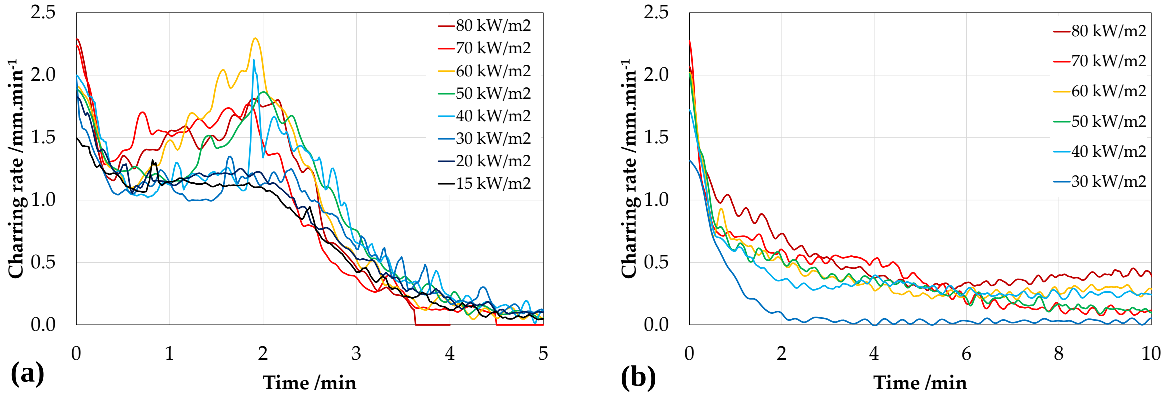

Figure 6. Calculated charring rates for 4.5 mm thick samples with (a) ceramic insulation and (b) aluminium block at the back face, subject to various incident radiant heat fluxes. Note the different time scales on the abscissa.

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Charring rates for thick samples present similar characteristic behaviour as thin samples, but with a different time scale (Fig. 7). The insulated samples present a first peak located between 1 – 2 mm·min^{-1} for heat fluxes between 20 – 80 kW·m^{-2}. This is followed by a decay with a quasi-steady state charring rate that is strongly dependent on the incident heat flux, followed by a steady increase achieving a final peak for heat fluxes larger than 15 kW·m^{-2}. Samples with a heat sink show an initial peak located at 1.3 – 2.2 mm·min^{-1} followed by a decay yielding something approximating well to a quasi-steady behaviour.

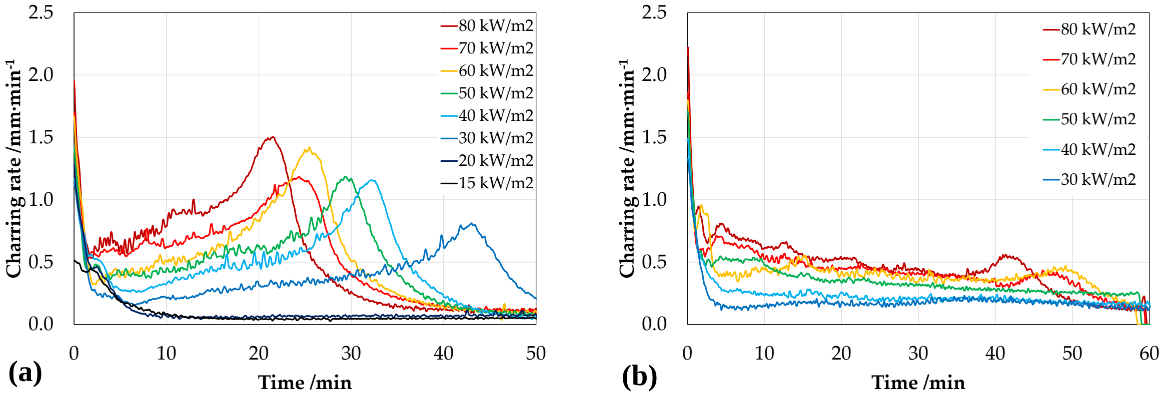

Figure 7. Calculated charring rates for 29 mm thick samples with (a) ceramic insulation and (b) aluminium block at the back face, subject to various incident radiant heat fluxes.

2.4. Discussion

The presented results clearly show that the charring rate strongly depends on the boundary condition at the back face of the CFRP. An approximately constant charring rate is only achieved when a heat sink is used. Furthermore, this rate is initially strongly dependent on the incident heat flux for thick samples, while there is a suggestion that it converges more quickly for thin samples when exposed to high heat fluxes (above 40 kW·min^{-1}). The quasi-steady state charring rate for this case is below 0.5 mm·min^{-1}, and even lower at reduced heat fluxes. For relevant scenarios, it is suggested that design practices might consider initial transient charring rates up to a maximum value of 2.3 mm·min^{-1} for heat fluxes up to 80 kW·min^{-1}. However, from the time when the thermal wave can be assessed as reaching the rear surface, a peak charring rate of 0.5 mm·min^{-1} might be justified for this material. While higher rates are observed for insulating rear surfaces, with much stronger dependence on the level of the incident flux, these conditions are expected to be of less relevance to many practical scenarios.

Clearly these results pertain to a given material and idealised exposure conditions, thus cannot be taken as definitive, nor to be assumed as applying in general. But in reality much greater uncertainties are associated with the specification of the exposed surface heat fluxes, which depend on an arbitrary fire boundary condition and may vary in both space and time. Thus, the current observations suggest potential simplifications in theoretical or modelling treatments arising from the fact that the insulating behaviour of the char limits regression rates at higher fluxes under some scenarios, provided that it can be assumed that any rear surface insulation effects are not significant. Considering also the significant uncertainties in the mechanical performance of the cylinder, including localised effects, the ability to specify a bounded parameter, i.e. realistic peak charring rates, might be justified under some conditions, potentially providing a great simplification of the overall coupled fire-thermal-structure problem.

3. Conclusions and future work

Predictions of charring rates for carbon fibre-polymer composites have been presented as a function of the external thermal exposure and unexposed face boundary condition. These predictions have been formulated as a function of mass loss data obtained at the sample scale. This method has potential application due to the strong relationship between mechanical properties and charred section, and may

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be used to improve the mechanical properties assessment during coupled thermo-mechanical analysis. Results presented herein show that steady state charring rates only occur in the case of substantial heat losses through the back face of the material. These are also strongly dependent on the incident heat flux for thick samples. An insulated condition yields an upper limit on the charring rate, with near peak values of 1.5 – 2.3 $\mathrm{mm \cdot min^{-1}}$ obtained for heat fluxes within the range of 30 – 80 $\mathrm{kW \cdot m^{-2}}$.

Further work is needed to evaluate the actual boundary conditions which may pertain at the back face of the vessel during use, i.e. when filled with high pressure gas, thus providing more confidence in the guidance on the bounds for the range of charring rates that would apply for end-use conditions. Additionally, an uncertainty assessment is required in order to evaluate the assumption of a thin reaction zone, and its effect on the mechanical behaviour.

Acknowledgments

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