Adhesive Joining of Zerodur–CFRP–Zerodur Sandwich Structures for Aerospace Applications

Adhesive joining of Zerodur™ - CFRP - Zerodur™ sandwich structures for aerospace applications

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Abstract

A high performance adhesive is used to join Zerodur™ to Carbon Fibre Reinforced Polymers (CFRPs) honeycomb (HC) in a sandwich structure for aerospace applications. The main problem of finding an adhesive with suitable thermomechanical stability and ease of application for use in large components, *together with a* lower curing temperature than 160 °C, in order to avoid detrimental effects on the CFRPs is resolved.

Two phenolic-based adhesives and one cyanate ester-based are considered. One phenolic-based adhesive that had already proven effective in the joining of carbon/carbon composites (C/C) is used to join CFRP slabs and Zerodur™ - CFRP - Zerodur™ in a sandwich structure.

Thermal analysis is conducted to characterise and compare the phenolic adhesive, cured at 150°C and at 260 °C, with a cyanate ester-based adhesive and a commercial phenolic-based one.

The phenolic adhesive cured at 150 °C results to be the most suitable joining material; the lap shear strength of the CFRP slabs joined at room temperature is measured after thermal cycling.

Zerodur™ - CFRP - Zerodur™ sandwich structures, joined by the phenolic adhesive cured at 150 °C, are tested in tensile and lap shear mode.

1. Introduction

Carbon Fibre Reinforced Polymers (CFRPs) honeycomb (HC) is used in aeronautical sandwich structures with ultra-stable glass-ceramic skins, such as Zerodur ™ [1], to build satellite components, thanks to its unique mass/property ratio: however, the performance of satellite components depends to a great extent on the adhesives used to assemble them. The environmental conditions can be particularly extreme for satellite applications, and severe thermal cycling can occur together with alternating exposure and non-exposure to sunlight. Therefore, the main requirement for the whole structure, in order to avoid signal distortions, is excellent thermal stability.

In order to fully benefit from the potential of Zerodur ™ and CFRPs, it is important to select a joining material that has a low thermal expansion coefficient, sound mechanical strength and a curing temperature that is suitable for both CFRPs and Zerodur ™. Moreover, the adhesive should be easy to apply in a cleanroom environment and on square meter sized components.

Inorganic solutions, for example, lead/bismuth-based low temperature glasses, and cements,

such as Vubonite™ (a phosphate cement) and Keraflex (a cement), have been found not to be suitable for application to these sandwich structures, mainly due to the high processing temperature of the selected glasses and to the low adhesion and, consequently, the low mechanical strength of the joints in the case of cements. [2]

The available solutions (i.e. commercial adhesives) also suffer from some drawbacks: first, they were not specifically designed to join CFRPs and Zerodur ™, but were instead developed to join aluminium honeycombs to carbon/epoxy or C/C skins. [3]

The currently adopted curing temperature of adhesives is too high for the specific case under study and therefore detrimental for the mechanical properties of both CFRPs and Zerodur ™. Moreover, their Coefficient of Thermal Expansion (CTE), which is higher than those of CFRPs and Zerodur ™, may cause distortions of the sandwich structure due to thermal and/or moisture expansion effects. [4]

The objective of this work has been to develop an advanced and highly performing adhesive that would be able to provide suitable mechanical strength to Zerodur™ - CFRP - Zerodur™ sandwich structures, coupled with suitable thermo-mechanical stability within the operative range, and the possibility of using the joint on large flat and curved surfaces.

2. Experimental section

The considered 6-ply CFRP plates were produced by NTPT (North Thin Ply Technology, Switzerland). They contained 50 volume % high modulus pitch carbon fibres (YSH 70A, Japan), orientated symmetrically at +60°/-60°/0° , six plies, and a cyanate ester NTPT CE380 matrix. The interlaminar shear strength (ILSS) was 35 MPa and the CTE in the 25-90 °C range for the unidirectional composite, perpendicular to the fibres, was 36.5 $x10^{-6}$ $°C^{-1}$, while it was -0.25 x 10^{-6} $°C^{-1}$ for the quasi-isotropic layup. [5]

The CFRP HC, which was also produced by NTPT, was manufactured with cyanate ester ThinPreg™ 380CE matrix, with the same fibres as above (YSH 70A, 50 volume % , six plies with symmetrical fibre orientations at +60°/-60°/0°); the density was 36 kg/m^3, with a cell size of 20 mm, while the wall thickness was in the 0.21 to 0.24 mm range and the HC thickness was 40 mm. The average CTE was - 0.26 x 10^{-6} °C^{-1}.[5]

A number of 2.5 mm thick Zerodur ™ slabs were supplied by Schott, Germany: these were glass ceramic slabs with 70 to 78 % of quartz micro-crystallites that were 50 to 80 nm in size embedded in a glassy phase. Zerodur ™ has a thermal expansion of nearly zero, which is achieved with an accuracy of 0 ± 0.007 x 10^{-6} °C^{-1} (in the 0 °C - 50 °C range) and a Young Modulus of 90 GPa. The additional properties of Zerodur can be found in [1] .

A commercially available adhesive that is suggested for joining carbon-based materials, that is, Graphi-Bond™ 551-RN from AREMCO Products, Inc. (USA) (referred to as GB in this paper), was used in this work: the main components are graphite and graphite fibres in a phenolic resin, and, according to the data sheet, it has a CTE = 7.4 x10^{-6} °C^{-1} . [6]

Cured bulk GB samples (50 mm x 20 mm x 5 mm) were prepared with a curing cycle of 0.3°C/min heating to 130°C, followed by 4 hours dwelling at 130°C and 2 hours at 260°C (in air), as reported in [7] .

A phenolic-based adhesive (referred to as PH in this paper) and one cyanate ester-based one (referred to as CY in this paper), that had already been proven effective in joining C/C, were prepared by M.D.P Materials Design & Processing S.r.l. - Italy, and their characteristics, which are reported in [8] , are summarised briefly hereafter.

Their compositional range (wt %) is:

- 55 – 75 wt % phenolic resin (Hexion - Resole based Bakelite 1211, Germany), 1-4

wt % Carbon black (Cabot, grade Vulcan 7H, UK), 1-4 wt % Milled Carbon Fibres (SIGRAFIL C10 M250 UNS by SGL Carbon, UK), 5-20 wt % Graphite (Cecchi, grade A20 microshield, Italy), 10-25 wt % ethanol as a solvent.

- 65 – 85 wt % cyanate ester (Lonza PT 30, Germany), the same fillers as above, no added solvent.

The typical curing cycle for phenolic adhesives involves heating at 0.3 °C/min up to 130 °C, a dwell time of 4 hours, followed by heating to 260 °C at 0.3 °C/min , a dwell time of 2 hours, and then cooling (referred to as PH260 in this paper).

The phenolic adhesive was also cured with a lower temperature curing cycle (referred to as PH150 in this paper): 4 hours at 130°C, followed by 10 hours at 150°C (heating rate: 0.3°C/min), in order to avoid any detrimental effects of curing at 260 °C on CFRPs.

The curing of the cyanate ester was faster, and involved heating up to 150 °C, a dwell time of 1 hour, followed by heating to 200 °C at 10 °C/min, a dwell time of 3 hours, and a last step at 270 °C, with a dwell time of 3 hours.

The curing processes were conducted in air in a muffle furnace (Nabertherm LH 60/40, Germany) with different thermal cycles, according to the composition of the adhesive.

The commercial adhesive (GB), the phenolic one with both curing cycles (PH260 and PH150) and the cyanate ester (CY) adhesives were cured inside moulds in order to obtain bulk cured adhesives (175 mm x 50 mm x 3 mm) for dilatometry (Netzsch, DIL 402 PC/4) and thermogravimetric analyses (TGA) with differential thermo-gravimetry (DTG) and Thermo-Gravimetric-Evolved Gas analyses (TGA-EGA). The thermal stability of the samples was assessed by means of thermogravimetric/evolved gas analysis (TGA/EGA). An ultra-microbalance (sensitivity 0.1 µg), connected to a time/temperature-resolved FTIR, was

employed for TGA. The samples were ground in an agate mortar for these tests. Fragments of the samples (ca. 15 g) were placed in an open platinum pan and heated, from 30 to 1000 °C, at a rate of 20 °C/min under a dynamic inert atmosphere (100% N_2, flow rate: 35 mL/min) in a Pyris 1 TGA (PerkinElmer, Waltham, MA, USA). The gas that was produced during the heating ramp was piped (gas flow 65 mL/min), via a pressurized heated transfer line (Redshift S.r.l. Vicenza, Italy), and analysed continuously by the FTIR (Spectrum 100, Perkin Elmer), equipped with a conventional thermostatic gas cell. Temperature/time-resolved spectra were acquired, over the 4000-600 cm^{-1} wavenumber range, at a resolution of 0.4 cm^{-1}, and analysed with the Spectrum software (Perkin Elmer). In order to minimise any interference with the gaseous species of interest that was produced during the thermal decomposition of the organic matrix, the H_2O spectra and any released CO_2 were automatically subtracted from each FTIR spectrum by applying a compensation algorithm during the recording. Temperature-resolved infrared profiles of each single moiety desorbed from the samples were obtained from the intensity of a representative peak of the investigated species. The gas that was produced from PH150 and PH260 during the main degradative process was automatically collected (ca. 100 µL) and injected into a Clarus 500S gas chromatograph (PerkineElmer) equipped with a standard non-polar ELITE 5MS fused silica capillary column (PerkineElmer). The eluted substances were identified by means of an integrated Clarus 560S mass spectrometer (PerkineElmer). Total Ion Count (TIC) chromatograms, normalised to the sample mass, were reported. The average mass spectra identified at the mid-height of the chromatographic peak were analysed with NIST MS Search Software.

CFRP HC was tested as above, by means of TGA-EGA, for comparison purposes.

Zerodur ™ slabs were joined with both the commercial GB adhesive and the phenolic adhesive cured with both high (PH260) and low (PH150) temperature curing processes to measure the indentation elastic modulus inside the joints, which was conducted by means of

nano-indentation, using the continuous stiffness measurement (CSM) method and a Berkovich indenter (Nano Indenter G200, Agilent Technologies).

CFRP slabs were abraded with SiC paper (#2500) to expose the first fibre layer (0°), then cleaned with ethanol, sonicated and dried prior to joining. They were joined with the phenolic adhesive cured at both high (PH260) and low (PH150) temperature curing cycles, with about 1 kPa to keep the samples in the correct position. The joint thickness, measured as the difference after joining, ranged between 140 to 200 microns.

The joints were tested, by means of the single lap offset shear test in compression (SLO), a modification of ASTM D1002-05, as in [9], to compare the two curing processes.

The tests were performed using a universal mechanical testing machine (SINTEC D/10), with a cross-head speed of 0.5 mm/min. The average lap shear strength in compression of the adhesive joined CFRPs was calculated by dividing the maximum load at failure by the joining area. The joining area of all the SLO samples was 25 mm x 12.5 mm = 312.5 mm^2. The tests were carried out on at least five samples.

The lap shear of these joints was also tested after a thermal treatment consisting of a first step of 24 hours at 80°C under vacuum, a second step (ageing) of 7 days at 45°C and 93% Relative Humidity (RH), and a third step of 64 thermal cycles [-30°C ; 70°C], as in **Table I**. [10]

Zerodur™ - CFRP - Zerodur™ sandwich structures (100 mm x 100 mm; 150 mm x 100 mm), joined with the low temperature cured phenolic adhesive (PH150), were tested in triplicate, in tensile and lap shear mode, respectively.

In order to obtain the sandwich structures, a CFRP honeycomb was cut to the Zerodur™ plate size, one side of the honeycomb was dipped into the phenolic adhesive (PH) at room

temperature, and the same side was then placed on the Zerodur™ plate; the thus assembled half was turned over and the other honeycomb side was dipped into the phenolic adhesive (PH); the same side was then placed on the second Zerodur™ plate; a small load was applied to the obtained assembly (around 1kPa) to keep it in position; the assembly was placed in a furnace for the modified, low temperature curing treatment (PH150).

The tensile and apparent shear values were calculated by dividing the load at fracture by the entire Zerodur™ area or by dividing it by the calculated CFRP HC bonded area, as discussed hereafter .

The polished cross-sections of the joints and fracture surfaces after the lap shear tests were observed by means of Field Emission Scanning Electron Microscopy, equipped with an Energy Dispersive Spectroscopy device (FESEM-EDS SUPRATM 40, Zeiss and Merlin Gemini Zeiss, Germany).

2. Results and discussion

The relatively low maximum temperature (160°C) that was considered acceptable for the CFRPs used in this work depends on the fact that no post-curing treatment was performed during its production to avoid any possible detrimental effects in the moisture expansion coefficient [10] . As a consequence, the glass transition of this "non-post-cured" CFRPs is lower than in the case of the post-cured one.

For this reason, most of the highly performing adhesives that have been developed for aeronautical and space applications, which have typical curing temperature of about 250-260 °C, could not be used.

Another constraint is related to the necessity of being able to spread the adhesive easily, in a cleanroom environment, during the production of the Zerodur™ - CFRP - Zerodur™ sandwich structures (**Figure 1**). The use of a cyanate ester adhesive, such as CY, would be more difficult, even in the case of low temperature curing, because the adhesive must be kept at a temperature of at least 70 °C in order to have a suitably low viscosity for the joining process [8] . This is not the case of phenolic-based adhesives, as they can be used at room temperature.

In consideration of all that has been discussed above, attempts were made to reduce the curing temperature to 150 °C, while increasing the curing time to 10 hours, on one of the phenolic adhesives used in this work, (PH), since it had already been fully characterised in case of curing at 260°C in [8].

It was considered worth comparing the properties of the low temperature cured adhesive PH150 with those of the other adhesives cured at higher temperatures.

The commercial adhesive, referred to as GB in this paper, was considered because it had previously been used by some of the authors to join C/C composites, and its properties, which were discussed in [7], were known . GB joined C/C composites were lap shear tested and a sound value of 14±3 MPa was obtained for the SiC paper abraded C/C, while a value of only 7±4 MPa was obtained for the as-received C/C. The elastic modulus inside the C/C joint was measured by means of a Nanoindenter XP (depth limit 2000 nm) and 18±3 GPa was obtained. [7]

The GB adhesive required curing at 260 °C, and the cyanate ester required it at 270 °C, but both temperatures were too high for the thermo-mechanical integrity of the CFRP joints. However, bulk samples of these adhesives were cured as slabs in order to test to measure their CTE, by means of dilatometry, for comparison purposes with PH260 and PH150.

As can be seen in **Figure 2**, the extensive porosity of the bulk samples made it difficult to obtain suitable samples for the dilatometry tests. Therefore, smaller specimens were cut from these larger ones, in an attempt to avoid large pores. In this way, it was possible to test the CTE of PH150, PH260 and GB. However, any attempt to obtain suitable samples from CY failed.

Figure 3 shows the huge variation is CTE measurements for the six bulk samples of PH150. The CTE measured between 25 and 100 °C ranges between 82 and 33 x 10^{-6} °C^{-1}. The porosity of each sample is the most likely source of this deviation. The CTE of PH260 is at about 50 x 10^{-6} °C^{-1} and in the 16-24 x 10^{-6} °C^{-1} range for GB (the curves are not reported here). There is a certain difference between the GB CTE on the data sheet (7.4 x 10^{-6} °C^{-1}) and that measured in this work (16-24 x 10^{-6} °C^{-1}): again, porosity may be responsible, but there is no indication on the data sheet [6] of how the GB CTE was measured.

As a result of the uncertainty of the CTE measurements of the bulk cured adhesives, it was decided to characterise them with other techniques in order to compare their behaviour.

TGA-EGA analyses were conducted on the CFRP HC, the commercial adhesive (GB), the phenolic one obtained with both curing cycles (PH260 and PH150) and on the cyanate ester (CY) (**Figure 4, 5**).

In order to fully characterise the thermal behaviour of the selected phenolic resin with the modified curing process at 150 °C (PH150), which was necessary to preserve the mechanical properties of CFRP, TGA-EGA was used to investigate the chemical nature of the gaseous species that evolved during its heating with FTIR [11,12] and to compare them with those obtained from the typical curing at 260°C (PH260) (**Figure 4**). The same analysis was conducted on the cyanate ester resin cured at 270 °C (CY) , on the commercial carbon-based adhesive cured at 260 °C (GB), and on the CFRP HC used in this work, for comparison

purposes.

The thermal behaviour of the samples was studied over a 30-1000 °C temperature range in an inert atmosphere (N_2 100%, heating rate 20 °C min^{-1}). **Figure 4** reports the thermograms and the relative derivative curves (D-TG) obtained for the PH150 (blue curve), PH260 (red curve), CY (green curve), GB (orange curve) and the CFRP HD (grey curve) samples. The gas released during the heating was continuously analysed, by means of FTIR, to identify the main species: NH_3, CH_4, phenol (C_6H_5OH) and alkyl isocyanates (RCNO). In order to avoid any interference from water or from any CO_2 released during the heating, the signals of such species were subtracted during the FTIR recording by applying a compensation algorithm. Four temperature ranges were considered for the thermograms: 30-190 °C (I); 190-325 °C (II); 325-500 °C (III) and 500-1000 °C (IV). PH150 and PH260 exhibited virtually the same thermal behaviour between 30 °C and 190 °C, and it was characterised by a mass loss of 1%. GB underwent a mass loss of 0.1%. The observed mass loss was assigned to the evolution of physisorbed/chemisorbed water. No other volatile species were detected. CY and CFRP HC were thermally stable.

PH150 was subject to a higher mass loss of between 190-325 ° C (3%), due to a well-defined process, as evidenced by the minimum on D-TG at ca. 250 °C , and which was characterised by the release of NH_3. The release of NH_3 indicates that some nitrogen containing precursors (most likely urea, according to the decomposition temperature, [13] are present in the adhesive as additives, as observed by Brobowski et al. [14] PH260 lost 1% of mass, possibly due to water release (not measured). The absence of an NH_3 release indicates that the curing process at a higher temperature (260 °C) induced the decomposition of any nitrogen containing precursors. The mass of CY, GB and CFRP HC remained virtually constant over the same range, thus evidencing the thermal stability of such samples over this temperature range. PH150 and PH260 underwent mass losses of 8.1% and 8.6% between 325-500 °C,

respectively. The main species that were produced were NH_3 and R-NCO. Again in this case, the evolution of nitrogen containing species is consistent with the presence of urea and isocyanate in the phenolic resins. [14] GB was characterised by a mass loss of ca. 8.2%, due to at least one main process, as evidenced by the minimum on D-TG at ca. 400 °C, which was superimposed onto the tail of a second process that occurred at a higher temperature. The release of C_6H_5OH started in this range. The recorded FTIR profile for this sample did not account for the measured weight loss or for the evident peak on D-TG at ca. 400 °C. This could be explained by considering a further release of water (not measured) from the sample due to thermally induced condensation reactions. CY and CFRP exhibited similar behaviour, with a mass loss of ca. 12.8% and ca. 7.5%, respectively. Both of the samples underwent a fast decomposition process characterised by the evolution of NH_3.

PH260 and PH150, which exhibited similar thermal behaviour over the 500-1000 ° C range, with a weight loss of ca. 21.0% and ca. 18.1%, respectively, produced virtually the same amount of C_6H_5OH. Furthermore, both PH260 and, albeit to a lesser extent, PH150 released CH_4, possibly as a result of the recombination of residual C and H. CY (mass loss ca. 17.3%) and CFRP (mass loss ca. 8.9 %) produced NH_3 and R-NCO. CY also released CH_4, likely due to the recombination of residual C and H. GB showed a mass loss of ca. 23.0 %, as a result of the production of C_6H_5OH and CH_4.

The main thermal degradative process of PH15 and PH260 is represented in more detail in **Figure 5** (a), where the mass loss and the FTIR profiles are reported. In order to univocally assess the gaseous species released during the main degradative process of the cured phenolic adhesives, the produced gas was sampled at 560 °C and analysed by means of GC-MS. The gas chromatograms, expressed as TIC/mg of sample (**Figure 5 b**), evidenced the release of a complex mixture of aromatic species (namely benzene, toluene, 1,3-dymethylbenzene, phenol, 2-methylphenol, 4-methylphenol, 2,6-dimethylphenol, 2,3-dimethylphenol) from both

PH150 (upper panel) and PH260 (lower panel). The intensity of each recorded peak is slightly higher for PH150 than for PH260. The intensity of the GC peak of each detected species is of the same order of magnitude for both of the samples. This indicates that the phenolic resin cured at 150 °C exhibited a similar thermal stability to that cured at 260 °C.

The phenolic adhesive cured at both a high (PH260) and low (PH150) temperature, and the commercial GB adhesive were used to join Zerodur ™ slabs and to measure the indentation elastic modulus, as obtained from nano-indentation, inside the joints to the fixed maximum penetration depth of 1500 nm [15] , **Figure 6** : values of 8.1 ± 0.8 GPa were measured for PH150, of 7.9 ± 1.3 GPa for PH260 and of 12.0 ± 2.8 GPa for GB. The value measured here for GB (12.0 ± 2.8 GPa) is slightly lower than that reported in [7] (18±3 GPa) inside the joined region, but the latter result was obtained with a different instrument. In order to test the suitability of the nano-indentation method, the indentation elastic modulus was also measured on Zerodur ™, and a value of 89.9 ± 0.9 GPa, which corresponds to what was reported in the data sheet [1], was observed .

As specified by ThalesAleniaSpace, , the elastic modulus of a joint layer must be higher than 500 MPa and it must be measured inside the joined region. Lower values cannot guarantee the rigidity of the final sandwich component. In this respect, PH150, PH260 and GB statisfied the requirements . No value of CY is available yet.

The PH phenolic adhesive obtained under both curing cycles (PH260 and PH150) was used to join CFRP slabs: the polished cross section of a typical joint is shown in **Figure 7 (a-c)**. The interface with CFRPs is continuous and free of pores, and the inorganic charges are clearly visible and well dispersed in the adhesive. However, as shown in **Figure 7 (a),** some large pores are still present, even though the curing was conducted at a very slow heating rate (0.3 °C/min). The interface between the adhesive and the CFRPs is barely distinguishable **(Figure**

7 b,c), and a perfect wettability of PH150 on CFRPs can be observed.

Figure 8 (a) shows the typical cohesive fracture obtained when CFRP slabs are joined with PH150, with an average lap shear strength (SLO) of 16 ± 1 MPa both before (a) and after (b) thermal ageing of the joints, as in **Table I**.

As reported in [8], the lap shear strength of the PH260 joined C/C was about 16 MPa, thus showing that this phenolic-based adhesive is effective as a joining material for C/C and CFRPs, for both curing cycles, at least from a mechanical point of view. Moreover, the cyanate ester adhesive joined C/C also gave a sound average lap shear value of 13 MPa, but the main drawback of this cyanate ester resin is the temperature necessary to apply CY to large structures, as discussed above. This drawback could be avoided by selecting a different CY with low viscosity at room temperature: some activities are ongoing in this direction.

Zerodur™ - CFRP - Zerodur™ sandwich structures, joined with the low temperature cured phenolic adhesive (PH150), were tested in triplicate in tensile mode (100 mm x 100 mm) (**Figure 1**) and in lap shear mode (150 mm x 100 mm) (**Figure 9**). The tensile test set-up, which was prepared at the Politecnico di Torino (Italy), is shown in **Figure 9**: sandwich structures were joined to metal fixtures with an epoxy glue spread over the whole surface of the fixtures. A cohesive/mixed fracture can be observed for the tensile tests, i.e. some adhesive is visible on Zerodur ™ and some on CFRP HC. Moreover, an average tensile strength of 0.78 ± 0.28 MPa was measured by dividing the maximum load at failure by the total joining area, i.e. the Zerodur™ area (100 mm x 100 mm).

When the joining area was calculated by considering the honeycomb wall area joined to Zerodur™, i.e. by multiplying the total number of honeycomb walls in each sandwich (79) by the area of a single wall, the single wall area was derived from the average thickness (0.22 mm) and length (11.55 mm) of a honeycomb wall. The average tensile strength was

calculated by dividing the maximum load at failure by the honeycomb wall area, which resulted in 39 ± 14 MPa.

The shear test set up prepared at ThalesAleniaSpace is shown in **Figure 10**: again, the fracture is cohesive/mixed as before. An average lap shear of 0.66 ± 0.1 MPa was obtained by dividing the maximum load at failure by the total joining area, i.e. the Zerodur™ area (150 mm x 100 mm). The apparent shear strength calculated by dividing the maximum load at failure by the honeycomb wall area is 33 ± 0.5 MPa.

3. Conclusion

The aim of this work was to develop and test a low curing temperature and high performance adhesive that would be able to join Zerodur™ to Carbon Fibre Reinforced Polymer (CFRP) honeycomb (HC) in a sandwich structure for aerospace applications.

Two phenolic-based adhesives and one cyanate ester-based one were tested and compared with a commercial adhesive. The phenolic-based adhesive cured at 150°C showed the same thermo-mechanical characteristics after curing at 260°C; the properties were obtained by means of dilatometry, thermogravimetric analysis (TGA) with differential thermo-gravimetry (DTG), Thermo-Gravimetric-Evolved Gas analysis (TGA-EGA), and elastic modulus tests of the indentations inside the joined region.

The phenolic adhesive cured at 150 °C was considered the most suitable to join the CFRPs to Zerodur ™ and it was mechanically tested by measuring the lap shear strength of CFRP slabs joined at room temperature and after thermal cycling.

Zerodur™ - CFRP - Zerodur™ sandwich structures, joined with the phenolic adhesive cured at 150 °C, were also tested in tensile and lap shear mode.

Further activity is foreseen to reduce the curing temperature of the other two adhesives i.e., the cyanate ester (CY) and the commercial phenolic-based adhesive (GB).

Finally, an improvement in the joining process could be obtained by using a robotised machine that would be able to spread a thin line of adhesive, with a hexagonal honeycomb pattern, directly onto Zerodur skins. After this step, the honeycomb could be placed between the two skins before the structure is introduced into the curing furnace. Mechanisation of the dipping, adhesive deposition and honeycomb handling procedures could help in the realisation of larger prototypes of the final component.

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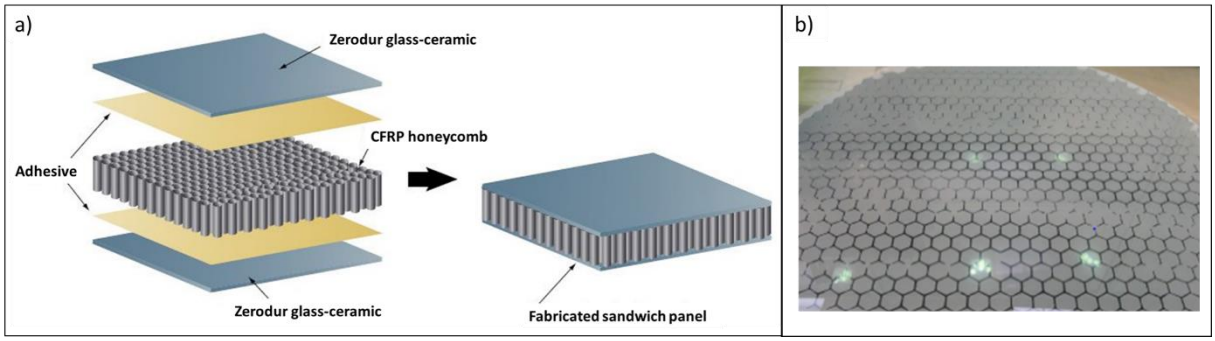

Figure 1. Sketch of the sandwich structure (a) and the final prototype (b) with face sheets made of Zerodur ™ and CFRP honeycomb in between. The adhesive joint between CFRPs and Zerodur ™ is visible.

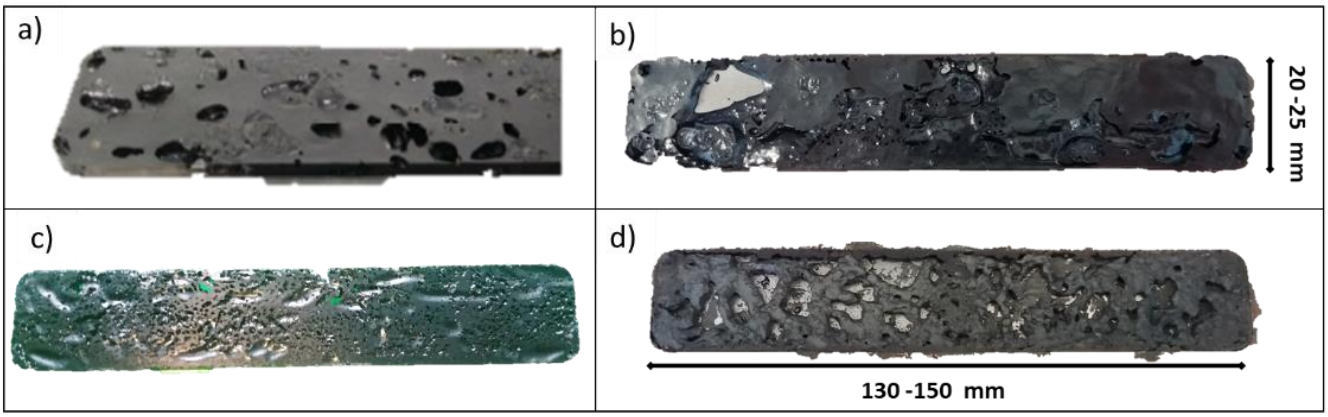

Figure 2. Bulk adhesives: the phenolic adhesive cured at 150 °C (PH150) (a), at 260 °C (PH260) (b) , the cyanate resin cured at 270 °C (CY) (c), and the commercial adhesive cured at 260 °C (GB) (d).

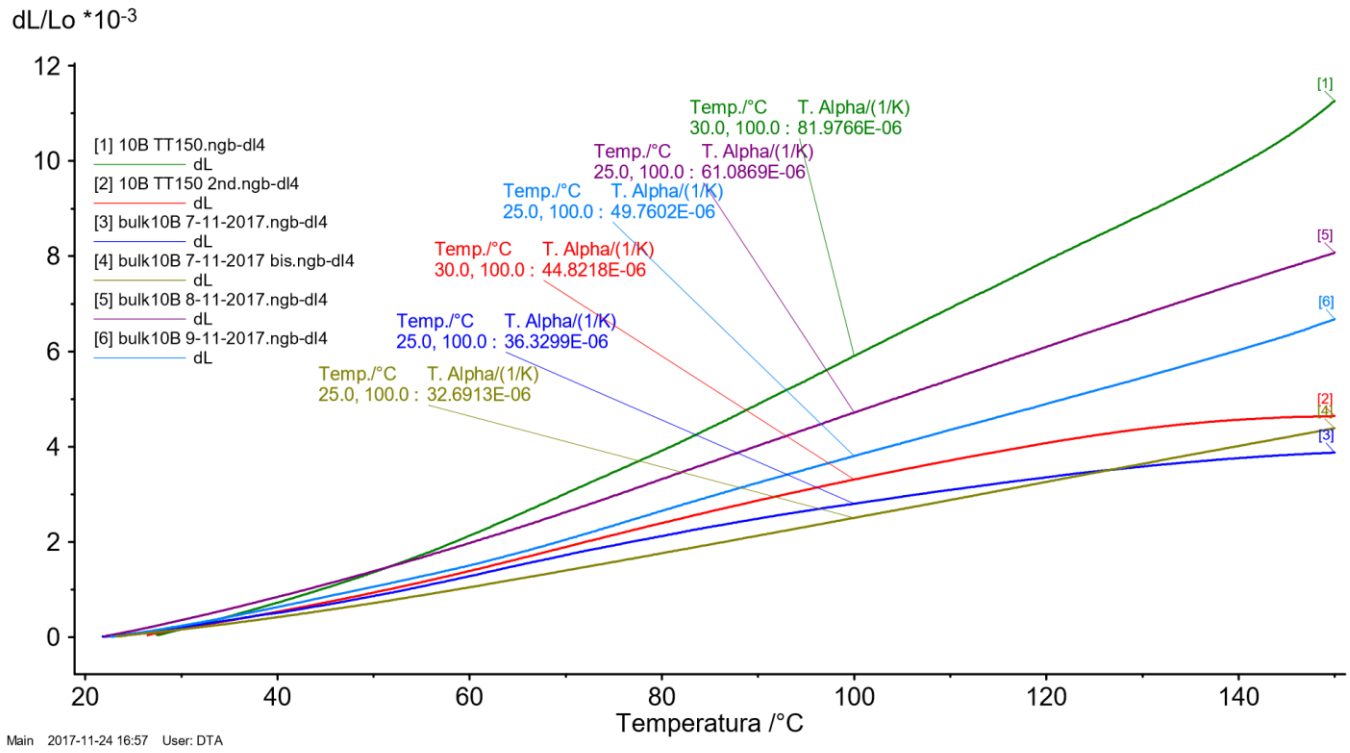

Figure 3. CTE of the phenolic adhesive cured at 150 °C (PH150) measured on 6 different bulk samples, showing a large variation of results

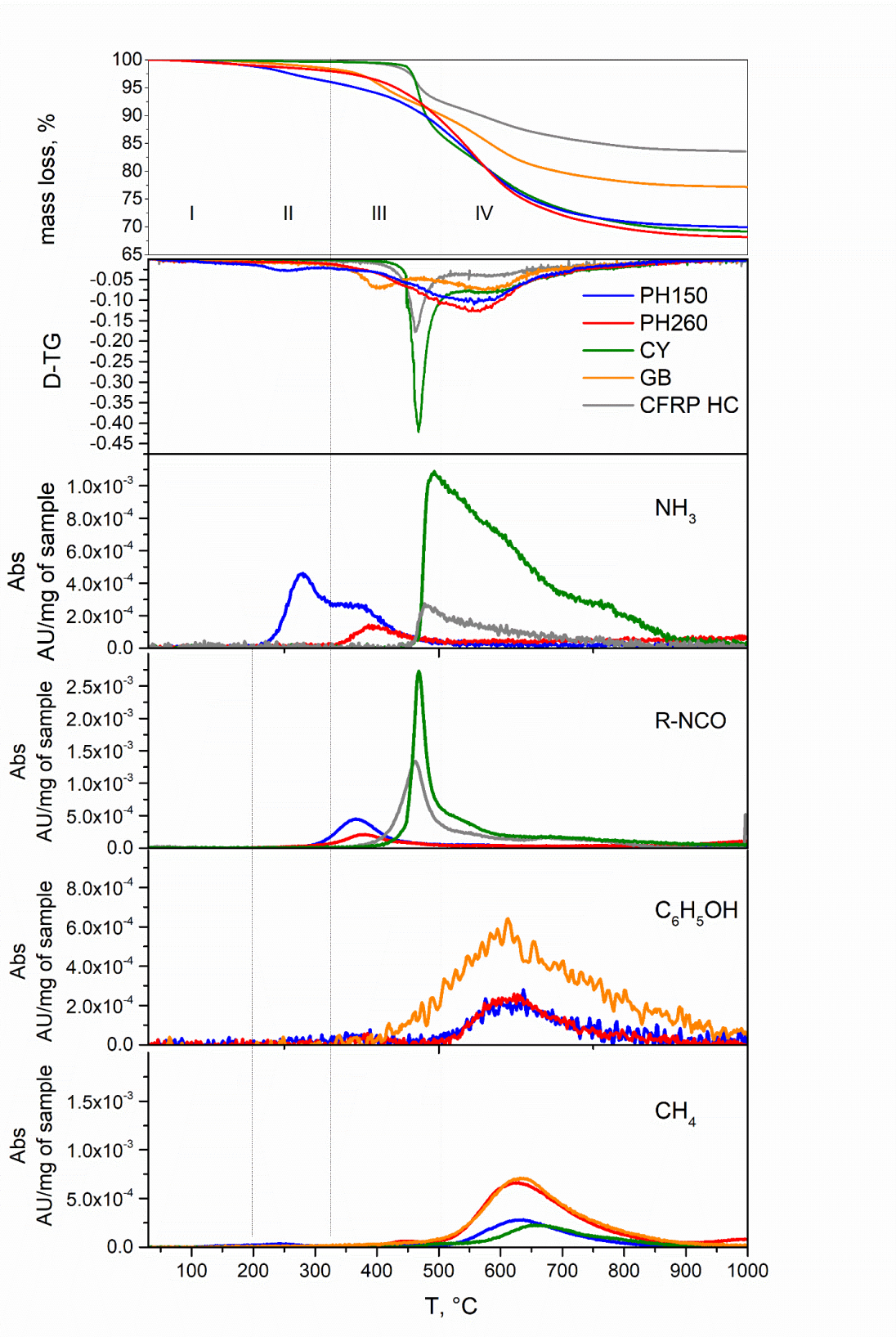

Figure 4. Thermograms (mass loss %) and derivative curves (D-TG) recorded after heating PH150 (blue line), PH260 (red line), CY (green line), GB (orange line) and CFRP HC (grey line) under an N 2 dynamic atmosphere at temperatures ranging from 35 to 1000 °C (20 °C/min). FTIR profiles of the NH_3, R-NCO, C_6H_5OH and CH_4 releases are reported as a function of the temperature.

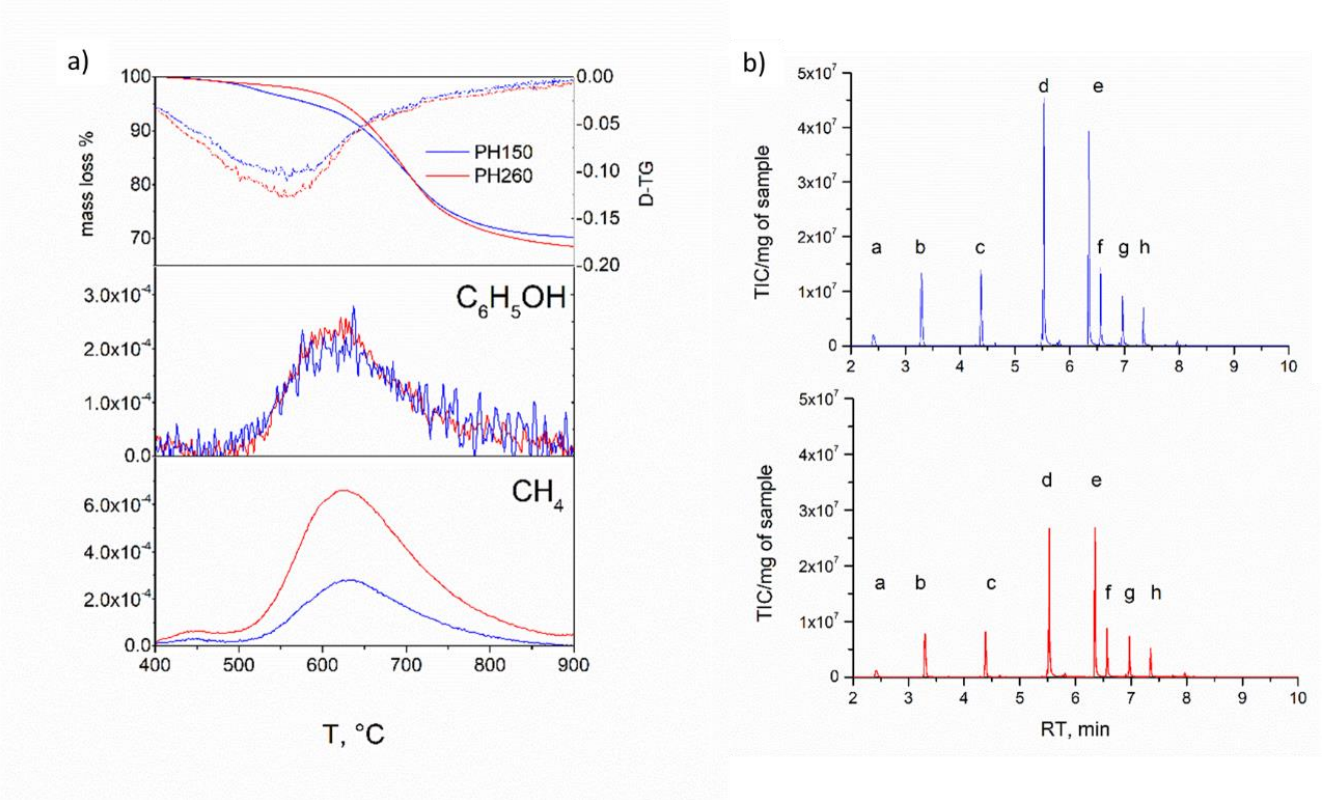

Figure 5. (a) Mass loss %, derivative curves (D-TG) and FTIR profiles of the release of the gaseous products over the 400-900 °C temperature range (a) and (b) gas chromatograms of the gas that was produced for the phenolic adhesives cured at 150 °C (PH150) and at 260 °C (PH260) at ca. 560 °C. The GC curve are normalised to the mass of the samples. The GC peaks correspond to a) benzene; b) toluene; c) 1,3-dymethylbenzene; d) phenol; e) 2-methylphenol; f) 4-methylphenol; g) 2,6-dimethylphenol; h) 2,3-dimethylphenol.

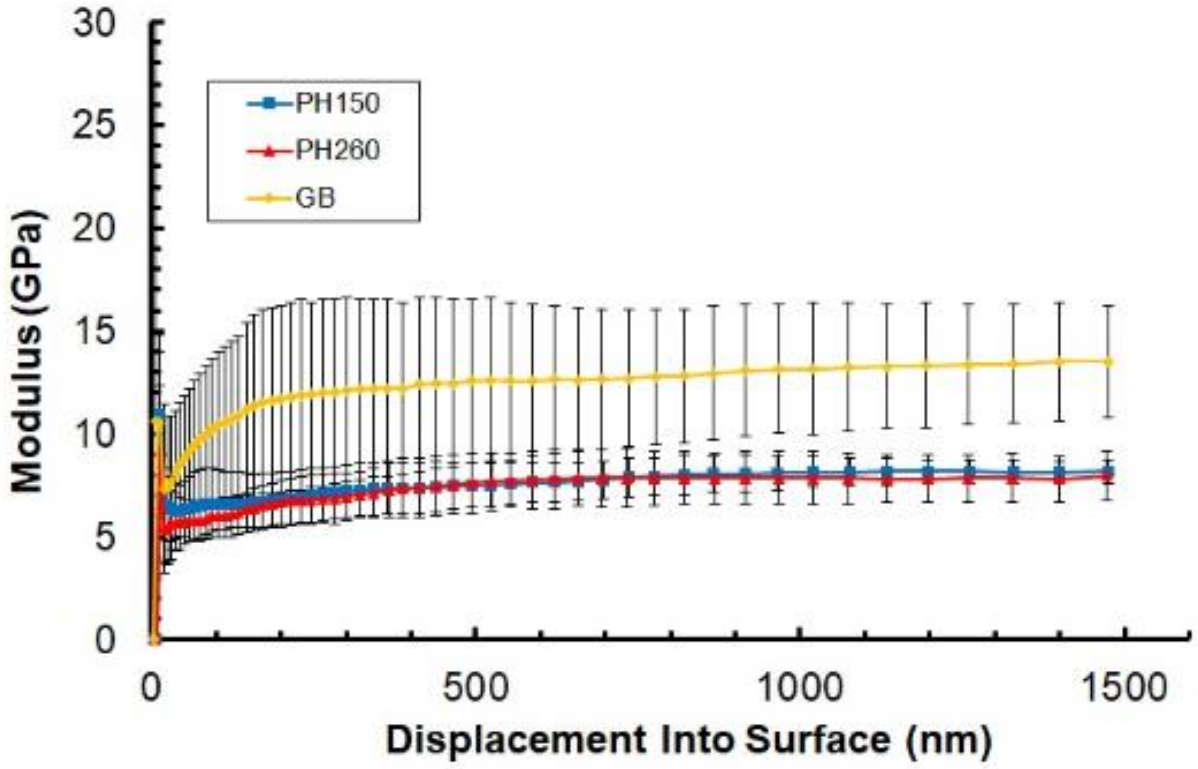

Figure 6. Elastic modulus measurements obtained from the nano-indentation test: comparison of Zerodur™ joined with the phenolic adhesive cured at 150 °C (PH150) and at 260 °C (PH260) and the commercial adhesive (GB).

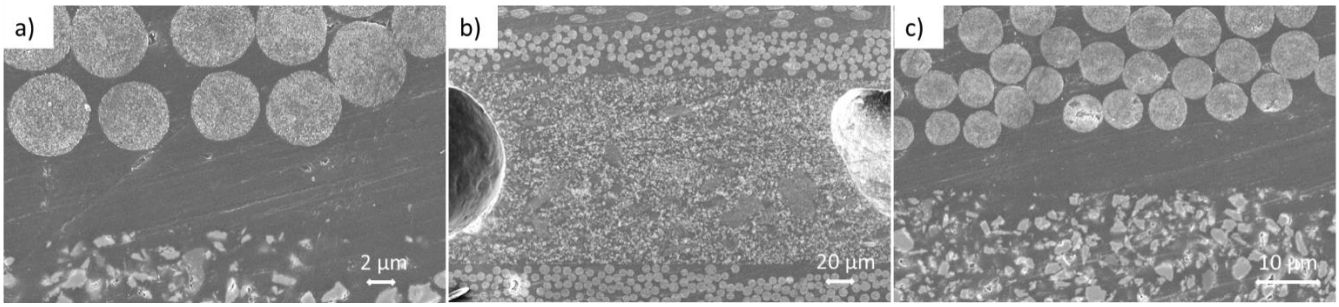

Figure 7. Phenolic adhesive (PH150) bonded CFRPs: SEM polished cross sections at increased magnification showing the residual porosity in the phenolic adhesive (a) and the perfect wettability at the adhesive/ CFRPs interface (b,c); inorganic charges in the phenolic adhesive are also visible in all the pictures.

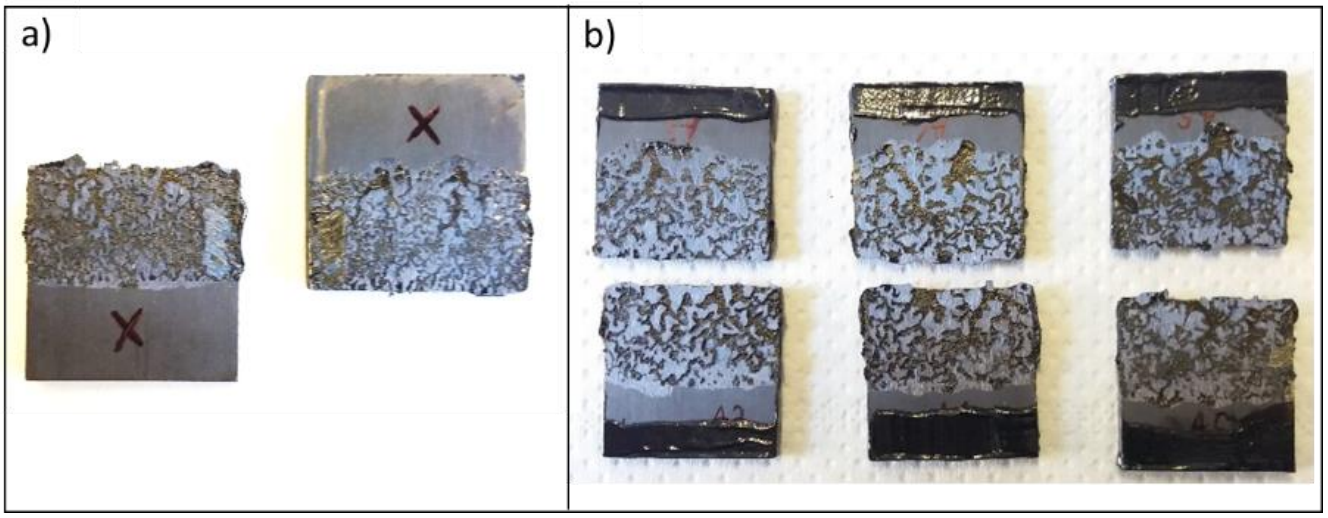

Figure 8. Cohesive fracture surfaces of the phenolic adhesive (PH150) bonded CFRPs after the Single Lap Offset test, showing 16 ± 1 MPa for both before (a) and after (b) thermal ageing

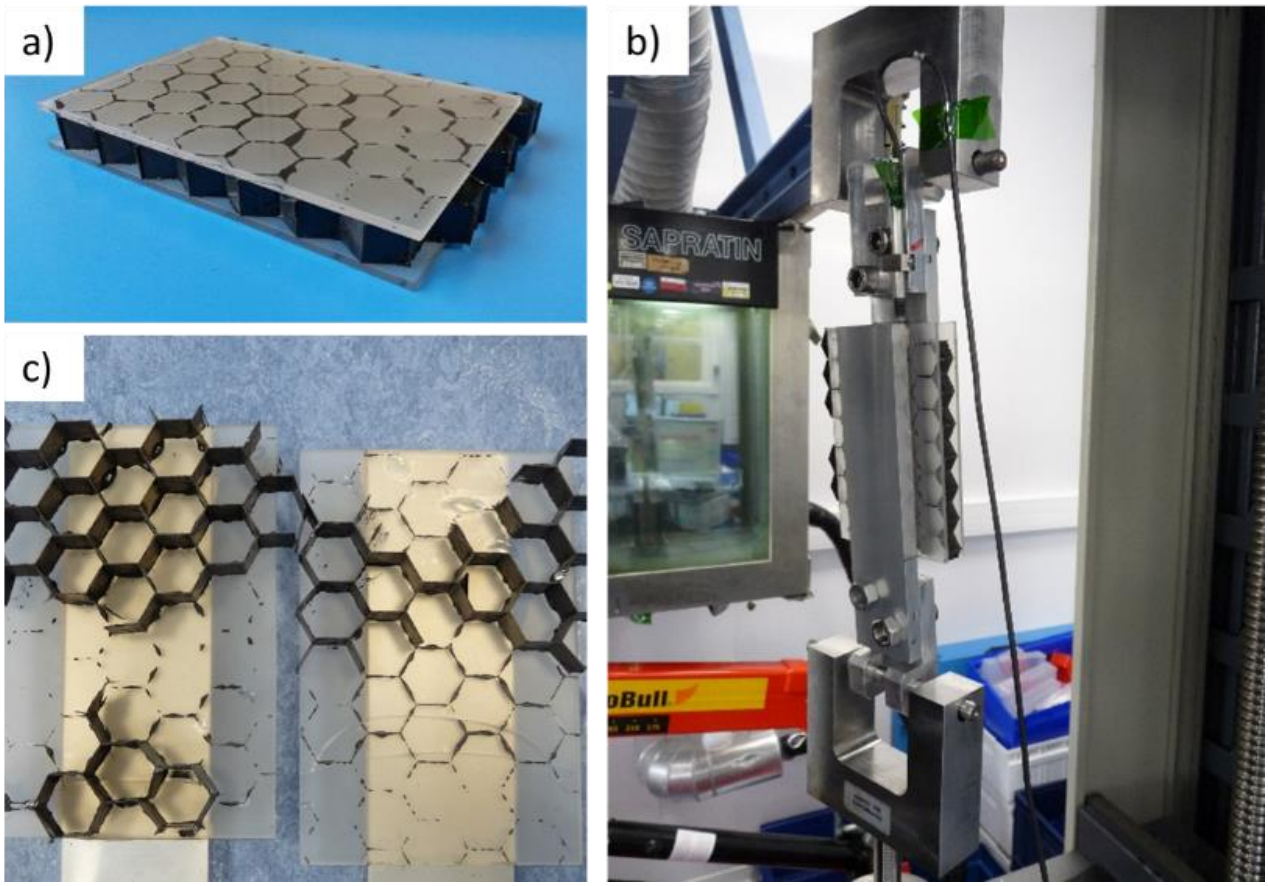

Figure 9. Phenolic resin bonded (PH150) Zerodur ™-CFRP honeycomb-Zerodur ™ sandwich assembly (100 mm x100 mm) (a) for a tensile test (b) and the fracture surface of sandwiches after a tensile test (c)

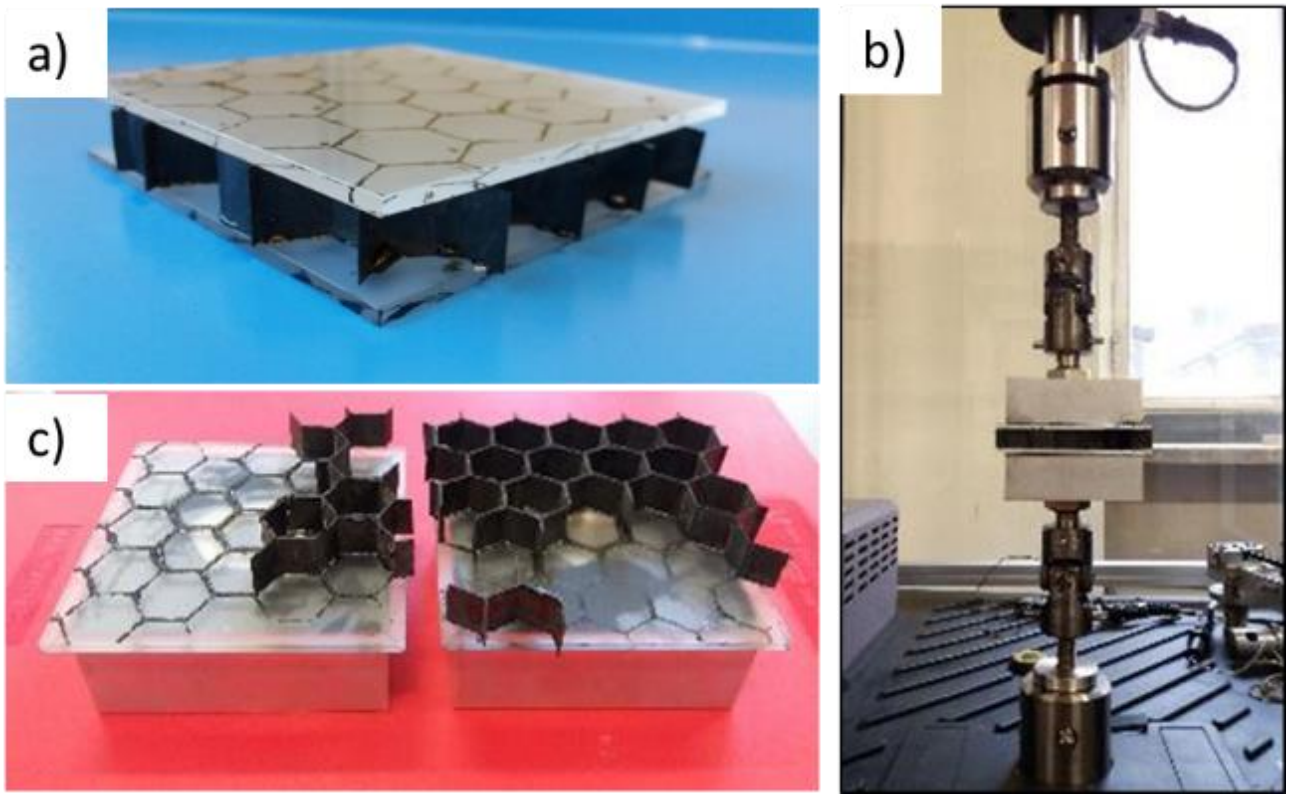

Figure 10 : Phenolic resin bonded (PH150) Zerodur ™-CFRP honeycomb-Zerodur™ sandwich assembly (150 mm x100 mm) (a) for a shear test (b) and the fracture surface of the sandwiches after a tensile test (c)

Table 1. Thermal cycling of joined samples for the lap shear tests.

Step 1: 24 hours at 80°C	Vacuum, pressure < 2 x 10-5 mbar at room temperature (RT) Temperature ramp: between 0.3 et 0.5°C/min until 80° ± 2°C Dwelling at 80°C for 24 hours Cooling to RT at 5°C/min
Step 2: ageing	7 days at 45±3 °C and 93±5 %HR
Step 3: thermal cycling	64 cycles [-30°C ; 70°C] : Temperature ramp: 5°C/min (both for heating and cooling) 30 minute step at -30°C and at 70°C, starting from a first cycle at 70°C

Table of contents

The design of high performance adhesives is presented for the joining of Zerodur™ to Carbon Fibre Reinforced Polymer (CFRP) honeycomb (HC) in a sandwich structure of carbon fibre reinforced composites (C/C) for ultra-stable aerospace applications. A phenolic-based adhesive appears promising as it shows suitable thermomechanical stability, ease of application on large components and a low curing temperature, which are compatible with CFRP substrates.

Keyword : joining

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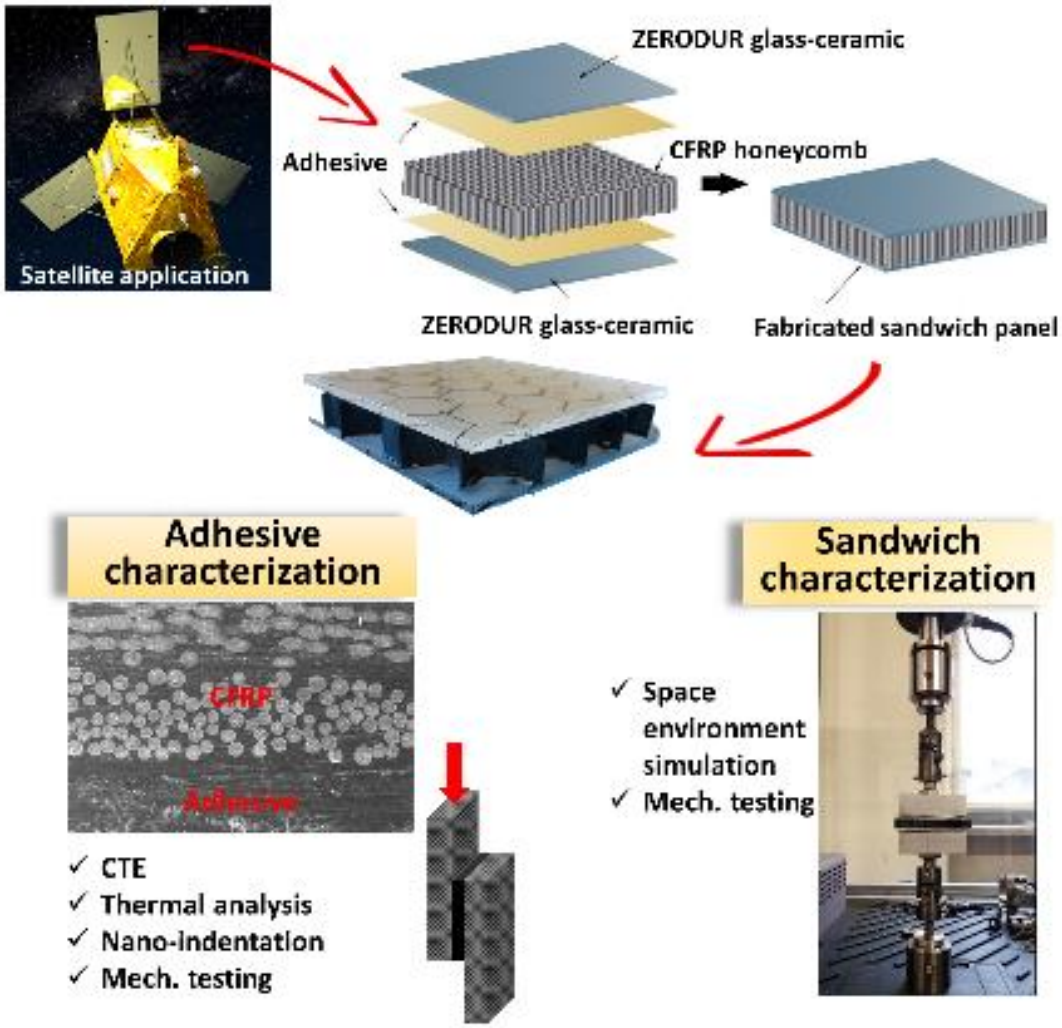
Adhesive joining of Zerodur™ - CFRP - Zerodur™ sandwich structures for aerospace applications


Satellite application
ZERODUR glass-ceramic
Adhesive
CFRP honeycomb
ZERODUR glass-ceramic
Fabricated sandwich panel
Adhesive characterization
CFRP
Adhesive
✓ CTE
✓ Thermal analysis
✓ Nano-Indentation
✓ Mech. testing
Sandwich characterization
✓ Space environment simulation
✓ Mech. testing