MANUFACTURING AND MECHANICAL CHARACTERISATION OF CARBON NANOTUBE ENHANCED CYANATESTER BASED CARBON FIBRE REINFORCED COMPOSITES FOR HIGH TEMPERATURE SPACE APPLICATIONS

Volker Liedtke(1), Hans Georg Wulz(2), Anneliese Poenninger(1), Carsten Schoeppinger(3)

(1) Austrian Institute of Technology, Aerospace and Advanced Technologies, A-2444 Seibersdorf, +43 50550 3346, volker.liedtke@ait.ac.at; +43 50550 3368, anneliese.poenninger@ait.ac.at
(2) EADS Astrium GmbH, D-88039 Friedrichshafen. +49 7545 8 2282, hansgeorg.wulz@astrium.eads.net
(3) INVENT GmbH, Christian-Pommer-Straße 34, D-38112 Braunschweig, +49 531 2 44 66 50, carsten.schoeppinger@invent-gmbh.de

1 ABSTRACT

High temperature resistant CFRPs for application temperatures up to 400 °C have been manufactured by addition of carbon nano-tubes (CNTs) for enhanced thermal stability. Their mechanical properties, namely bending strength and interlaminar shear strength, show that they fulfill the requirements for the BepiColombo mission to Mercury.

2 INTRODUCTION

The need for development of CFRPs able to withstand temperatures exceeding 300 °C originates from the specifications of the BepiColombo mission. The BepiColombo Mission to the planet Mercury is implemented as a cornerstone of the Cosmic Vision Scientific Program under the responsibility of the European Space Agency. The mission which is considered to be one of the most exciting and most challenging in the history of space exploration to date will commence in 2013 with the launch of the Mercury Composite Spacecraft on Soyuz Fregat.

The mission consists of two separate spacecraft that will orbit the planet, i.e. the Mercury Planetary Orbiter (MPO to be built by ESA, and the Magnetospheric Orbiter (MMO) which is contributed by Japanese space agency ISAS/JAXA. The MPO will study the surface and internal composition of the planet and the MMO will study Mercury's magnetosphere, see Fig. 1.

Following a long interplanetary cruise, powered by the Mercury Transfer Module (MTM), the Mercury Planetary Orbiter (MPO) and the Mercury Magnetospheric Orbiter (MMO) will be inserted to their planetary orbits in 2019. The nominal mission will be completed by the end of 2020 with a possible extension of one more year.

With two spacecraft, BepiColombo is a large and costly mission, within ESA's long-term science programme. The key challenges of the mission are to provide a safe transfer of the spacecraft carrying the scientific instruments to Mercury and to ensure successful science operations of both orbiters under extreme environmental conditions, [1].

Fig. 1: Artist's impression of the four main elements of the Mercury Composite Spacecraft. Left to right: Mercury Magnetospheric Orbiter (MMO), Sunshield, Mercury Planetary Orbiter (MPO) and Mercury Transfer Module (MTM). (Copyright: ESA. Image by AOES Medialab)

2.1 The High Gain Antenna

The High Gain Antenna Reflector Assembly (ARA) which will be mounted on the MPO is one of the most critical subsystems of the BepiColombo mission since it constitutes the heart of the telecommunication subsystem. It provides the communication of the Spacecraft under extreme environmental conditions with earth and the BepiColombo Radio Science Experiment.

The ARA is composed of a Main Reflector, a Sub Reflector with mounting struts, the Antenna Hold Down and Release Mechanisms and the Support Structures that attach the Antenna onto the MPO. The ARA is designed to withstand the extreme environmental conditions which have been defined for the cruise phase beginning with the launch, the travel to the
planet Mercury and the Mercury orbit environment, the required downlink data rate, Ka-band pointing stability and the phase stability required by the Radio Science Experiment (RSE), [2].

The ARA design concept is illustrated in Fig. 2:

![Design Concept of the HGA Antenna Reflector Assembly (ARA). Courtesy Astrium GmbH](image)

Special attention is drawn in particular on thermo-mechanical design and material technology selection to meet the following key design drivers for the ARA:

- Mission environment with temperatures ranging from \(-200^\circ\)C to as much as \(+400^\circ\)C, UV radiation, about 10 times of the solar constant, and in addition high solar proton fluxes and energetic particle impacts (micrometeorites)
- High reliability in a long duration mission in this challenging environment
- Low distortion to meet the stringent requirements on data downlink (X-band and Ka-band use and simultaneous operation of uplink/downlink), antenna pointing stability and phase stability needs of the Radio Science Experiment (RSE)
- Low mass and limited envelope, constrained by the spacecraft accommodation capability
- High stiffness in stowed and deployed configuration

2.2 ARA Structural Components of High Temperature CFRP

The ARA Support Structure and the Antenna Frame, see Fig. 2, both will be fabricated of High-Temperature CFRP, which is reported in this paper. Selection of a high temperature resistant composite material reduces thermal gradients and provides a very stiff and thermally stable basis for the titanium antenna reflector.

A special carbon fibre reinforced polymer (CFRP) composite material has been developed at Astrium GmbH in particular for high-temperature application on ARA of the BepiColombo mission. The material has been characterized in depth in the timeframe from October 2007 to February 2008 at Austrian Institute of Technology (AIT).

The applied resin, a high temperature cyanate ester has been selected to be the basis material for modification by dispersion of specially treated (“functionalized”) multiwall carbon nanotubes (CNTs). Even without any modification by CNTs, the composite material shows outstanding mechanical features at a temperature range up to 350°C and excellent thermoelastic stability, i.e. thermal “zero-expansion” within the specified operational temperature range.

Further improvement activities with that composite material system are running. The development process is continuing in a well proceeding cooperation between Astrium and AIT with cyanate ester resins modified by differently functionalized CNTs [3].

3 MANUFACTURING OF TEST PLATES

3.1 Nanofillers applied

In order to provide suited chemical compatibility between the nanofillers, i.e. the CNTs and the polymeric matrix material, the surface of the CNTs had been treated in such a way that it well interacts with covalent bonds of the polymeric matrix material.

Different types of chemical treatment have been reported in literature. Figure 3 presents some frequently applied types of functionalisation with CNTs.

![Functionalisation of Carbon Nanotubes (CNTs); courtesy of FutureCarbon GmbH, Bayreuth (Germany)](image)

The respective CNTs (thermally oxidised, carboxylized, and as manufactured, i.e. without further surface treatment) were added to PT-30 resin as commercially available from LONZA, Switzerland. The amount of CNTs was always 0.5 weight% of the resin.
3.2 Fabrication of CFRP Laminates for Material Characterization

For characterisation, UD reinforced composites have been manufactured. The reason for choosing UD composites is the ease of obtaining the properties of other fibre architectures, e.g. quasi-isotropic (0/45/90/-45°) symm, (0/60/-60°) symm, (0/90°) and others, by application of laminate theory. Furthermore, the processing of UD reinforced composites was deemed favourable because of easier process control.

The manufacturing process consisted of two steps:

1. Preparation of prepregs by winding the M55 carbon fibres around a heated drum (70°C), followed by wetting with resin, either neat and modified by CNTs. This step is depicted in Fig. 4:

2. Laminating 9 UD fibre layers to a composite by means of compression and thermal treatment in a steel tool, as depicted in Fig. 5. This process step had been carried out in an autoclave.

By this process, three different plates were fabricated:
- Plate 1: PT-30 + 0.5gew.-% MWCNT thermally oxidized
- Plate 2: PT-30 + 0.5gew.-% MWCNT functionalized (carboxylized)
- Plate 3: PT-30 + 0.5gew.-% MWCNT as produced

3.3 Preparation of Test Plates

Test plates in the respective dimensions (for ILSS 20x10x2.3 mm³, for bending tests 80x10x2.3 mm³) were cut by water jet.

Samples were selected from different locations of the test plates in order to average any local differences of the material properties.

3.4 Cryogenic Thermal Cycling Tests

One set of samples (i.e. 5 ILSS, 5 bending) of each test plates were subject to 10 cryogenic thermal cycles by submerging the samples into liquid nitrogen for 5 minutes, then taking them out and blowing them to ambient temperature by a fan for another 5 minutes. The procedure was repeated for 10 cycles in total.

4 MECHANICAL CHARACTERISATION

All mechanical tests were made on a universal test machine Shimadzu AG-10TC. For the bending tests, the displacement had been measured by means of an inductive transducer type HBM W1T3. Tests at elevated temperature were performed in a split drum furnace.

Two types of tests had been performed:
- Bending tests according to EN 2562, with crosshead speed of 5 mm/min
- Interlaminar shear strength (ILSS) tests according to EN 2562, with a crosshead speed of 1 mm/min, except for tests at 400 °C, where crosshead speed of 5 mm/min had to be applied to compensate for the plastic deformation of the samples at this temperature.

4.1 Bending test results

Results of the bending tests are summarised in the following Figs. Fig. 6 shows bending strength and Young’s modulus of samples from the three different plates. Results at RT, at 300 °C, 400 °C, and RT after 10 cryogenic thermal cycles, have been shown.
At RT, both as received and after cryogenic cycling, the three plates show only small differences that are well within the scattering of data, as indicated by the error bars in Fig. 6. At 300 °C, it becomes clear that Plate 1 has significantly less strength compared to Plates 2 and 3. At 400 °C it becomes evident that Plate 3 has the best high temperature strength, though the differences to Plate 2 could be within the scattering of data. The same results are however found for the Young’s modulus, indicating a better performance of Plate 3.

Strain data are presented in the following Fig. 7:

The strain at maximum load and the strain at failure are identical for tests at room temperature, irrespective the fact that samples had been cryocycled or not. At 300 °C, the strain at failure is slightly higher than the strain at maximum load, caused by some plastic deformation before final failure. Only at 400 °C, the sample fails in a plastic way, with strain-to-failure of 0.8% for Plate 3, 1.8% for Plate 1, and 2.0% for Plate 2. The scattering of these values is however very large, though a different failure mode caused by a notable softening of the matrix could clearly be determined.

This observation becomes more obvious when looking at the respective stress/strain plots. In Fig. 8, typical results for Plate 1 at RT and at 400 °C are presented.

The ILSS is a very efficient tool for assessing the matrix properties of a CFRP. The results are presented in the following Fig. 9:

Results of ILSS confirm the conclusions already drawn from the bending tests:
- Plate 3, manufactured with as produced, i.e. not surface modified, CNTs shows best properties at high temperatures
- At RT, the 3 plates do not differ significantly
- 10 cryogenic cycles do not change the properties

4.2 Interlaminar shear test results

Fig. 9: Apparent interlaminar shear strength at RT, 300/400 °C, and RT after 10 cryogenic thermal cycles
4.3 Summary – Mechanical properties

The decrease of the mechanical properties bending strength, Young’s modulus, and ILSS with temperature and after cryogenic cycling is additionally compiled in the following Fig. 10. Here, the percentage of residual strength is depicted.

![Fig. 10: Bending strength, Young's modulus, and ILSS at 300/400 °C and after cryocycling compared to as received properties](image)

The data presented in Fig. 10 reveal that Plate 1 shows a significant strength reduction at 300 °C, while Plates 2 and 3 retain more than 80% of their bending strength and more than 90% of their Young’s modulus at that temperature.

At 400 °C, Plate 3 shows a higher residual strength compared to Plate 2.

Summarising all the aforesaid, Plate 2 and 3 are the materials of choice for high temperature applications.

Regarding bending strength and Young’s modulus, all three plates are virtually unaffected by 10 thermal cycles between LN2 and RT. Only their ILSS seems to be slightly reduced beyond the scattering of test results.

5 MICROSTRUCTURAL INVESTIGATIONS

For further understanding the different behaviour of the three different CNT surface modifications on the composite’s mechanical performance, microstructural investigations were carried out.

5.1 Stereomicroscopy – Cryogenic cycling

The cross sections of samples before and after cryogenic cycles have been investigated by stereomicroscopy. As examples, the ILSS test samples of Plate 1, shown in Fig. 11, have been investigated.

![Fig. 11: Cross sections of Plate 1 ILSS samples before (top) and after 10 times cryogenic cycles (bottom)](image)

As already assumed from the small differences in mechanical data, there is no visible degradation of the composites. Namely no delaminations had been observed in any of the specimens investigated, not even at the edges.

5.2 Non-destructive testing by ultrasound

The non-destructive investigations were intended to identify defects, e.g. delaminations and voids, and to identify possibly faulty samples prior to mechanical tests.

The most relevant finding is the very different response of the plates to ultrasonic scanning. Despite applying identical parameters, it was found that the back wall echo could not be recorded on any of the samples manufactured from Plate 2. The other two plates could easily be scanned, i.e. they could be penetrated by the ultrasonic signal.

Results are presented in the following Fig. 12.
Despite initial assumptions, it was not feasible to correlate the NDI findings with the mechanical test results. Initially it had been expected that a poor signal transmission of a single test specimen can be attributed to faults, thus resulting in comparably lower strength.

5.3 Scanning electron microscopy

Scanning electron microscopy was employed for assessing the overall structural homogeneity of the samples and to identify CNTs inside their structure. Scans of typical specimens made of the different plates shall be presented.

In Fig. 13, the investigation of Plate 1 reveals a large delamination of about 500 µm length and up to 80 µm width had been found. Otherwise, no pores or delaminations could be detected. Even in larger magnification, no CNTs could be detected.

The micro-structure of the Plate 2 sample, depicted in Fig. 15, is different from the one presented in Fig. 13. Numerous voids and structural imperfections can be detected. A close look reveals that the CNTs are only found in matrix spots inside the carbon filaments that are larger than approx. 5-10 µm in size.

High magnification reveals that the CNTs are well dispersed in the matrix, and not clustered or clogged. This is shown in Fig. 14.
The micro-structure of samples made of Plate 3 is very similar to that of Plate 2 specimens; this is presented in Fig. 16. Pores are however larger and not aligned along the layers, as it was found for Plate 2 samples.

Summarising the SEM results, it seems that the size and amount of pores does not significantly influence the mechanical properties of the samples investigated. At least these correlations are anything than obvious, as Plate 3 material performs best at high temperatures despite the large pores, and Plate 2 material does not exhibit a particularly low ILSS.

5 SUMMARY AND OUTLOOK

Despite the fact that further detailed investigations – namely fatigue tests and extended tests at low temperatures – are still open, the addition of CNTs to PT-30 cyanate ester resin significantly improves the high temperature mechanical properties. The CNT functionalisation is a critical factor, and these results indicate that any oxidative surface treatment may reduce the high temperature strength.

Other prospective fillers like POSS have already been discarded [4], so the full potential of CNTs to cyanate ester based matrices shall be further investigated. Novel resin formulations, like the “toughened” types DT-4000 and DT-7000, could be improved further to achieve better properties for cryogenic applications, though their upper temperature limit is clearly below 300 °C.

The complete understanding of resin/CNT/carbon fibre interaction, namely chemical compatibility of CNT surface treatment and matrix, seems to require some more work. The manufacturing process for the PT-30 seems mature, though improved cyanate esters currently being developed and with improved performance, might request some changes in the processing route.

For the requirements of the BepiColombo mission, the PT-30 resin with CNT addition currently seems to be the most promising approach and should thus be further investigated and fully space qualified, to be ready for the flight to Mercury in due time!

5 LITERATURE