HEDGE

HIGH SERVICE TEMPERATURE ADHESIVES AND COMPOSITES FOR THERMAL SHIELDING IN ATMOSPHERIC ENTRY"

ESA Contract no. 4000124051/18/NL/KML

EXECUTIVE SUMMARY REPORT – ESR:

Mars entry and Earth re-entry probes have a Thermal Protection System (TPS) designed to survive in harsh environments. The Front Heatshield Shield is made of cork based outgassed Norcoat® liège and carbon/phenolic Asterm® ablative materials. Both thermal protections are suitable for Mars entry and Earth re-entry, respectively (Figure 1) and have been provided by ArianeGroup SAS.

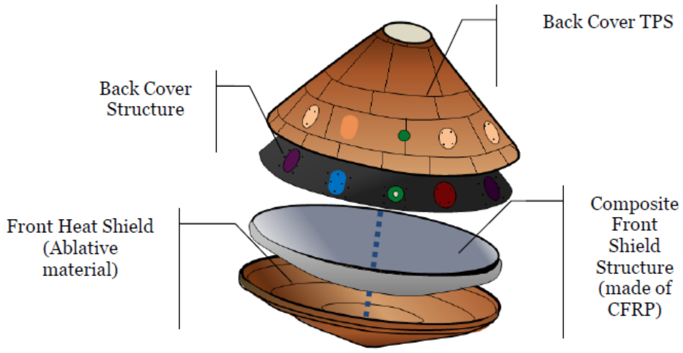


Figure 1. Schematic drawing of a planetary probe based on the ExoMars Demonstrator Module (Bouilly, J. M. et al. "Ablative thermal protection systems for entry in Mars atmosphere. A presentation of materials solutions and testing capabilities" (2006))

These ablatives are directly bonded to the Composite Front Shield Structure, made of Carbon Fibre Reinforced Polymer (CFRP) skins with an operational temperature of 160-180ºC. The adhesives used for the bonding the ablatives with the CFRP usually are thermosetting polymers with an operational temperature of 150-180ºC. In order to reduce the ablative thickness, what will allow reducing the weight of the TPS and the weight of the capsule, alternative adhesives and CFRP with wider thermal range have been proposed for this project.

The objective of the HEDGE project is to identify the requirements of CFRP and bonding materials for TPS applications in spacecrafts with an operational temperature up to 250ºC, select the most promising CFRP and adhesives materials according to the consolidated requirements and relevant criteria, apply them using suitable manufacturing methods and characterize mechanical, physical, thermal and adhesive properties of samples and representative breadboards to evaluate their technical feasibility in a future Mars entry and Earth re-entry mission.

The ablative materials used for atmospheric Mars entry and Earth re-entry are specially designed for each scenario because the requirements to pass through the atmosphere of each planet are different. For this reason, one of the requirements of the alternative CFRP and adhesives to be selected in the project have been the need to be compatible with the used ablative materials for both scenarios: Mars entry (NORCOAT®) and Earth re-entry (ASTERM®). Other requirements have been divided in these main categories: technical and functional properties, availability and restriction, processability, safety and sustainability. All requirements needed for materials and processes have been collected and used for the exhaustive market screening and trade-off. The trade-off has been performed in two differentiated stages. During the first stage, most important characteristics such as service temperature, low outgassing, and availability in the European market (and possible ITAR restrictions and REACH regulation issues) have been considered as a first filter. During the second stage, selection criteria have been quantified using weighing factors and thresholds per property have been stablished. At the end of the trade-off, these values have been compared and discussed to select the CFRP: CFRP#1 (Toray RS-8HT; Bismaleimide, BMI), CFRP#2 (Toray TC420; CE, Cyanate Ester), and adhesives: Adh#1 (Momentive RTV566; liquid silicone), Adh#2 (Toray TC4015; CE, film adhesive) materials to be investigated in the project (Table 1).

Reference name	Material type	Supplier	Full reference
CFRP#1	Fabric prepreg (T300/Bismaleimide)	Toray	D-RS-8-HT HS0804 42% T300 3k
CFRP#2	Fabric prepreg (T300/Cyanate ester)	Toray	TC420-00 HS0804 42% T300 3k
Adh#1	Adhesive (liquid silicone)	Momentive	RTV566 001-kit
Adh#2	Adhesive (Cyanate ester film)	Toray	TC4015U 0.060 psf 12”
Norcoat®	Ablator (cork-based)	ArianeGroup	Outgassed Norcoat® liège 10mm
Asterm®	Ablator (carbon felt/phenolic resin)	ArianeGroup	Asterm® 20mm

Table 1. List of sample materials and references

	Raw semi-finished materials				Combinations of materials											
Ablatives	-	-	-	-	-	-	-	-	Norcoat®	Norcoat®	Norcoat®	Norcoat®	Asterm®	Asterm®	Asterm®	Asterm®
Adhesives	-	-	Adh#1	Adh#2	Adh#1	Adh#1	Adh#2	Adh#2	Adh#1	Adh#1	Adh#2	Adh#2	Adh#1	Adh#1	Adh#2	Adh#2
CFRP	CFRP#1	CFRP#2	-	-	CFRP#1	CFRP#2	CFRP#1	CFRP#2	CFRP#1	CFRP#2	CFRP#1	CFRP#2	CFRP#1	CFRP#2	CFRP#1	CFRP#2

Table 2. Combination of materials used for sample manufacturing

A third CFRP, CFRP#3 (HexPly® F655™; Bismaleimide, BMI, from Hexcel), and a third adhesive, Adh#3 (RTV-S 691; silicone, from Wacker), have been selected as an alternative to mitigate possible risk of not reaching the expected requirements. Table 2 indicate the reference names and a short description for all configurations of samples that have been manufactured.

Other three adhesives, DELO MONOPOX HT760 (epoxy resin, from DELO), LOCTITE® EA 9497™ (epoxy resin, from Henkel), and FM® 300 (epoxy film, from Solvay), have been used to attach the aluminium tabs to flatwise samples. A silicone-based adhesive primer, SS4155 (silicone, from Momentive), has been applied to CFRP panels and ablatives for improving bonding when using RTV566 (silicone, from Momentive) adhesive and avoiding a damaging heat post-processing.

Manufacturing of samples for analysing: i) thermal and hygroscopic properties (Glass transition temperature, Outgassing of volatiles, Specific heat, Thermal diffusivity, Coefficient of Moisture Expansion); ii) physical properties (Fibre volume fraction, Density); iii) mechanical and fracture properties (Tensile 0º, Compression 0º – with tabs), (Shear rail, Interlaminar Shear Strength (ILSS) – without tabs) (Double Cantilever Beam, DCB) (Single Lap Joint, SLJ) (Flatwise joint strength). For mechanical and fracture properties evaluation, three environmental conditions are considered: i) room temperature ambient (RTA) defined as 23 ± 2 ºC, ii) High Temperature Ambient (HTA): 250 ºC (0 /+5 ºC), and iii) High Temperature Heat Exposure (HTH): 250 ºC (0/+5 ºC), after a high temperature exposition of 250 ºC (-0/+5 ºC) during 20 min (-0/+2 min).

The two main problems encountered during the manufacture of flatwise specimens are explained below, as well as the solution applied: 1) *Need of a primer for RTV566 silicone adhesive:* Primer SS4155 have been applied successfully to ablatives and CFRP panels for avoiding a thermal post-processing that has previously degraded RTV566 adhesive in DCB, SLJ and flatwise joint strength tests; 2) *Not suitable behaviour of Delo Monopox HT760 adhesive:* Delo Monopox HT760 have not been processed properly for sample testing of mechanical properties. FM® 300 and EA9497™ have been used as potential alternatives. FM® 300 has presented a lack of adhesion. However, EA9497™ adhesive has presented suitable adhesive properties between aluminium tabs and CFRP panels.

Given the experience acquired during the manufacture of the samples, the following guidelines have been proposed for the suitable manufacture of breadboards: a) the use of SS4155 primer before application of RTV566 adhesive is recommended; b) a vacuum bag system (Figure 2) is required for curing the adhesive interface with the ablative and the CFRP.

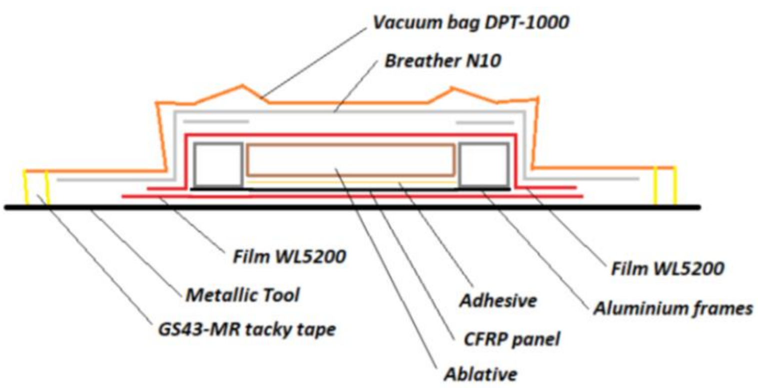


Figure 2. Vacuum bag scheme for manufacturing of sandwich structures: flatwise samples and breadboards

Mechanical strength at RTA, HTA, and HTN conditions have been evaluated for composites (Figure 3, left). In tension, both composites behave similarly at RTA. However, for HTA and HTH cases, CFRP#2 is strongly degraded. In compression, CFRP#1 outperforms CFRP#2 at any temperature. In contrast, CFRP#2 shows a major reduction in compression, especially at HTH that reaches a 50% reduction (Figure 3, left).

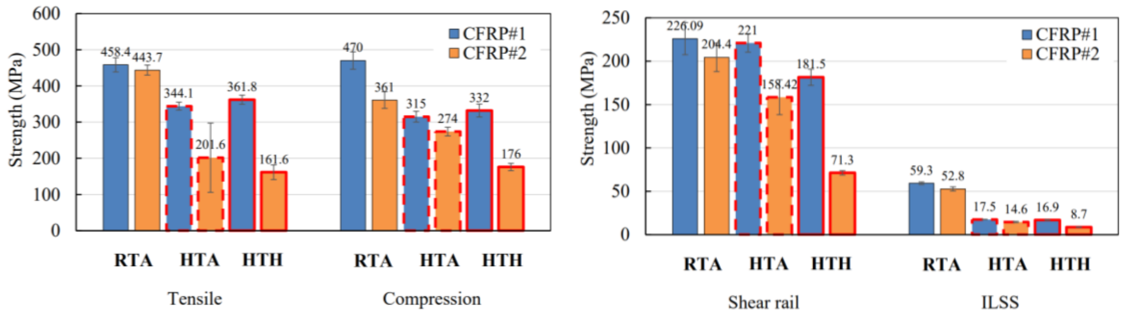


Figure 3. Tension and compression strengths for different test conditions and materials (left); shear rail and interlaminar shear strengths for different test conditions and materials (right)

Shear strengths obtained in the shear rail and interlaminar shear (ILSS) tests for both composites at different test conditions have been evaluated (Figure 3, right). At RTA, both composites result in similar in-plane shear strengths, but again the effect of heat exposure (HTH) is severely affecting CFRP#2 (Figure 3, right). The interlaminar strength is similar in both composites at any temperature (Figure 3, right).

Adhesive properties for samples have been analysed (Figure 4). Fracture toughness and Single-lap shear (SLS) strengths for combinations of CFRPs with Adh#1 (silicone) were much higher than with Adh#2 (CE) at room temperature (RTA). However, these values decrease severely when heating (HTA, HTH) (Figure 4). Fracture toughness and SLS stress for combinations using CFRP#2 have been significantly higher than those using CFRP#1 (Figure 4).

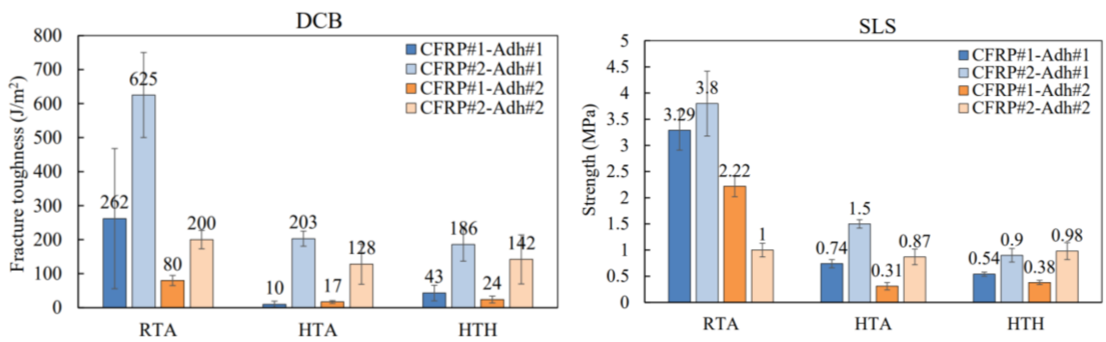


Figure 4. Mode I fracture toughness for different test conditions and material combinations (left); single-lap shear strength for different test conditions and materials (right)

Valid and invalid failure modes considered within the analysis are shown (Figure 5, left) for flatwise samples. Two examples of valid (Figure 5, center) and invalid (Figure 5, right) failure modes considered within the analysis are presented.

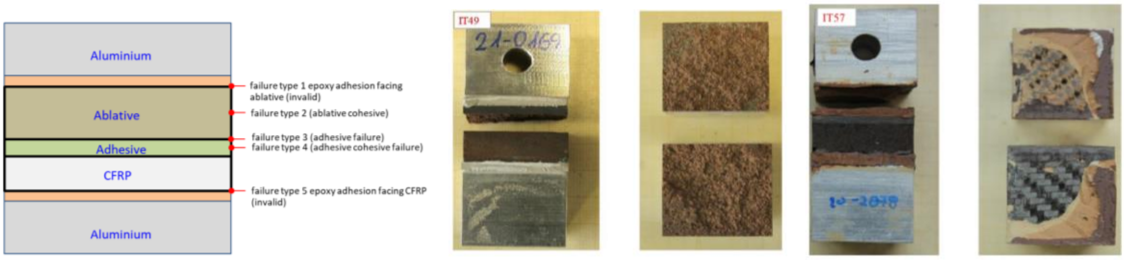


Figure 5. Failure mode identification of flatwise specimens (left); Norcoat®-Liege failure type 2 (ablator failure) at RTA conditions (center); Norcoat®-Liege failure type 5 (aluminium blocks adhesive) at HTH conditions (right)

Flatwise joint strengths for both ablators and combinations of CFRP panels and adhesives at different test conditions (RTA, HTA, HTH) have been characterized (Figure 6). Flatwise strength for NORCOAT® combinations (Figure 6, left) are much higher than those obtained for ASTERM® (Figure 6, right), particularly at RTA. In both cases, flatwise strength is significantly reduced after thermal treatment (HTA and HTH). For NORCOAT® combinations, flatwise strength is slightly higher when using Adh#2 (Figure 6, left). While when using ASTERM®, all combinations present very low values for flatwise strengths (Figure 6, right).

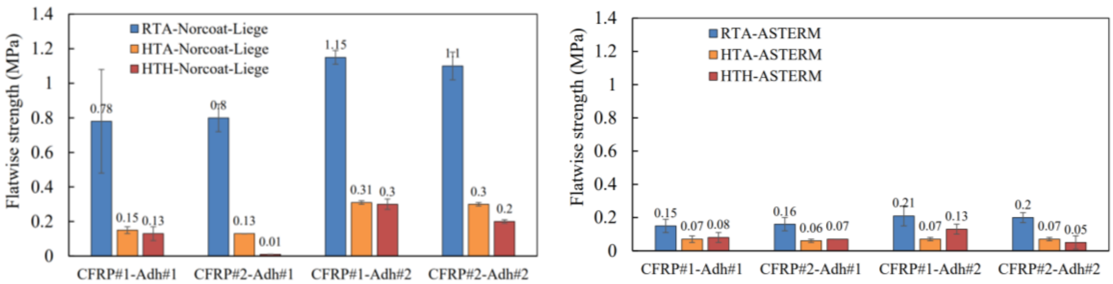


Figure 6. Flatwise strength for Norcoat®-Liege (left) and for ASTERM® (right) and all material combinations at different test conditions

On one side, the more pronounced thermal degradation of CFRP#2 in comparison with CFRP#1 has been observed at tensile strength levels higher than 100 MPa (Figure 3, left). However, flatwise strength is below 2 MPa in all cases (Figure 6), what means that the limitation of mechanical performance for flatwise panels is associated to ablatives and/or adhesives. On the other side, the failure mode identified for flatwise panels was mainly based on ablative cohesion (type 2), sometimes on adhesive failure (invalid, type 5), and rarely on adhesive failure (type 3) (Figure 5). Moreover, adhesive properties of combinations using CFRP#2 have been much better than those using CFRP#1 (Figure 4). *Therefore, combinations with CFRP#2 with both ablatives, NORCOAT® and ASTERM®, and both adhesives, Adh#1 and Adh#2, are recommended for up-scaling when manufacturing breadboards.*

The design of the breadboards consists of four specimens covering the best candidates of material combinations selected according to the results obtained previously for characterization of samples. Table 3 summarizes the four tested breadboards, materials, and identification codes.

Specimen ID	Materials	Ablator
01/S21028	CFRP#2/Adhesive#2	ASTERM®
02/S21028	CFRP#2/Adhesive#2	Norcoat®
03/S21028	CFRP#2/Adhesive#1	ASTERM®
04/S21028	CFRP#2/Adhesive#1	Norcoat®

CFRP#2: TC420/CE, Adh#1: RTV566/silicone, Adh#2 : TC4015/CE

Table 3. Test specimen and identification

A comprehensive literature review focused on vibration testing, thermal cycling, and non-destructive inspection methods for the evaluation of the adhesive bonding of breadboards has been carried out. The detailed sequence has been considered as the most suitable for evaluating breadboards in the project. It consists of an initial inspection step based on carrying out photomicrographs at 20x magnification in all the edges of the breadboard and tap test of pristine breadboards. Secondly, a random vibration test (Table 4) followed by a thermal cycling test in inert atmosphere using dry N_2 (Table 5).

Frequency band (Hz)	Reference level (g)
5-2000	0.5
Sweep rate 2oct/min	
1 sweep up	

Frequency band (Hz)	Qualification level (g^2/Hz)
20	0.0913
100	0.273
400	0.273
2000	0.069
Overall level	17.19grms
Duration	30s

Table 4. Low sine vibration test levels (left); and random vibration test levels (right)

Test parameter	Requirement
Hot temperature	+100ºC±5 ºC
Cold temperature	-100ºC±5 ºC
Temp. slope	10ºC/min
Nº cycles	25
Min. Dwell time	5 min after stabilization
Stabilization criterion	Temperature of all thermocouples must be with the tolerance

Table 5. Thermal-cycling test parameters

Inspection based on a low-level sine vibration test with dynamic response has been done for all breadboards before and after random vibration and thermal cycling tests. A final inspection for all breadboards including again photomicrographs at 20x magnification in all the edges of the breadboard and tap test of pristine breadboards has been carried out in the project.

Specific parameters representing the application in Mars entry and Earth re-entry for future spacecrafts have been specified for low sine vibration, random vibration, and thermal cycling tests.

All breadboards have been manufactured properly according to procedures already established for flatwise panels previously. No major problems have been detected during their manufacturing (Figure 7).

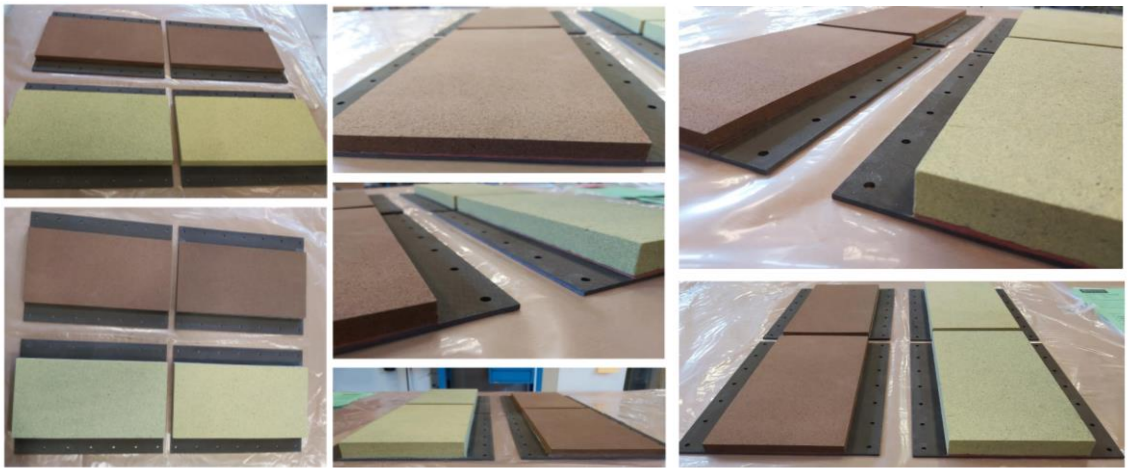


Figure 7. Final manufactured breadboards

It is important to highlight the sizing effect when testing thermal protection systems, since the thermal-induced strains on the breadboards became much more important than at coupon level. After the random vibration and thermal cycling tests, breadboard 02/S21028 (CFRP#2, Adhesive#2/Norcoat®) displays severe adhesive damage at the edges but the other breadboards seem to be intact with no evidence of damage (Figure 8).

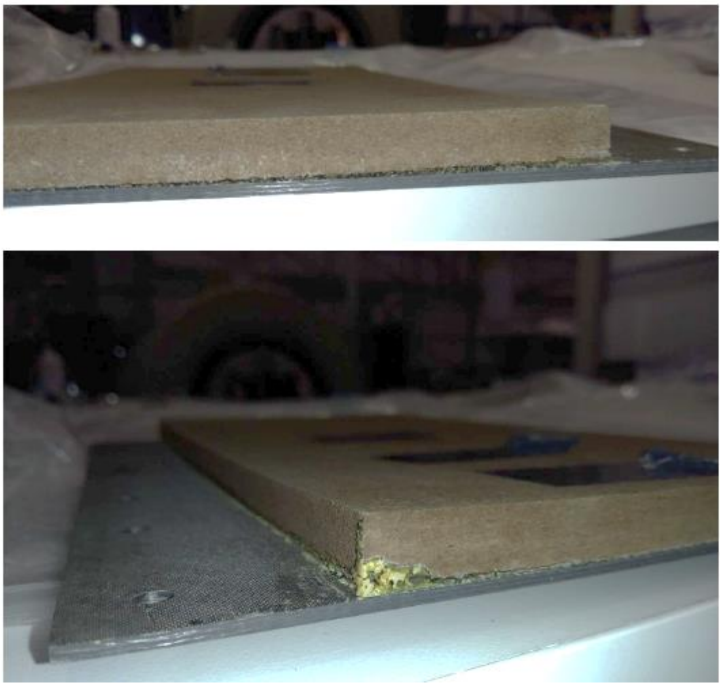


Figure 8. Detailed view of edge debonding on specimen 02/S21028 reported by CTA

After the thermal endurance test at 250ºC during 20min, the breadboards 02/S210028 and 04/S21028 are severely damaged with adhesive cracking but also with some major delamination within the composite (Figure 9).

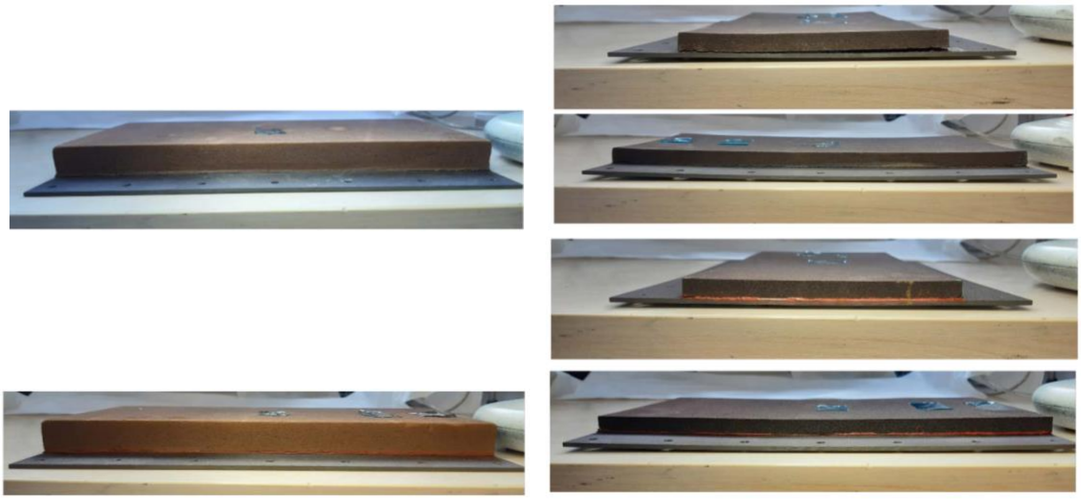


Figure 9. Breadboard 01/S21028 (left, up), 02/S21028 (right, up), 03/S21028 (left, down), and 04/S21028 (right, down) after endurance test at 250ºC

The thermal induced strains during the test distorted the samples and created warping. It is reasonable to think that the composite got distorted after heat exposure and bended the NORCOAT®. However, this is just an assumption that could not be confirmed during the test. What seems clear is that breadboards 01/S21028 and 03/S21028 with ASTERM® kept their flatness and did not show any major evidence of damage, which means that the thermal response and interaction of the materials in these assemblies were good (Figure 9).

This type of test could be used to define the maximum size of the ablator tiles and its thickness. The residual flatwise strengths showed reasonable levels and pointed out that the NORCOAT® is stronger than the ASTERM®, but in general, the thermal response of the breadboards with ASTERM® was much better than with NORCOAT®. Nevertheless, the ASTERM® material seems to be the weakest part under flatwise tension, which might compromise the structural integrity in case of a tension load acting on the TPS. In this regard, both adhesives (RTV566 and TC4015) would be suitable for bonding the ASTERM® ablator to the composite as they show high enough bonding strength, at least higher than the ablator itself.

As expected from the tap test performed before, the images taken from the longitudinal cut reveal significant damage on breadboards 02/S21028 and 04/S21028 (Figure 10, right-up) and Figure 10, right-down, respectively). Note that both breadboards have not only adhesive damage but also a large delamination within the CFRP substrate, which is especially visible on breadboard 02/S2102 (Figure 10, right-up). The rest of the images do not reveal any other damage location.

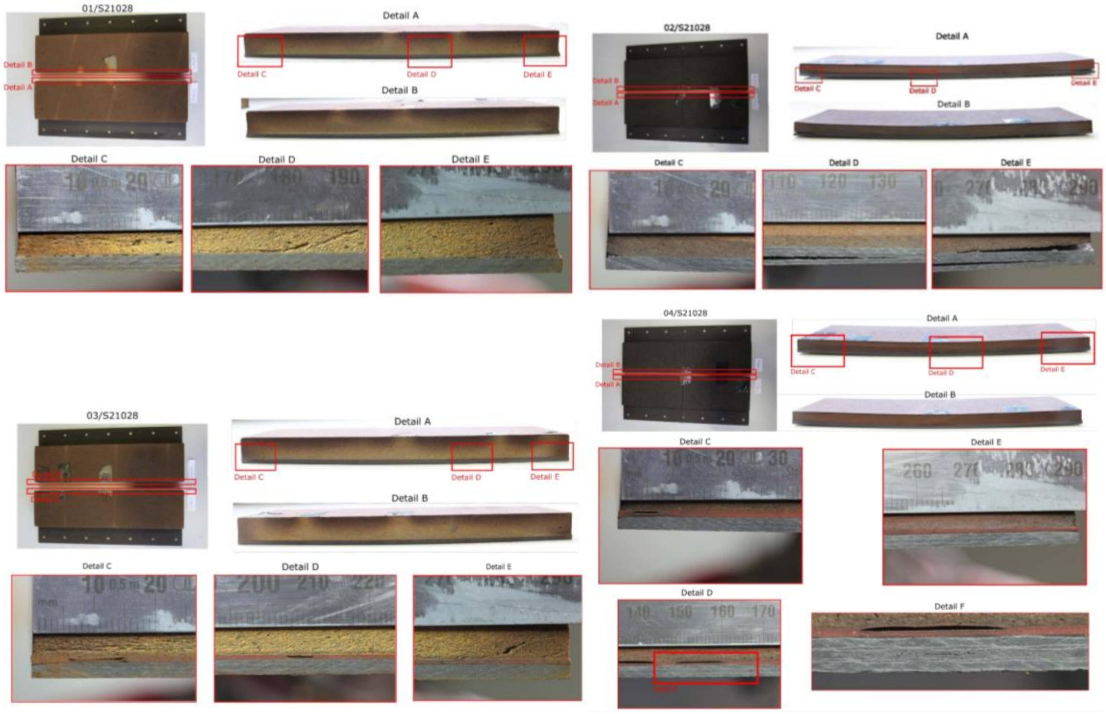
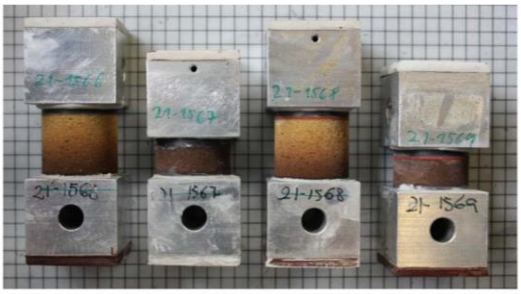


Figure 10. Inspection at the longitudinal section cut of breadboard 01/S21028 (left, up), 02/S21028 (right, up), 03/S21028 (left, down), and 04/S21028 (right, down) after thermal endurance test

After the longitudinal cut, only breadboards with observed damage (02/S21028 and 04/S21028) were cut transversally. More evidence of delamination cracks in breadboard 04/S21028 was observed.

After the inspections, one circular flatwise specimen was taken out as close as possible to the central part of the breadboards to evaluate its residual strength (Figure 11, up). Besides the change in the geometry of the specimen (circular vs prismatic), the residual flatwise strengths are like their respective values obtained at RTA previously (Figure 6).



Specimen	Breadboard	Materials	Residual strength (MPa)	Flatwise strength (MPa)	Failure mode
21-1566	01/S21028	CFRP#2 Adhesive#2 ASTERM	0.26	0.2±0.03 (RTA) 0.07±0.01 (HTA) 0.05±0.04 (HTH)	Ablative failure
21-1567	02/S21028	CFRP#2 Adhesive#2 NORCOAT	0.85	1.1±0.08 (RTA) 0.03±0.01 (HTA) 0.2±0.01 (HTH)	Ablative failure
21-1568	03/S21028	CFRP#2 Adhesive#1 ASTERM	-	0.16±0.04 (RTA) 0.06±0.01 (HTA) 0.07 (HTH)	Broken before test, during assembly (ablative failure)
21-1569	04/S21028	CFRP#2 Adhesive#1 NORCOAT	0.72	0.8±0.08 (RTA) 0.13 (HTA) 0.01 (HTH)	Adhesive and ablative failure

CFRP#2: T300/CE, Adhesive#1 (silicone): RTV566, Adhesive#2 : TC4015

21-1566: CFRP#2/Adhesive#2/ASTERM
21-1567: CFRP#2/Adhesive#2/NORCOAT
21-1568: CFRP#2/Adhesive#1/ASTERM
21-1569: CFRP#2/Adhesive#1/ NORCOAT

Figure 11. Residual flatwise tension strengths (up); images of post-mortem flatwise samples (down)

The main conclusions derived from the execution of the project are highlighted below:

- Samples and breadboards based on selected alternative CFRP panels and adhesives with wider thermal range and/or state-of-the-art ablative materials have been successfully manufactured. Their thermal, physical, mechanical, and adhesive properties have been evaluated and compared to identify the most suitable combination of materials with suitable performance at operational temperature up to 250ºC and accomplishing the requirements for TPS applications in spacecrafts for a future Mars entry and Earth re-entry mission.

- Manufacturing of flatwise panels has been particularly challenging. Silicone primer Momentive SS4155 has been shown as a successful solution to avoid permanent damage to the ablative (curvatures, partial cracks, degradation, etc.)

due to thermal post-treatment step when using RTV566 silicone adhesive. Curing of flatwise panels in a vacuum bag has been carried out successfully.

- A qualitative comparison between all tested sample material combinations has been carried out (Table 6).

		CFRP#1	CFRP#2
Individual performance		Better mechanical properties. Less temperature degradation (Tg=290ºC)	Severe temperature degradation (Tg=239ºC)
Bonded with…		CFRP#1	CFRP#2
Adhesive#1		Adhesive failure (poor adhesion). Large scatter. Huge reduction in toughness due to temperature (5-20x)	Cohesive failure better adhesion). Far less reduction in toughness due to temperature (~3x)
		Reasonable shear strength but important reduction due to temperature	Reasonable shear strength and lower reduction due to temperature
Adhesive#2		Cohesive failure. Very high porosity. Lower toughness than Adhesive#1 but less degradation due to temperature (Tg=251ºC)	Cohesive failure. Large scatter. Very high porosity. Lower toughness than Adhesive#1 but less degradation due to temperature. Higher toughness than combined with CFRP#1 (2-6x)
		Lower shear strength in comparison with Adhesive#1 and important reduction due to temperature	Lower shear strength in comparison with Adhesive#1 and less reduction due to temperature
Flatwise		CFRP#1	CFRP#2
Norcoat® Liège	Adhesive#1	Reasonable flatwise strength and marked reduction due to temperature	Reasonable flatwise strength and marked reduction due to temperature. At HTH only one flatwise strength reported with very low value
	Adhesive#2	Higher flatwise strength that Adhesive#1 and marked reduction due to temperature	Higher flatwise strength that Adhesive#1 and marked reduction due to temperature
Asterm®	Adhesive#1	Poor properties compared to Norcoat®. Similar strength regardless of temperature and conditions	Poor properties compared to Norcoat®. Similar strength regardless of temperature and conditions
	Adhesive#2	Similar to Adhesive#1	Similar to Adhesive#1

Best	
Medium	
Worst	

Table 6. Pros and cons of each test for all sample material combinations

- The selection of the most suitable material combinations to be used for manufacturing breadboards (representative demonstrators including CFRP, adhesive and ablator materials) has not been obvious as the results do not clearly evidence any candidate for all test conditions and material properties. Considering the adhesive joint as the main design parameter, the best candidates are CFRP#2 (Toray TC420; Cyanate Ester) and Adh#1 (Momentive RTV566; liquid silicone). CFRP#1 (Toray RS-8HT; Bismaleimide) is better in terms of mechanical properties, but has a poorer interaction with the adhesives investigated, which is a strong argument to discard CFRP #1 and stick to CFRP#2 for the breadboard-level analyses. It must be noted, however, that the glass transition temperature of CFRP#2 is slightly below 250ºC, and the laminate resin-dominated properties were significantly degraded at high temperature. However, these residual properties may be considered enough for the load-bearing capacity of the structure.

- Breadboard 01/S21028 (CFRP#2/Adhesive#2/ASTERM®) and 03/S21028 (CFRP#2/Adhesive#1/ASTERM®), both including ASTERM® ablator in their structure, performed well and the inspections did not reveal any major indication of adhesive degradation or composite failure.

- Breadboard 02/S21028 (CFRP#2/Adhesive#2/ NORCOAT®), including NORCOAT® ablator and cyanate ester-based adhesive, showed adhesive cracking all along the external edges, a large delamination crack at the laminate and significant warping.

- Breadboard 04/S21028 (CFRP#2/Adhesive#1/NORCOAT®), including NORCOAT® ablator and silicone-based adhesive showed adhesive cracking at the corners and some interior regions, a large delamination crack at the laminate and warping.

- After thorough testing and evaluation, material selection and tuning of the bonding process of the breadboards, it can be concluded that the operational temperature of the ablators bonded to the CFRP must be limited for the NORCOAT® ablator, being 250ºC on the interface seems to be far from realistic especially after the thermal endurance test.

Finally, several recommendations have been identified at the end of the project. They are focused on optimization and up-scaling of the results obtained, together with definition of several research strategies for developing novel high-performance adhesives, ablatives, and composites.