THERMAL AND REACTION TO FIRE PROPERTIES OF CFRP UNDER VARIOUS HEAT IMPACT SCENARIOS -SPECIFIC HAZARDS

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Abstract

This work addresses specific dangers originating from CFRP structures under thermal load. It investigates effects of various types of heat loads on epoxy based CFRP, starting below the max. operational temperature limit (ca. 135°C), up to rapid matrix degradation (ca. 350°C) in thermal equilibrium or rapid heat up during one sided irradiation. Heat flux ranges from developing and fully developed fires (50 and 80 kW/m^2) up to heat fluxes typical for nuclear heat blasts (up to 5000 kW/m^2). Additionally the impact of improvised fire accelerants and the formation of respirable fiber fragments are investigated.
Solutions for a safe application are offered, focusing on:
- Definition of threshold energies for minimum thermal impact, necessary for a safety relevant drop of residual strength. Infrared spectroscopy as a non destructive testing method for visually or ultrasonically not observable heat damage.
- Characterization of degradation processes with respect to temperature and strain gradients throughout the panels, dependent on type of heat load and heat flux levels.
- Definition of critical conditions in various fire scenarios (including improvised fire accelerants) for the evolution of respirable carbon fiber fragments and loss of mechanical integrity.

1. Introduction

Carbon fiber reinforced plastics (CFRP) are widely used in lightweight construction. However their thermal performance is limited. Several dangers arise during heat load, challenging a safe application of components especially for highly threatened systems such as military aircraft. For a moderate thermal load starting below the operational temperature limit, a significant drop of residual strength may occur without visually or ultrasonically observable incipient heat damage [1]. Possible causes for local thermal overload are typically pipe bursts, malfunctions in electric equipment, accidental overheat during repair, engine overheating or impingement of engine exhaust, lightning strikes or fires etc. [2]. Additionally there is a difference with respect to thermal damage whether the heat load occurs in a thermal equilibrium or by means of a rapid heat up. Reaction to hot air or one sided irradiation may differ dependent on heat flux.
This work addresses specific dangers originating from CFRP structures under thermal load and offers solutions for a safe application, focusing on:
- Definition of threshold energies for minimum thermal impact, necessary for a significant drop of residual strength. Infrared spectroscopy as a non-destructive testing method for visually or ultrasonically not observable heat damage.
- Characterization of degradation processes with respect to temperature and strain gradients throughout the panels, dependent on type of heat load and heat flux levels.

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- Definition of critical conditions in various fire scenarios (including improvised fire accelerants) for the evolution of respirable carbon fiber fragments and loss of mechanical integrity.

2. Material

All tests were carried out with the carbon fiber reinforced epoxy system HexPly® 8552/IM7 from Hexcel Composites GmbH (Stade, Germany). The matrix system consists of an aromatic epoxy resin (EP, ~29 wt.%), which is toughened with a temperature resistant thermoplastic polyether sulfone (PES, ~6 wt.%) [3]. The fiber content is ~65 wt.%. The investigated laminates consist of 16, 32, 48 uni-directional plies resulting in 2, 4, 6 mm thick quasi-isotropic (QI) lay-ups: [[0/45/90/-45]2]S etc.. The prepregs were cured in an autoclave according to the manufacturer's recommended conditions. Ultrasonic C-scans were performed to ensure that the laminates were free of delamination, voids and fiber orientation errors. The cured laminates were cut with a water-cooled diamond wheel saw.

3. Experimental

One sided irradiation of 2, 4, 6 mm thick 100 x 100 mm^2 samples is carried out with a cone shaped electrical heater of a cone calorimeter (see below) at heat fluxes of 50 and 80 kW/m^2 for various exposure times from 3s to 80s prior to ignition. Heat fluxes between 500 and 1750 kW/m^2 are applied by a Xenon lamp on 20 x 10 x 2 mm^3 samples for 0.5s to 5 s [4]. Laboratory scale experiments with fire accelerants are performed on horizontally orientated 2, 4, 6 mm thick 100 x 100 mm^2 panels with various amounts (5g to 50g) of a mixture of 90% diesel fuel and 10% petroleum ether [5].
Changes in the composition of the polymer matrix due to the thermal load were analyzed by micro attenuated total reflection Fourier Transform Infrared Spectroscopy (µ-ATR-FTIR). Spectra were recorded with a Bruker Tensor 27 spectrometer and a Harrick ATR cell with a silicon crystal (diameter: 0.1 mm) on the specimen's surface.
Interlaminar Shear Strength (ILSS) tests for the specimen with a thickness of 2 mm were performed in accordance to EN 2563 [6].
Reaction-to-fire characteristics such as heat release, mass loss, smoke, soot etc. were analyzed with a cone calorimeter (Fire Testing Technology) according to ISO 5660 [7].
A JEOL JSM-6480 LV scanning electron microscope was applied for the determination of fiber diameters. For each given value 20 fibers were measured and averaged.

4. Results and discussion

4.1. Visually not observable damage by moderate thermal load under equilibrium conditions

Moderate thermal load starting below the max. operational temperature limit (ca. 135°C) may cause damages which cannot be observed visually. As no delaminations or other severe defects occur, also ultrasonic scans are not able to identify a significant loss of residual strength. Fig. 1 depicts ultrasonic scans of several samples which were conditioned at 240°C and 280°C for various periods of time. Additionally the relative interlaminar shear strength after thermal load is given. For samples conditioned at lower temperatures than 240°C no defects are indicated by ultrasonic analysis at all, even for periods of time up to one year when minimum residual strength of 50 % are obtained [1]. Thermo-oxidative matrix degradation starts at the samples` surface in contact to air and penetrates the bulk material for prolonged ageing, but severe degradation is limited to areas close to the surface (ca. 100 µm for 200 days at 200°C [3]). However, the fiber-to-matrix adhesion is also reduced in the bulk material in the absence of air. Fiber-to-matrix adhesion, as the weakest factor to retain residual interlaminar shear strength, dominates the performance of a CFRP after thermal load.
Infrared spectroscopy is very sensitive to a matrix degradation and therefore is able to detect moderate thermal load. This technique allows characterizing changes in the chemical composition of the matrix

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non-destructively. Thermally loaded 8552/IM7 samples typically show a preferred degradation of the epoxy resin compared to the polyethersulfon toughener [3], indicated by the relative intensity ratio of IR-bands characteristic for the epoxy resin (1512 cm^{-1}) and the polyethersulfone (1486 cm^{-1}). Fig. 1 additionally provides the relative content of the epoxy resin next to the polyethersulfon toughener. Infrared spectra were recorded at the samples` surface after thermal loading. Therefore infrared spectroscopy provides an easy to use, non-destructive tool to predict residual strength for moderate thermal load [8].

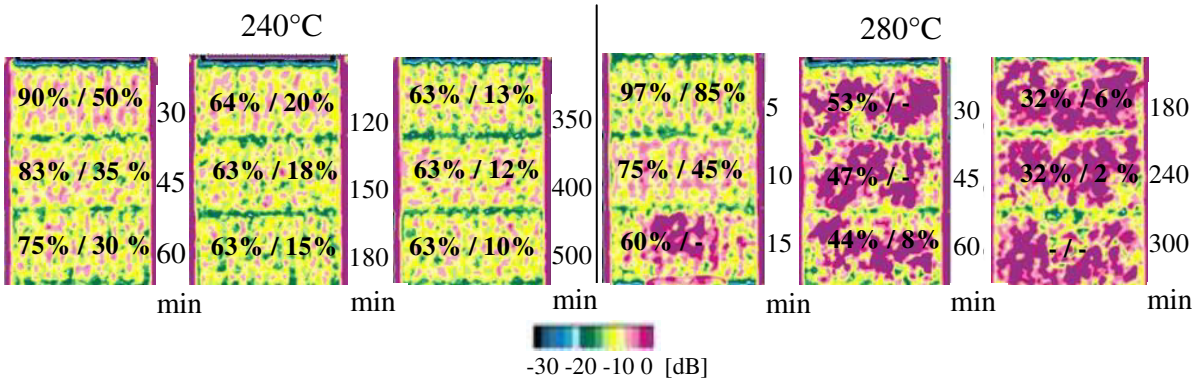

Figure 1: Ultrasonic C-scans of thermally loaded CFRP specimens with given residual ILS strength (left value) and residual epoxy resin to polyethersulfon ratio at the surface determined by IR-spectroscopy (right value)

4.2. Differences in degradation mechanisms by a rapid heat up under one-sided irradiation

Under conditions of a thermal equilibrium, predominantly the occurring temperature determines the degradation progress for a specific polymer matrix. During a rapid heat up as for example by one-sided irradiation, a damage of a CFRP material is influenced by additional parameters. Heat absorption and reflection, heat capacity, heat conduction through the material, formation of temperature and strain gradients accompanied by delaminations characterize the degradation process [9]. During a short term heat up close to ignition temperature (400°C), typically temperature and strain gradients forming delaminations are responsible for a significant decrease of mechanical strength.
Heat fluxes of 50 and 80 kW/m^2, which are typical for developing and fully developed fires, respectively, do not lead to a significant drop of residual strength, as long as a certain threshold value for the applied heat energy per volume is not exceeded (see Fig. 2). For the investigated material, an applied energy per volume of ca. $5 \cdot 10^5$ kJ/m^3 defines a limit, up to which no severe damage of a CFRP component is expected. This threshold value is independent of the material thickness, irradiation time and heat flux. However, for a higher range of heat fluxes characteristic for nuclear heat blasts (500 to 1750 kW/m^2) this threshold is shifted to a higher value by nearly one order of magnitude. The main reason for this shift is the lower irradiation time (<5s). With increasing heat flux the damage process is increasingly limited to areas close to the surface, as the polymer matrix provides limited heat conduction.
Therefore maximum energy per volume levels, allowing a safe application of CFRP, have to be determined for various heat flux scenarios.

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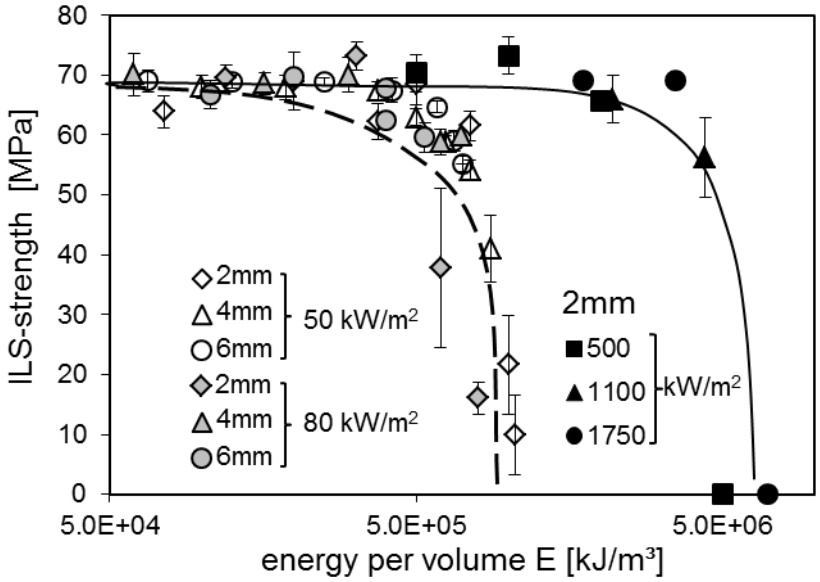

Figure 2: ILS-strengths plotted vs. energy per volume for CFRP 8552/IM7 irradiated at significantely different heat flux levels (< 100 kW/m^2 and > 500 kW/m^2)

4.3. Impact of improvised fire accelerants

Laboratory scale tests with fire accelerants show a significant loss of residual strength dependent on the amount of fire accelerant and the thickness of the 100 x 100 mm^2-panels (Figure 3). For 2 mm thick panels, 15 g of the fire accelerant are sufficient for a nearly complete loss of the panels´ mechanical integrity, whereas 6 mm panels retain about 80% of their initial strength. Combustion of the polymer matrix leads to a relative mass loss of max. 5% for the 2 mm panels and 1 % for the 6 mm panels, which does not significantly contribute to the heat release of the fire accelerant [10]. Damaged areas indicated by delaminations increasingly penetrate the material with increasing amounts of fire accelerant. Temperatures on the backside of the panel reach maximum values of 350°C for 2 mm thick samples and ca. 260°C for 6 mm thick samples. Front side temperatures are assumed to be beyond 400 °C, typically necessary for ignition [10]. Therefore, thin panels and sandwich structures are prone to failure due to the impact of improvised fire accelerants. When 500 ml of a fire accelerant is applied on an aircraft sandwich structure (see Fig. 4), severe damage is observed. After combustion lasting several minutes, the top CFRP layer is delaminated and detached from the honeycomb core. At the backside no delaminations are observed.
In consequence, users of CFRP systems have to be aware of the fact, that these systems can be easily damaged by arson attacks.

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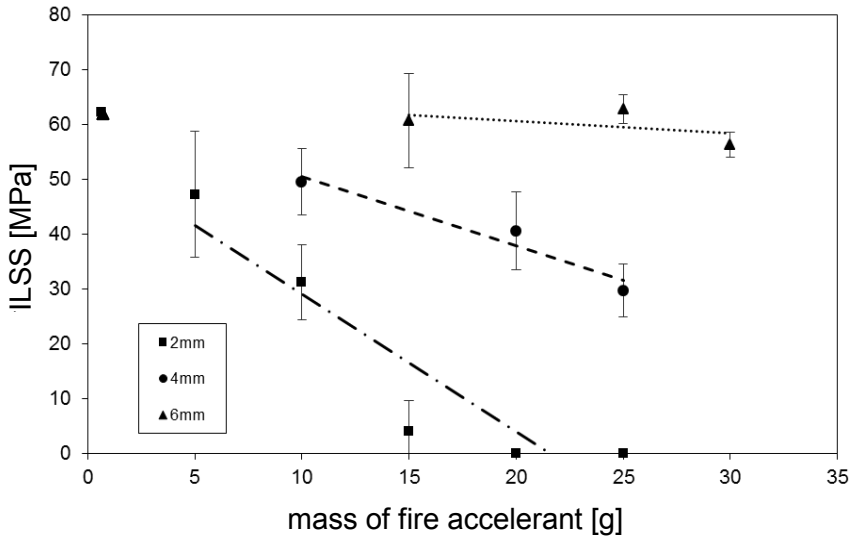

Figure 3. Residual Interlaminar shear strength (ILSS) in the center of various thick, horizontally positioned 100 x 100 mm^2 panels after application of various amounts of a fire accelerant

Figure 4. Helicopter CFRP sandwich structure during application of improvised fire accelerant

A non-destructive evaluation of the panels after the laboratory scale tests is carried out by infrared (IR) spectroscopy. IR-spectra recorded on the backside of the panels allow a correlation of the matrix degradation with the observed maximum temperatures. Figure 5 presents this empirical correlation by the relative intensity ratio of IR-bands characteristic for the epoxy resin (1512 cm^{-1}) and the polyethersulfone (1486 cm^{-1}). It is clearly indicated, that higher temperatures correlate to a preferred degradation of the epoxy resin.
In principle this technique can be used to determine the residual strength of a thermally loaded CFRP. Chemometric analyses of IR spectra additionally allow a separate estimation of the temperature and the duration of a heat impact [11].

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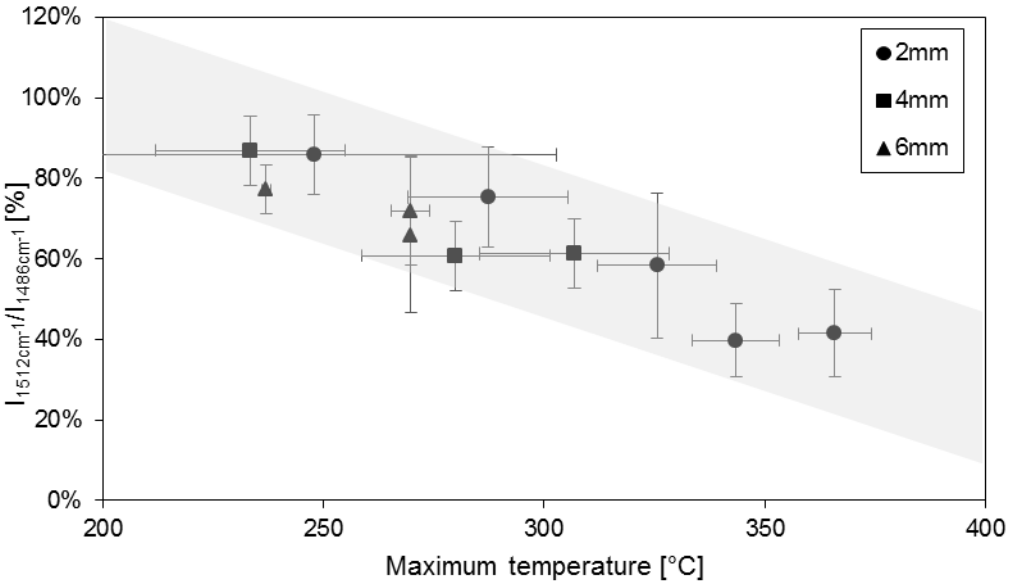

Figure 5: Correlation of resin degradation (intensity ratio of infrared spectroscopic bands characteristic for epoxy resin (1512 cm^{-1}) and polyethersulfon (1486 cm^{-1}) with reached backside maximum temperatures during application of various amounts of fire accelerant on 2 - 6 mm thick CFRP panels

4.4. Formation of respirable carbon fiber fragments

Recently, elevated concentrations of respirable fiber dust were detected during handling of combusted carbon composite material after fire [12, 13], requiring personal protective equipment especially for rescue forces and police [14]. Fibers are considered to be respirable according to the definition of the world health organization (WHO), when they are thinner than 3 µm, longer than 5 µm and the length to diameter ratio is more than 3. Thermal degradation of carbon fibers is accompanied by an overall decrease of the fiber diameter and the formation of surface defects, which form large holes with prolonged thermal load and let the fibers break easily [15]. Fig 6 shows a pair of an IM7 carbon fiber, with an initial diameter of 5.3 µm. After 20 min of thermal treatment at 650°C the diameter is reduced to ca. 2 µm. A minimum temperature of ca. 600°C for a significant reduction of the fiber diameter was observed. Therefore a real fire is prone to form respirable fibers only when it is fully developed and high fuel loads occur.
In contrast to a fire, where fibers thinner than 3 µm may be formed, fiber fragmentation by mechanical processing such as drilling, cutting and milling starts from thicker fibers with initial diameters typically more than 5 µm for commercial fibers. A fragmentation forming respirable fibers with dimensions according to the WHO definition is less likely without thermal load. Guidelines for a safe mechanical processing are given in [16].

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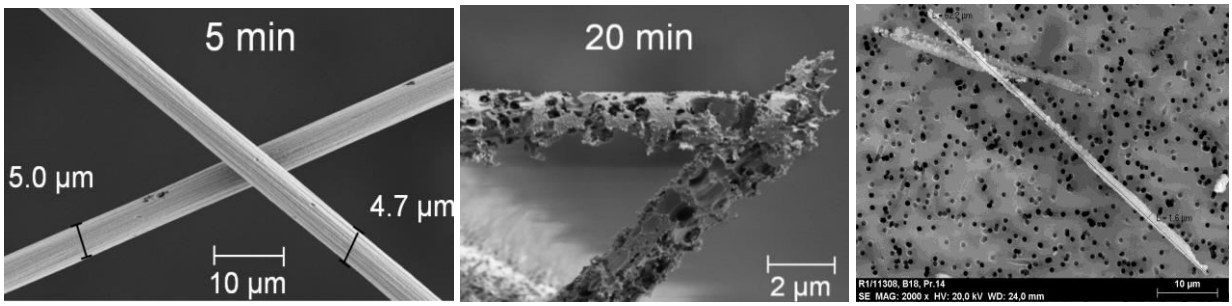

Figure 6: Scanning electron micrographs of a IM7 fiber pair after thermal treatment at 650°C for 5 and 20 min and a fiber fragment after a fully developed kerosene fire (right side) [13]

5. Conclusion

CFRP imply various hazards when exposed to thermal load. Especially for military aircraft a high risk of thermal damage exists. Various scenarios have to be considered, which reveal the material´s weaknesses.
CFRP may significantly loose strength even due to a moderate thermal load, which is not accompanied by visually detectable damage. Also ultrasonic scans are not sensitive enough to identify a possible need of repair. Infrared spectroscopy provides a non-destructive testing technique, which is able to reliably predict residual strength for samples with unknown, incipient heat damage.
Damage mechanisms are distinctively different for thermal loads under equilibrium conditions or for rapid heat up. The formation of temperature and strain gradients, which may form delaminations, dominates the degradation mechanism during rapid heat up. For one-sided irradiation, threshold energies for minimum thermal impact are defined, necessary for a significant drop of residual strength. As long as this energy is not exceeded, a safe application of a component is guaranteed. However, this threshold value is not constant for significantly different heat flux ranges, characteristic for fires or nuclear heat blasts
Improvised fire accelerants may cause severe damage on CFRP structures. Especially sandwich components are vulnerable in this context.
Respirable fiber fragments may be formed during a fire, as the diameter of the carbon fiber decreases with thermal load. However, a possible health hazard is limited to scenarios with temperatures beyond ca. 600°C, which are characteristic for fuel fires.

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