LONG-TERM HIGH TEMPERATURE AND FIRE DEGRADATION OF CARBON/POLYIMIDE COMPOSITES

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1. Introduction

In aero-engine applications, the high durability requirements necessitate for composites that can efficiently withstand a combination of complex mechanical and hygrothermal loads over their service life. High performance epoxy-based composites are nowadays being utilised in structural components in the front "cold" section of aero-engines such as fan blades, fan containment cases and ducts [1]. Nevertheless, the inherently low thermal stability of epoxies in temperatures over 180°C renders them unsuitable for components in the engine sections (past the fan) with higher thermal requirements [1-3]. Such limitations hinder the wider exploitation of polymeric fibre-reinforced composites to even further decrease weight of components and as a consequence achieve CO_2 emission reductions aligning thus with the Flightpath 2050 Europe's Vision for Aviation [4].

Organic resins with higher thermal stability such as Bismaleimides (BMI), Cyanate Esters (CE), Polyimides (PI) and Phthalonitriles have been readily available for a long time and successfully used in the electronics, energy, machinery and aerospace sectors [5-8]. Along those lines, the authors have previously reported the development and assessment of a thermoset polyimide-based composite system (T650/NEXIMID® MHT-R) with a glass transition temperature (T_g) of approximately 370°C (up to 420°C) suitable for high temperature aero-engine applications [9-13]. The study presented here reports preliminary results on the effect of long-term thermal exposure on the performance of these polyimide-based composites as well as their response to fire exposure.

2. Experimental

2.1. Material systems and manufacturing

The composites used in this study were made of CYTEC Thornel® T650/35 8HS carbon fibre weave (370 g/m^3) featuring a 1% UC.309 epoxy-compatible sizing and NEXIMID® MHT-R thermoset polyimide (NEXAM Chemical AB) [9]. Quasi-isotropic laminates (350×350 mm) with a $[(-45/45)/(90/0)]_{2S}$ layup (eight bi-axial fabric layers) were manufactured using Resin Transfer Moulding, with a thickness of approximately 3.2 mm and a fibre volume fraction of 58±1% [9].

2.2. Thermal Ageing

For the thermal ageing of the T650/MHT-R composites, two batches of six specimens were thermally aged in a temperature-controlled environmental chamber for 500hrs and 1000hrs at 320°C in air

environment and subsequently tested in tension, compression and Short-Beam Shear (SBS) at ambient temperature.

2.3. Mechanical Testing

To evaluate the effect of elevated temperature and long-term thermal exposure on the mechanical performance of composites two sets of tests were carried out: tensile, compression, SBS tests at 200°C and 320°C (set 1) as well as tensile, compression, SBS tests at ambient temperature on specimens aged for 500hrs and 1000hrs in air at 320°C (set 2).

Tensile testing was carried according to ASTM D3039 standard [14] for six specimens at a constant cross-head speed of 1 mm/min using an Instron 5801 servo-hydraulic machine equipped with a 100 kN load cell. The loading scheme comprised loading of the specimens up to catastrophic failure. Compressive testing was conducted on six specimens using a fixture that transfers load through a combination of shear and end loading, i.e. Mixed Load Transfer (MLT) on six 80×12 mm specimens [15] at a 1 mm/min rate up to catastrophic failure using the same testing configuration as in tension (see above). The elastic modulus in bothe tension and compression while the stiffness was determined by linear fit of stress vs. strain curves in the elastic region of the stress-strain curve (0.1–0.3% strain). SBS testing was carried out in three-point bending with a 4:1 span-to-depth ratio using an Instron 5801 servo-hydraulic machine equipped with a 1 kN load cell (ASTM D2344) [16]. To facilitate testing at elevated temperature an Instron environmental chamber with temperatures capability from -150°C to 350°C was fitted in the aforementioned testing apparatus. For tension and compression, strain measurement was carried out using Digital Image Correlation (GOM Aramis).

2.4. Fire Reaction Testing

For the assessment of the fire-reaction properties of the T650/MHT-R composites, Cone Calorimetry (CC) was employed. CC is a bench-scale test which measures fire reaction properties of combustible materials in oxygen environment and provides a series of fire reaction properties, heat release rate, time-to-ignition, smoke density, and yields of CO_2 and CO, to name a few. In the CC fixture used in this study, the specimen with dimensions 100×100 mm was fixated on a metal sample holder which was placed on the load cell that monitored the weight of the sample during the experiment. The cone was mounted horizontally and the edges of the sample were closed. The testing was carried out according to ISO 5660-1 standard at 50 kW/m^2 and 70 kW/m^2 on three specimens per heat flux. The tests were performed on conditioned specimens (7 days) at 23±2ºC and 50±5% relative humidity [17].

3. Results & Discussion

3.1. Mechanical performance of T650/MHT-R Composites

An overview of the results from the experimental procedure described in the previous section is presented in Table 1. In particular, for tension and compression the change in modulus, strength and failure strain is shown whereas for SBS only strength values are presented.

With regards to the performance of T650/MHT-R composites at elevated temperature: the increase in temperature did not have any effect on the fibre-dominated properties, i.e. tensile properties. Note that no tensile testing was conducted at 200°C since at 320°C no significant change on the properties was observed. However, the matrix and fibre/matrix interface-dominated properties (compression and SBS) were affected by the increased temperature. As can be seen in Figure 1, where normalised modulus and strength are shown, at 200°C the T650/MHT-R composites lose approximately 20% of their stiffness and 30% of their strength in compression. While further increase of temperature from 200°C to 320°C has no significant influence compressive performance; nevertheless the SBS strength continues to decreases even more rapid above 200°C.

Table 1. Performance comparison of the T650/MHT-R composites at different temperatures and after thermal ageing.

Property	*RT*	*200°C*	*320°C*	*500hrs at 320°C*	*1000hrs at 320°C*
Tension					
Modulus (E_t), GPa	45.0±0.5	N/A	41.2±0.9	41.9±0.5	35.2±1.7
Strength (F^{tu}), MPa	488.1±34.6	N/A	496.0±17.3	455.1±5.1	293.2±14.9
Strain-to-failure (ε_f), %	1.3±0.0	N/A	1.3±0.0	1.2±0.0	1.0±0.0
Compression					
Modulus (E_c), GPa	46.2±1.6	38.9±1.4	37.0±0.8	38.8±1.2	28.7±9.6
Strength (X^C), MPa	393.0±20.3	268.3±3.4	272.6±31.6	170.0±13.7	45.4±17.7
Strain-to-failure (ε_f), %	0.9±0.1	0.8±0.1	0.8±0.1	0.5±0.1	0.2±0.1
Short Beam Shear					
Strength (F^{sbs}), MPa	41.3±1.7	38.2±1.5	28.1±3.7	18.2±2.2	6.5±0.1

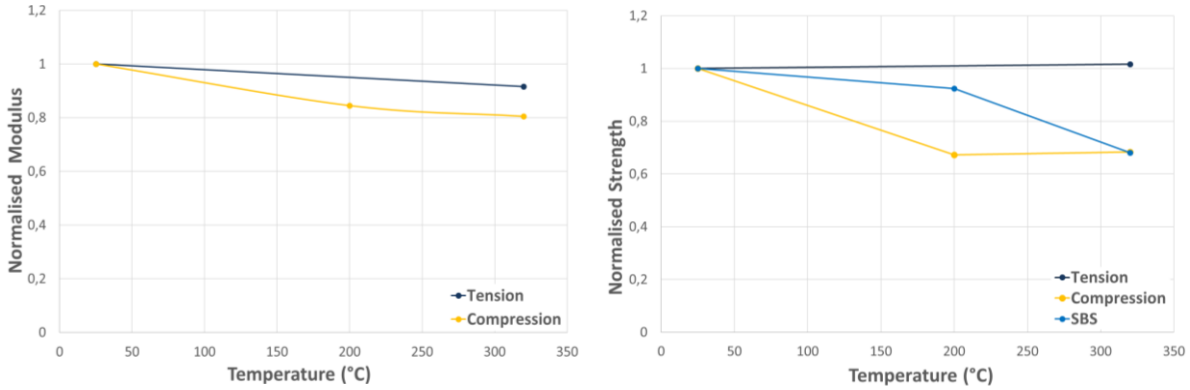

Figure 1. Normalised modulus and strength for tension and compression at ambient temperature, 200°C and 320°C.

As for the thermal ageing, considering Table 1 and Figure 2, it seems that the exposure to 320°C has a quite detrimental effect especially on the matrix and fibre/matrix interface-dominated properties. After 1000hrs of exposure to 320°C, the T650/MHT-R composites lose approximately 80% of their stiffness and strength in compression and Short-Beam Shear.

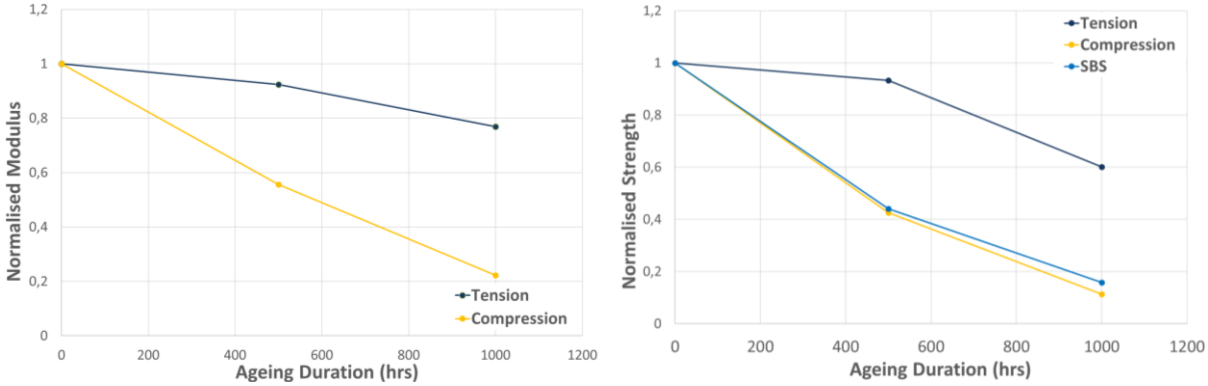

Figure 2. Normalised modulus and strength for tension and compression for no ageing and after ageing for 500hrs and 1000hrs at 320°C.

Similarly in tension, past 500hrs exposure the T650/MHT-R composites lose approximately 20% of the modulus and 40% of their strength. It should be noted that after 1000hrs of exposure to 320°C, a weight loss of approximately 8% throughout the samples was noted (less than 2% after 500hrs). The degradation of the polyimide observed mainly on the surface and free edges of the samples seems to have played a significant role on the degradation of the mechanical performance.

3.2. Fire Reaction of T650/MHT-R Composites

The results from the Cone Calorimetry testing at 50 kW/m^2 and 70 kW/m^2 of T650/MHT-R specimens are presented in Table 2 while the Heat Release Rate and Smoke Production Rate plots and tested samples for both exposures are shown in Figure 3 to Figure 6. Considering the fire reaction properties presented in Table 2, it can be seen that the 50 kW/m^2 heat flux was not adequate to ignite the specimens whilst the heat release was remarkably low, approximately 7 kW/m^2. By the end of the test, the specimens had lost approximately 9% of their original weight. As can be seen in Figure 6, the front face in all three specimens a degradation of the MHT-R resin was observed. Approximately 90s after the flame exposure, cracking sounds were recorded and after 2.5 min smoke was observed emanating from the rear side of the specimens. The visual observation of the specimens after the exposure indicated that delamination had occurred mainly on the front (two out of three specimens) and less on the rear side (one out of three specimens) of the specimens. Even though no dissection and optical microscopy was performed, the visual observation suggested that delamination had formed between the surface and the adjacent ply.

Table 2. Cone Calorimetry test results of T650/NEXIMID® MHT-R specimens at 50 kW/m^2 and 70 kW/m^2.

Property	50 kW/m^2	70 kW/m^2
Flashing t_{flash} (min:s)	-	-
Ignition, t_{ign} (min:s)	No ignition	3:08
All flaming ceased, t_{ext} (min:s)	-	-
Test time, t_{test} (min:s)	10:00	30:00
Peak heat release rate, q_{max} (kW/m^2)	7	29
Average heat release 3 min, q_{180} (kW/m^2)	-	21
Average heat release 5 min, q_{300} (kW/m^2)	-	20
Total heat produced, THR (MJ/m^2)	1.2	44.8
Peak smoke production, SPRmax (m^2/m^{2}s)	<0.05	0.1
Total smoke production over the non-flaming phase, TSP_{nofl} (m^2/m^2)	4.0	2.3
Total smoke production over the flaming phase, TSP_{fl} (m^2/m^2)	-	14.2
Total smoke production, TSP (m^2/m^2)	4	16.5
Sample mass before test, M_0 (g)	49.6	49.7
Sample mass at sustained flaming, M_s (g)	-	-

Sample mass after test (g)	44.9	48
Total mass loss, TML (g/m^2)	470	2106
Effective heat of combustion, ΔHc (MJ/kg)	-	21.1
Max average rate of heat emission, MARHE (kW/m^2)	2.2	15.5
Volume flow in exhaust duct, V (l/s)	24	24

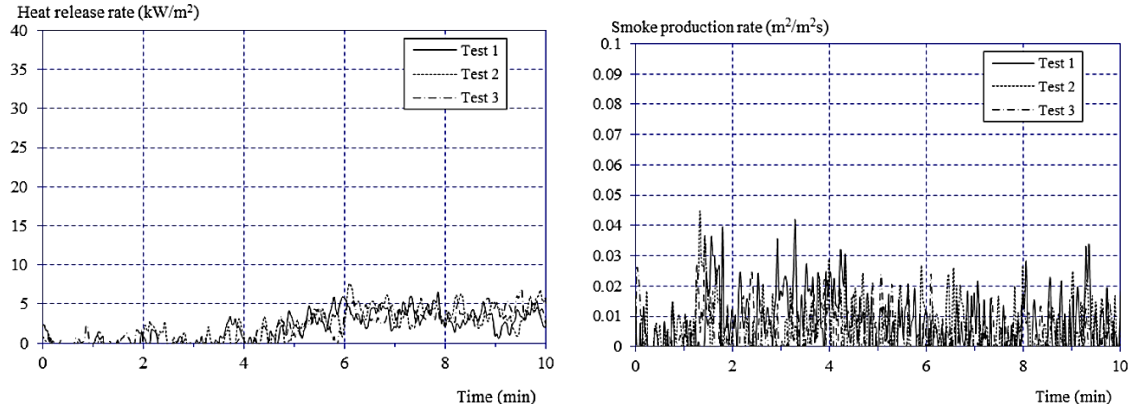

Figure 3. Heat Release Rate (left) and Smoke Production Rate (right) of the three T650/NEXIMID® MHT-R specimens exposed to 50 kW/m^2 heat flux.

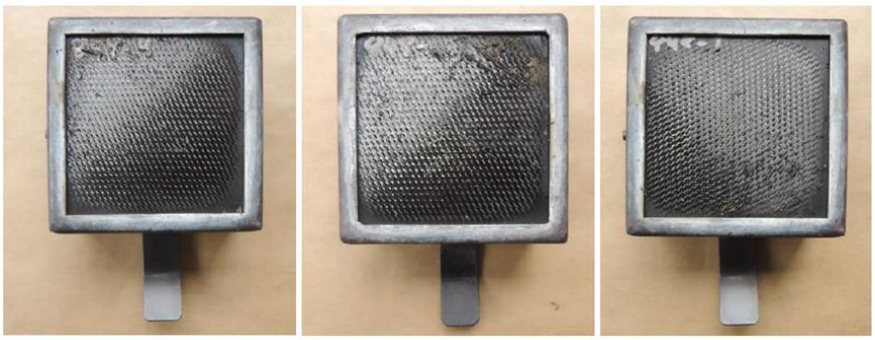

Figure 4. T650/NEXIMID® MHT-R specimens (100×100 mm) after exposure to 50 kW/m^2 heat flux.

In the case of 70 kW/m^2 exposure, the higher heat flux led to approximately three times larger heat release by the T650/MHT-R and weight loss than the case of 50 kW/m^2 heat flux (Table 2). As can be seen in Figure 6, apart from the polyimide resin burn significant deformation of the front ply/surface was observed. In particular, as soon as the specimens were removed from the holder, it was apparent that the surface plies had been displaced and moved towards the centre of the specimens. Cracking sounds and smoke from the rear side and edges were recorded much earlier in this case whilst a weak flame combustion continued at a stable rate after ignition and did not extinguish during the stipulated by the ISO 5660-1 standard time of the test. In all three specimens the central area throughout the thickness was found to be resin-starved and delaminations were observed throughout the specimen thickness.

In both cases, a characteristic heat release rate profile of a high charring and char yielding polymer was observed. Considering the heat release rate profile soon after ignition the HRR dropped as the char layer formed and increased in thickness. Essentially, the growing char layer insulated underlying polyimide from the heat flux the surface was exposed to and thus the net heat flux decreased with time.

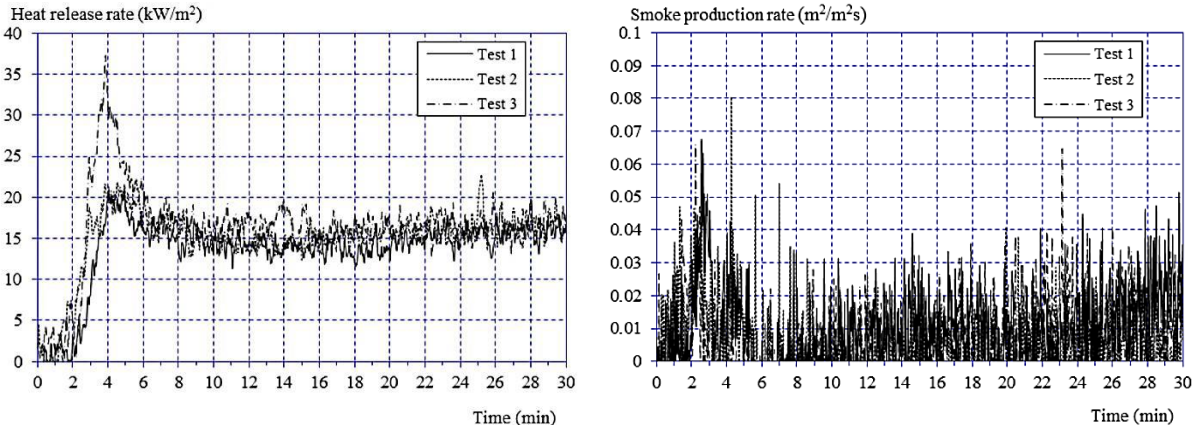

Figure 5. Heat Release Rate (left) and Smoke Production Rate (right) of the three T650/NEXIMID® MHT-R specimens exposed to 70 kW/m^2 heat flux.

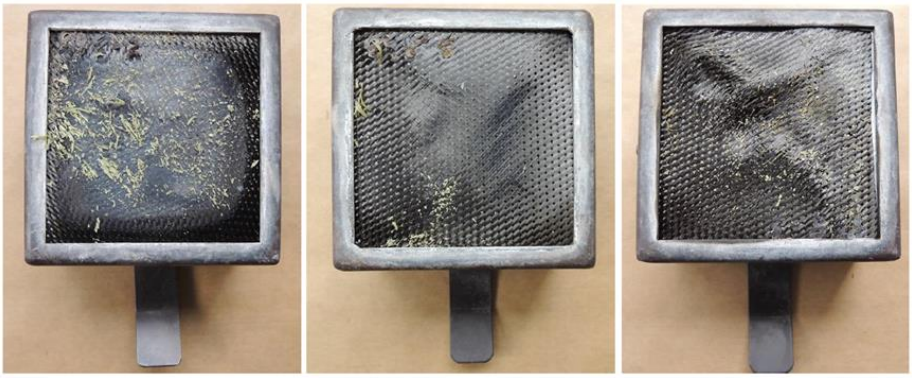

Figure 6. T650/NEXIMID® MHT-R specimens (100×100 mm) after exposure to 70 kW/m^2 heat flux.

3. Conclusions

In this study, the effect of elevated temperature and, long-term thermal exposure on the mechanical performance as well as the fire reaction of T650/MHT-R composites were assessed. From this assessment, the following conclusions can be drawn:

- Elevated temperature has negligible effect on the fibre-dominated properties of the T650/MHT-R composites – up to 320°C the T650/MHT-R composites retain their tensile stiffness and strength.
- At 200°C the T650/MHT-R composites lose approximately 20% of their stiffness and 30% of their strength in compression but from 200°C to 320°C the compressive performance is not affected further; Short-Beam Shear strength continues to decrease further beyond 200°C.
- Thermal ageing at 320°C for 500hrs affects mainly the matrix and fibre/matrix interface-dominated properties, while after 1000hrs both matrix and fibre-dominated properties are significantly degraded (up to 80%).
- At 50 kW/m^2 T650/MHT-R composites do not ignite while the peak HRR is approximately 7 kW/m^2. At 70 kW/m^2 fire exposure the system ignites after approximately 3 minutes and the peak HRR increases threefold.
- During fire exposure, a characteristic heat release rate profile of a high charring and char yielding polymer was observed. The lost T650/MHT-R composites approximately 9% of their original weight at 50 kW/m^2 and 25% at 70 kW/m^2 – most of the weight loss is due to the combustion of the polyimide resin in the surface and adjacent plies.

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