

Design, Realization, and Characterization of Advanced Adhesives for Joining Ultra-Stable C/C Based Components

Original

Design, Realization, and Characterization of Advanced Adhesives for Joining Ultra-Stable C/C Based Components / Casalegno, V.; De la Pierre des Ambrois, S.; Corazzari, I.; Turci, F.; Tatarko, P.; Damiano, O.; Cornillon, L.; Terenzi, A.; Natali, M.; Puglia, D.; Torre, L.; Ferraris, M.. - In: MACROMOLECULAR MATERIALS AND ENGINEERING. - ISSN 1438-7492. - 305:9(2020), p. 2000229. [10.1002/mame.202000229]

Availability:

This version is available at: 11583/2847045 since: 2020-09-29T16:32:50Z

Publisher:

Wiley-VCH Verlag

Published

DOI:10.1002/mame.202000229

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

Wiley preprint/submitted version

This is the pre-peer reviewed version of the [above quoted article], which has been published in final form at <http://dx.doi.org/10.1002/mame.202000229>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions..

(Article begins on next page)

Design, realization and characterization of advanced adhesives for joining ultra-stable C/C based components

Valentina Casalegno , Stefano De la Pierre des Ambrois, Ingrid Corazzari , Francesco Turci , Peter Tatarko, Olivier Damiano, Laurence Cornillon, Andrea Terenzi , Maurizio Natali , Deborah Puglia, Luigi Torre, Monica Ferraris*

Prof. V.Casalegno, S. De la Pierre des Ambrois, Prof. Monica Ferraris
*Department of Applied Science and Technology (DISAT), Politecnico di Torino
Corso Duca degli Abruzzi 24-10129 Torino, Italy*

Dr. I. Corazzari, Dr. F. Turci
*Department of Chemistry and “G. Scansetti” Interdepartmental Center for the Study of Asbestos and Other Toxic Particulates, Università degli Studi di Torino
Via Pietro Giuria 7- 10125 Torino, Italy*

Prof. Peter Tatarko
*Institute of Inorganic Chemistry, Slovak Academy of Sciences
Dubravska cesta 9, 845 36, Bratislava, Slovakia*

Dr. O. Damiano , Dr. L. Cornillon
Thales Alenia Space, 5 Allée des gabians, BP99, 06156 Cannes La Bocca Cedex, France

Dr. A. Terenzi , Prof. M. Natali , Prof. D. Puglia, Prof. L. Torre
*University of Perugia, Civil and Environment Engineering Department, Piazza Università -
06123 – Perugia, Italy*

corresponding author: valentina.casalegno@polito.it

Keywords: joining, ultra-stable adhesives, C/C, composites

Abstract

The aim of this work has been to develop high-performance adhesives to join carbon fibre reinforced composites (C/C) for use in aerospace applications; in order to guarantee sound mechanical strength, a low coefficient of thermal expansion and ease of application on large components. Several different adhesive formulations, based on phenolic or cyanate-ester resins (charged with the maximum experimentally feasible amount of carbon-based fillers), have been developed and tested. The measurements of the lap shear strength at room temperature of the C/C joined by means of one phenolic and one cyanate ester-based resin has demonstrated that these formulations are the most suitable for the given application. A complete characterisation, by means of viscosimetry, dilatometry and thermal gravimetric analysis, coupled with gas analysis by means of mass spectroscopy, has confirmed that the phenolic-based formulation is the most promising joining material. A nano-indenter was used to obtain its Young modulus and hardness, both inside the joint and as a bulk cured adhesive.

1. Introduction

The key aspects in aerospace applications are light-weight, high-strength, high-stiffness and fatigue resistance. Carbon/carbon composites (C/C) have been selected as key materials for space instruments because of their excellent properties, such as a thermal expansion coefficient close to zero, very high thermo-elastic stability, low density and moisture insensitivity.^[1]

Carbon-based composite materials, and sandwich structures in particular, have always been widely used in the space industry to build satellites, thanks to their unique mass/property ratio: however, the performance of satellites depends to a great extent on the chosen materials and in particular on the adhesives used to assemble their parts.

The environmental conditions for satellite applications can be extreme and severe thermal cycling can occur, thus the main requirement is an excellent thermal stability over a wide temperature range. [2] To fully benefit from the potential offered by C/Cs, it is important to select a joining material with the same properties as the C/C, together with sound mechanical strength.

Although joining methods for carbon materials have been studied extensively, very few papers have reported on the bonding of C/C composite parts using adhesives in recent years. [3-5]

The adhesives for such applications must fulfil very stringent requirements, mainly concerning the overall stability of the structure under operative conditions.

The advantage of the use of adhesives as a joining material are manifold: to cite a few, an overall weight reduction of the joined structure, and the absence of holes for bolts/screws, etc. Moreover, bonding is required not only during manufacturing, but also during repairs of the components: the use of adhesives facilitates the removal of damaged parts and their replacement. [6-9]

The existing solutions (i.e. commercial adhesives) suffer from some drawbacks, mainly related to distortions due to thermal and/or moisture expansion effects. However, the properties of adhesives for aerospace applications can be tailored with additives to obtain higher or lower viscosity, toughness and an optimized cure time.

The mechanical properties of the commercial structural adhesives reported in literature and on producers' data sheets are difficult to compare as they are based on lap shear tests, which depend on the joined sample size and shape. These properties range between 20-50 MPa at room temperature. However, the limiting factor for this work is the ILSS of the C/C composites, which is about 12 MPa, and thus represents the minimum mechanical strength considered suitable for the joints in this work. The objective of this work has been to develop an advanced and high-performant adhesive, able to provide suitable mechanical strength to

the C/C-based structure, coupled with a suitable thermo-mechanical stability over the operative range. ^[10]

2. Experimental section

Fourteen adhesives were prepared and tested to fulfil the requirements listed in Table 1 [Thales Alenia Space, private communication], twelve based on a phenolic resin and two on a cyanate ester one; their compositional range (wt %) is listed below:

- 60 – 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.
- 80 – 85 wt % cyanate ester (Lonza PT 30, Germany), the same fillers as above, but with no added solvent.

All the formulations were aimed at minimising the resin content and maximising the inorganic components: variations in the resins (ranging from 60-85 wt%) and in the ethanol as a solvent (absent in the cyanate ester composition and ranging between 12-20 wt % for the phenolic resin) were introduced to obtain a suitable viscosity.

The homogeneous dispersion of the fillers was one of the most important parameters for the formulation of each adhesive, together with the definition of the minimum resin content necessary to allow a good dispersion of all the fillers.

The best processing conditions for the dispersion of fillers in both adhesive families (phenolic resin and ester-based cyanate) were identified as follows: 15 rounds per minute (rpm), and 4 hours at room temperature in a planetary eight-litre capacity mixer.

The curing cycles and the chemical structure ^[11, 12] for the two different adhesive families are reported in **Figure 1** and were used to join 2D C/C composites (HITCO Carbon Composites, USA) (10 mm x 6 mm x 1.5 mm), which were polished before joining by means of a 600 grit abrasive paper to remove the 10 micron thick pyrolytic carbon deposited on them.

The C/C composites were produced by Chemical Vapour Infiltration (CVI) of a quasi-isotropic lay-up (0°/45°/-45°/90°) of ex-PAN fibres; an adequate high temperature treatment conferred a quasi-null CTE to the material. The composites had a tensile modulus of 60 GPa, a tensile strength of about 160 MPa at room temperature and an interlaminar shear strength of 12 MPa.

The C/C surface that had to be bonded was polished, ultrasonically cleaned in ethanol and then dried. Successively, the C/C composites were joined by a thin layer of adhesive, applied manually using a spatula; the process was performed at room temperature for the phenolic resin-based adhesives and at 70°C for the cyanate ester ones, which were heated on a hot plate to obtain a suitable viscosity. A pressure of about 1kPa was applied to keep the samples in the correct position during joining.

The curing process was conducted in a muffle furnace (Nabertherm LH 60/40, Germany) in air with different thermal cycles, according to the adhesive composition: the process took almost 20 hours for the phenolic-based adhesives, due to the low heating rate used to prevent the formation of porosity in the joint, while it took about 8 hours for the cyanate ester-based adhesives (**Figure 1**).

All the joined C/C had a joint thickness of about 100-200 microns (measured as the difference before and after joining): they were tested at room temperature by means of a Single Lap (SL) test under compression ^[13], that is, a modification of ASTM D1002-05. The tests were performed using a universal mechanical testing machine (SINTEC D/10), with a cross-head speed of 0.5 mm min⁻¹.

The lap shear strength of the adhesive joined C/Cs under compression was evaluated by dividing the force applied at failure by the joined area. The tests were carried out on at least five samples for each adhesive. The dimensions of the tested samples were about 6 mm × 10 mm × 1.5 mm. The joined samples were glued to the fixtures by an epoxy adhesive (Araldite AV 119).

The lap shear strength of the joints was used to down-select the two most suitable formulations (patent filed), a phenolic-based one and a cyanate ester-based one.

The viscosity of these two selected adhesives was measured before curing by means of a rotational rheometer with a parallel plate geometry and a 25 mm diameter at 30°C, under dynamic conditions, over a frequency range of 0.1-100 rad sec⁻¹, with a strain of 0.3%. The strain was calculated, by means of a preliminary strain sweep test, to measure the linear viscoelastic region of the material. The test was performed in an ARES G2, TA Instruments, UK.

The two selected adhesives were also cured as 50 mm x 20 mm x 5 mm bulk samples in a mold: due to the high porosity of the cured samples, smaller samples were cut from the large ones and tested by means of dilatometry (Netzsch, DIL 402 PC/4), thermogravimetric analysis (TGA) with differential thermo-gravimetry (DTG) and Thermo-Gravimetric-Evolved Gas analysis (TGA-EGA) at 10 °C min⁻¹ and 20°C min⁻¹.

An ultra-microbalance (sensitivity 0.1 µg), connected to a time/temperature-resolved FTIR, was employed for the TGA-EGA. The samples were ground in an agate mortar for this test. 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⁻¹ under a dynamic inert atmosphere (100% N₂, flow rate: 35 mL min⁻¹) in a Pyris 1 TGA (PerkinElmer, Waltham, MA, USA). The gas that evolved during the heating ramp was piped (gas flow of 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 thermostatic conventional gas cell. The

temperature/time-resolved spectra were acquired in the 4000-600 cm^{-1} wavenumber range at a resolution of 0.4 cm^{-1} and analysed using Spectrum software (Perkin Elmer). 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.

Furthermore, the gas that evolved from the sample during the main degradative process was automatically collected (ca. 100 μL) and injected into a Clarus 500S gas chromatograph (PerkinElmer), equipped with an Elite 5MS (PerkinElmer) standard non-polar fused silica capillary column. The eluted substances were identified by means of an integrated Clarus 560S mass spectrometer (PerkinElmer) used as a detector. Total Ion Count (TIC) chromatograms were recorded. Analyses of the average mass spectra that had been identified at the mid-height of the chromatographic peak were carried out with NIST MS Search Software.

The joint cross-sections and fracture surfaces were investigated, after lap-shear tests of the two selected adhesives, by means of Field Emission Scanning Electron Microscopy, equipped with Energy Dispersive Spectroscopy (FESEM-EDS SUPRATM 40, Zeiss and Merlin Gemini Zeiss).

The indentation elastic modulus and Martens hardness of the two adhesives were measured by means of the nano-indentation technique, using the continuous stiffness measurement (CSM) method, with a Berkovich indenter (Nano Indenter G200, Agilent Technologies). The indentation elastic modulus was calculated as in ^[14]. The properties were measured inside the joint and on the bulk after curing. The elastic modulus and the hardness were continuously measured up to a fixed maximum penetration depth of 1500 nm. The average values of the indentation elastic modulus and the Martens hardness of the adhesives were determined in the 500 – 1500 nm penetration depth region.

2. Results and discussion

All fourteen adhesives were formulated by adding the maximum experimentally feasible amount of carbon-based fillers, all of which were selected because of their well-known thermo-mechanical characteristics and ability to fulfil the CTE, and the mechanical and working temperature requirements of the adhesive, as summarised in Table 1. [15, 16]

The phenolic resin was chosen for this work because it can be applied at room temperature between the two C/Cs that have to be joined and then cured. The possibility of using an adhesive at room temperature is an advantage in the case of large C/C parts, provided that the gaseous products released during curing are controlled and the residual porosity minimised inside the joined region.

The cyanate ester resin-based adhesive offers the advantage of a faster curing process, without the release of an important amount of gaseous products; however, a higher temperature than 50 °C is necessary to obtain a suitably low viscosity, as will be discussed hereafter: after some preliminary experimental trials, 70°C was selected. Keeping the cyanate ester at 70 °C on a hot plate in a laboratory environment is not a problem, but it was considered an additional issue for the typically temperature-controlled, clean room environment of the aerospace industry clean room environment.

The curing process (**Figure 1**) was an important processing parameter that had to be optimised, in particular in the presence of a solvent (ethanol), as in the case of phenolic resin-based adhesives, which implied a severe gaseous production during the curing cycle. It was thus important to eliminate these gaseous products as much as possible in order to avoid excessive residual porosity in the adhesive and any consequent detrimental effects on the mechanical strength of the joints. To this aim, the first heating step was very slow (0.3 °C min⁻¹) so that the solvent would evaporate at 130 °C, when the adhesive was still at a low

viscosity, and this was followed by a further heating ramp at 0.3 °C/min up to the curing temperature of 260 °C.

The problem of gas formation was not an issue for the cyanate ester-based adhesives, and a much faster heating (10°C/min) was therefore selected, with two curing steps, at 150°C and 200 °C, before the final one at 270 °C.

Figure 2 (a-c) shows the lap-shear test set up, a typical force/displacement curve and the lap-shear test results at room temperature on the joined C/C. The lap-shear tests were not conducted to provide the pure shear strength of these joints, but were useful for comparative purposes and for down-selecting the most promising adhesives. A value of 12 MPa, corresponding to the interlaminar shear strength of these composites, represents the minimum mechanical strength requested for the joints in this work; thus, the down-selected adhesives were a phenolic-based adhesive (formulation 2) and a cyanate ester (formulation 2) (patent filed) , as shown in **Figure 2**.

The two selected adhesives were characterised, by means of a rheometer, before curing. **Figure 3** shows their viscosity curves versus frequency (rad s^{-1}) at 30°C; as expected, the viscosity of the cyanate ester adhesives was too high at this temperature: a temperature of at least 50°C is necessary to obtain a suitable viscosity for the envisaged applications; a temperature of 70 °C was selected for this work, and the cyanate ester was heated on a hot plate before use. It is interesting to note that the cyanate ester formulation showed a quasi-Newtonian type of behaviour over the analysed frequency range, whereas the phenolic-based formulation showed a pronounced decrease in viscosity versus shear, which makes the use of this adhesive much easier for the envisaged application on a large-scale component. In fact, the shear rate observed during the adhesive application on the C/C caused a viscosity reduction and eased its spreading on the C/C surface.^[17-20]

The dilatometry curves of the two cured bulk adhesives are shown in **Figure 4**: both the phenolic and cyanate ester adhesives show an almost linear behaviour up to 250 °C,

corresponding to a CTE of $50 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ measured over the 25-100 $^\circ\text{C}$ range: this value is one order of magnitude higher than the requested one indicated in Table 1. Work is in progress to reduce this value. Moreover, both adhesives resulted unstable after this temperature, with peaks due to both their softening and thermal decomposition, which are discussed in the following paragraphs.

Figure 5 shows the TGA and DTG curves of the two adhesives after their respective curing processes (Residual Mass % wt. on the left axis (solid curves) and differential curves on the right axis (dotted curves): a residual mass of about 70 % wt. (left axis) was measured for both adhesives after heating at 1000 $^\circ\text{C}$ (in a nitrogen atmosphere), corresponding to the content of the inorganic fillers of both adhesives and the char residual mass of the polymer systems.

The DTG curves (10 $^\circ\text{C}/\text{min}$) (**Figure 5**, dotted curves, right axis) allow the thermal decomposition of both adhesives, after curing, to be better understood: the phenolic adhesive shows a weak gaseous production before 200 $^\circ\text{C}$, a more intense thermal decomposition between 370 $^\circ\text{C}$ and 620 $^\circ\text{C}$, and an almost complete decomposition at about 850 $^\circ\text{C}$. The cyanate ester adhesives show a sharp, intense peak with the onset of decomposition at about 400 $^\circ\text{C}$, a smaller one at 600 $^\circ\text{C}$, and the process is almost completed at about 850 $^\circ\text{C}$. [21-23]

In order to investigate the chemical nature of the gaseous species that evolved during the heating, a well-established TGA-EGA approach was employed. [24, 25]

The analysis was carried out on both of the cured adhesives (**Figures 6 a,b**).

The thermo-gravimetric behaviour of both the cured adhesives that can be observed in **Figure 6** (20 $^\circ\text{C min}^{-1}$) confirms the previously discussed results (**Figure 5**, 10 $^\circ\text{C min}^{-1}$). The FTIR analysis on the phenolic cured adhesive allowed NH_3 , phenol (Phe-OH), CH_4 and alkylisocyanates (R-NCO) to be identified. The FTIR profiles of such species are reported in **Figure 6 a** as absorbance at a characteristic wavenumber (namely 965 cm^{-1} for NH_3 , 748 cm^{-1} for phenol, 3015 cm^{-1} for CH_4 and 2280 cm^{-1} for R-NCO), expressed as a function of the

temperature. The decomposition started at ca. 200 °C, with a first process during which the release of NH₃ and R-NCO was observed. In analogy to what has been observed in a recent work by Brobowski et al ^[26], the detection of nitrogen containing species indicates that the phenolic binder contains urea. The release of CH₄ and phenol (Phe-OH) was also observed for a higher temperature (ca. 500 °C) up to ca. 800 °C.

The same experiment carried out on the cured cyanate ester evidenced the evolution of NH₃, R-NCO and CH₄ (**Figure 6 b**). In this case, NH₃ and R-NCO were observed during the main degradative process, which started at ca. 400 °C. A lower amount of such species was also detected at higher temperatures (from ca. 550 up to 850 °C). Moreover, during this process, CH₄ was also produced, likely via the combination of residual carbon and hydrogen.

In order to univocally assess the gaseous species released during the main degradative process, the produced gas was sampled at the temperature at which the main degradative process of the cured phenolic and cyanate ester adhesives reached the maximum speed (560 °C and 465 °C, respectively) and then analysed by means of GC-MS. The gas chromatogram for the phenolic adhesive (**Figure 7 a**) evidenced that the main degradative process was a complex mixture of aromatic species (namely benzene; toluene; 1,3-dimethylbenzene; phenol, 2-methylphenol; 4-methylphenol; 2,6-dimethylphenol; 2,3-dimethylphenol or 2,4-dimethylphenol).

The same analysis, but carried out on the cured cyanate ester adhesive, revealed that some aromatic compounds (namely benzene, toluene, phenylisocyanate, phenol; 2-methylphenol; 4-methylphenol) were released during thermal degradation.

After carefully considering all the above discussed results, the phenolic-based adhesive was selected as the most suitable option to join C/C, in particular because the phenolic-based adhesive offered the advantage of having a suitable viscosity at room temperature, hence making the adhesive spreading process before curing much easier, even for large C/C parts.

The cyanate ester resin-based adhesives in fact offered the advantage of a faster curing, without releasing important amounts of gaseous products, although keeping this adhesive at about 70°C was considered an additional issue for a cleanroom environment in the aerospace industry.

The following characterisations were conducted on the phenolic resin joined C/C.

The interfaces between the C/C and adhesives were continuous and crack free, as can be seen in **Figure 8 a**: it is worth pointing out that the C/C polishing prior to joining was necessary to remove the chemical vapour deposited pyrolytic carbon layer: the wettability with the adhesives was found to be much lower without polishing as, consequently, was the resulting mechanical strength (not reported).

The strength of these joints was comparable to, or even slightly higher than the interlaminar shear strength of the C/C, and fracturing occurred inside the joint volume without any delamination of the composite.

The typical fracture surfaces showed the presence of adhesive on both sides, thus indicating a cohesive fracture; in some cases, the C/C was detected on the fracture surfaces, thus indicating a mixed fracture mode, i.e. partly adhesive and partly cohesive.

Figure 8 b evidences the phenolic resin-based adhesive fracture surface after mechanical testing, where the presence of well-dispersed carbon fibres inside the resin can be observed.

The indentation elastic modulus and the Martens hardness of the bulk phenolic resin-based adhesive and the adhesive inside the joint were measured by means of nano-indentation. The aim was to verify whether the properties of the adhesive were retained when it was confined and cured between the two facing surfaces (i.e. in a joint).

The continuous stiffness measurement (CSM) technique was used, as it allows the mechanical properties to be measured at any point along the loading curve, and not just at the unloading point, as in the conventional measurement technique. It has also been reported that,

due to a significantly smaller time constant, this technique is particularly useful for measuring the properties of polymeric materials, as in ^[14] .

Figure 9 shows the indentation elastic modulus of both the bulk phenolic resin and the adhesive in the joining area measured to a maximum penetration depth of 1500 nm. Both curves reached a plateau for greater penetration depths of the indenter than 200 nm, and constant elastic moduli of 7.9 GPa and 6.8 GPa were observed for the adhesive in the joining volume and the bulk adhesive, respectively. A slightly higher average elastic modulus was measured for the phenolic resin when it was confined between the two surfaces of the C/C in the joint. This was most likely caused by the different space orientation of the polymeric chains of the adhesive cured between the two surfaces, compared to the unconstrained bulk adhesive.

On the other hand, the different space orientations of the polymeric chains did not affect the Martens hardness values. **Figure 10** shows the Martens hardness of both the bulk phenolic resin and the adhesive in the joining volume, as measured to a maximum penetration depth of 1500 nm. In this case, both curves reached a plateau after exceeding the penetration depth of ~ 500 nm. The hardness of the adhesive in the joint was the same as that of the bulk adhesive (~ 0.48 GPa).

The results of the mechanical properties are summarised in Table 2.

3. Conclusion

Two adhesives, based on phenolic and on cyanate-ester resins, for the joining of carbon fibre reinforced composites (C/C) for use in aerospace applications, have been developed and thoroughly characterised.

Both adhesives fulfilled most of requirements necessary to join C/C, except for the CTE, which was one order of magnitude higher than expected. The main advantage of the

selected phenolic-based adhesive is that it can easily be applied to large C/C surfaces at room temperature, while the cyanate ester adhesive has to be kept at temperatures of about 70°C.

A slow curing procedure was developed to avoid porosity in the phenolic-based joints, and the requested higher apparent lap shear strength than 12 MPa at room temperature was thus reached. Work is in progress to reduce the CTE of both adhesives.

The mechanical properties of the phenolic resin-based adhesive, such as the indentation modulus and Martens hardness, were investigated for the bulk adhesive and the adhesive in the joint. The indentation modulus of the adhesive inside the joint was ~ 1 GPa higher than that of the bulk, probably due to the different orientations of the polymeric chain within the cured adhesive between the two surfaces, and to the interaction between the adhesive and the two surfaces on which the adhesive is placed. However, further research is necessary to confirm such a supposition. On the other hand, the same hardness values of the adhesive were measured regardless of whether the adhesive was confined between the two surfaces of the C/C in the joint or not.

Acknowledgements

Stefano Rizzo is kindly acknowledged for his help with the adhesive joining activity.

The TGA-FTIR-GC-MS measurements were obtained with equipment acquired by “G. Scansetti”, thanks to a grant from the Compagnia di San Paolo, Torino, Italy.

One of the authors (P.T) gratefully acknowledges the financial support of the APVV-17-0328 project.

One of the authors (S.DLP) would like to thank KMM-VIN for providing him with a Research Fellowship 2017 for the nano-indentation measurements.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

References

- [1] Z.S. Toor, *J. Spacecr. Technol.* **2018**, 8, 1.
- [2] C. Scarponi, *Adv. Compos. Mater.* **2016**, 385-412.
- [3] J. Wang, H. Jiang , Q, Guo, L. Liu, J. Song, S. Bau, S. Qiao. *J. Adhes. Sci. Technol.* **2009**, 23, 1.
- [4] M. Wang M , X. Hu , X. Xu . Z. Yun. J. Liu, H. Du, A. Guo. *Mat. Des .* **2015**, 86.
- [5] M. Salvo M, V. Casalegno, Y. Vitupier, L. Cornillon, C. Pambaguian, M. Ferraris. *J.Eur. Cer. Soc.* **2010**, 30.
- [6] M.Wang, J. Liu, H. Du , A. Guo, X. tao, X. Dong, H. Geng. *J. Alloy Compd.* **2015**, 633.
- [7] M. Wang, J. Liu , A. Guo, L. Zhao, G. Tian, S. Shen. S. Liu. *Int. J. Appl. Ceram. Technol.* **2015**, 12 ,4.
- [8] J. Li , R. Luo , Y. Bi, Q. Xiang, C. Lin, Y. Zhang, N. An. *Carbon.* **2008** , 46.
- [9] M. Wang , J. Liu , H. Du, F. Hou, A. Guo, S. Liu, X. Dong. *Ceram. Int.* **2014**, 40.
- [10] W.K., Goertzen, M.R. Kessler. *Compos. Part A-Appl. S.* **2007**, 38.
- [11] A. J. Guenther., M.C. Davis, K.R. Lamison, G. R. Yandek, L. R. Cambrea, T.J. Groshens , L. C. Baldwin , J. M. Mabry. *Polymer* **2011**, 52, 3933.
- [12] L. Pilato. *React. Funct. Polym.* **2013**, 73, 270 .
- [13] M. Ferraris , A.Ventrella , M.Salvo M, M. Avalle, F.Pavia, E. Martin. *Compos. Part B Eng.* **2010**, 41, 2.
- [14] X. Li, B. Bhushan. *Mater. Charact.***2002**, 48,11.
- [15] J.K. Koo, M. Natali, J. Tate, E. Allcorn *Int. J. Energetic Materials Chem. Prop.* **2013**,12.

- [16] J. H. Koo, H. Stretz, A. Bray, W. Wootan, S. Mulich, B. Powell, T. Grupa, J. Weisfenning, in Phenolic-Clay Nanocomposite for Rocket Propulsion Systems, Int'l SAMPE Symposium and Exhibition, **2002**, 47.
- [17] E.C. Botelho, N. Scherbakoff, M.C. Rezende, *Mat. Res.* **2000**, 3, 2.
- [18] D. Mourant, B. Riedl, D. Rodrigue, D. Q. Yang, C. Roy *J. Appl. Polym. Sci.* **2007**, 106, 2.
- [19] X. Yang, C.E. Frazier. *Int.J. Adhes. Adhes.* **2016**, 66.
- [20] T.J. Wooster, S. Abrol, D.R. MacFarlane. *Polymer* **2005**, 46, 19.
- [21] C. Chang, J. R. Tackett. *Thermochim. Acta* **1991**, 192, 12.
- [22] M.L. Ramirez, R. Walters, R.E. Lyon, E.P. Savitskis. *Polym Degrad Stabil.* **2002**, 78, 1.
- [23] Q. Lin, L. Qu, Q. Lü, C. Fang. *Polym. Test* **2013**, 32, 2.
- [24] I. Corazzari, R. Nisticò, F. Turci, M. G. Faga, F. Franzoso, S. Tabasso, G. Magnacca. *Polym. Degrad. Stabil.* **2015**, 112.
- [25] F. Franzoso, R. Nisticò, F. Cesano, F. I. Corazzari, F. Turci, D. Scarano, A. Bianco Prevot, G. Magnacca, L. Carlos, D.O. Mártire. *Chem. Eng. J.* **2017**, 310.
- [26] B. Artur, D. Droyński, G. Beata, *China Foundry*, **2018**, 15, 145.

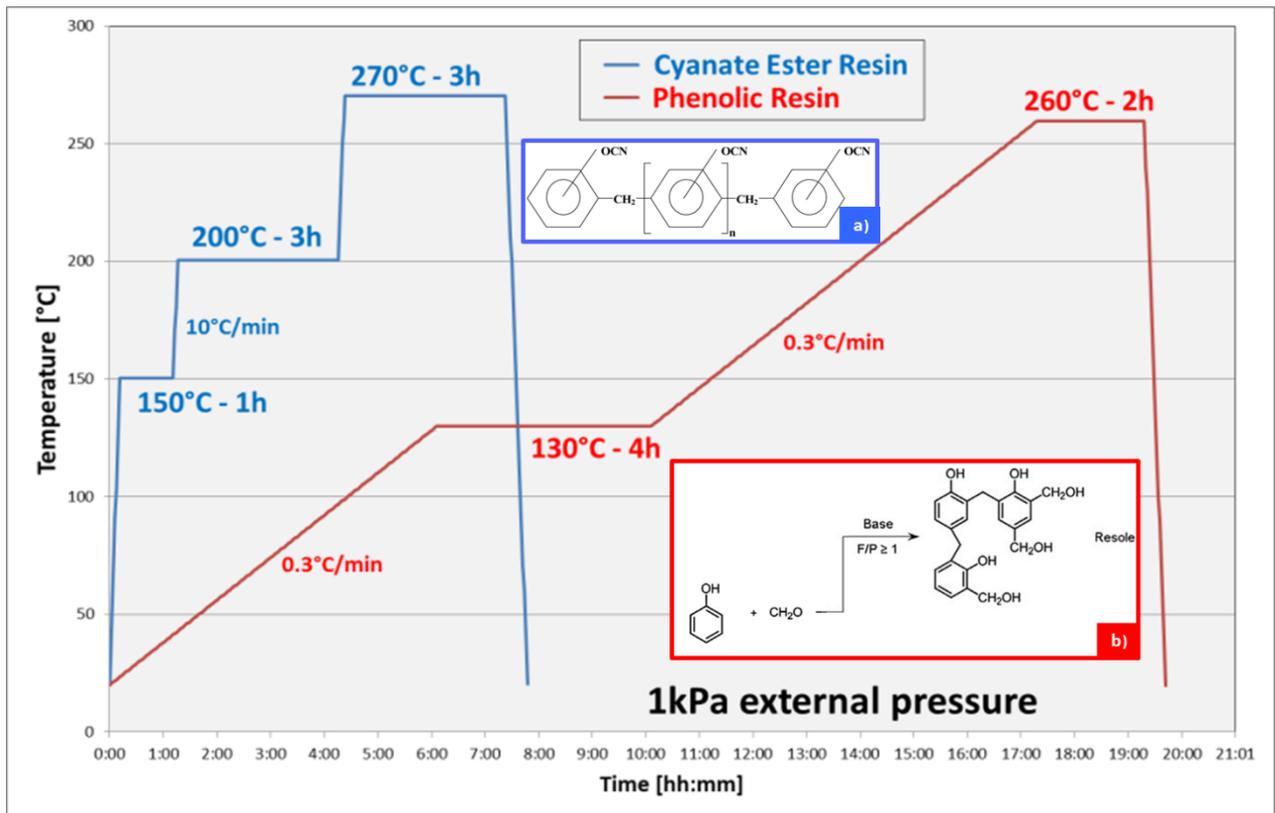


Figure 1. Curing processes and chemical structure of the cyanate ester resin (blue) and phenolic resin (red)-based adhesives. Inset (a): structure of the Lonza Primaset PT-30 cyanate ester ^[11]; inset (b): structure of a resole ^[12].

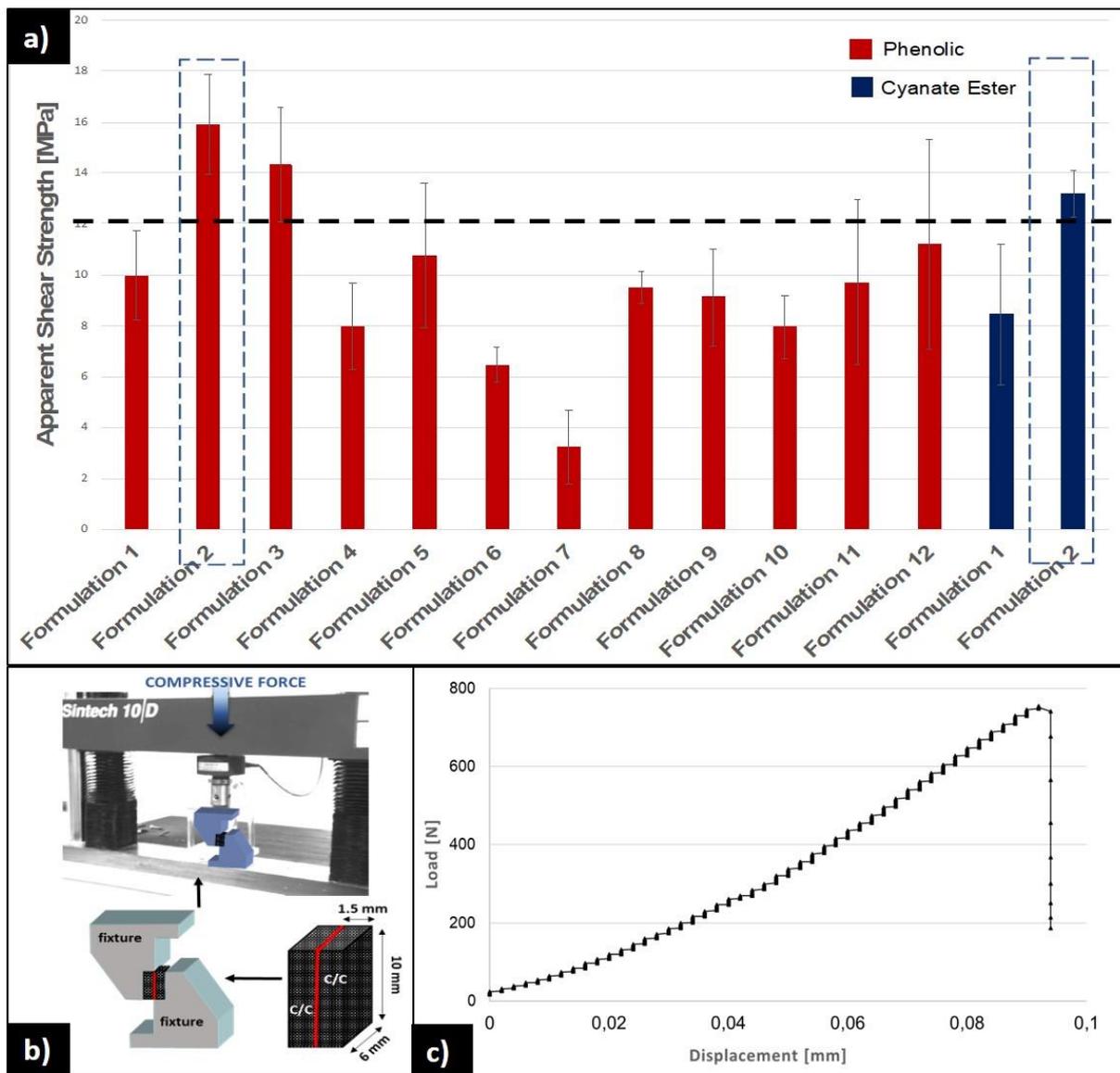


Figure 2 . Results obtained at room temperature on adhesive joined C/Cs (a), Set up of the lap-shear test (b), a typical load/displacement curve (c): the line at 12 MPa evidences the minimum requested mechanical strength; the two selected adhesives are highlighted.

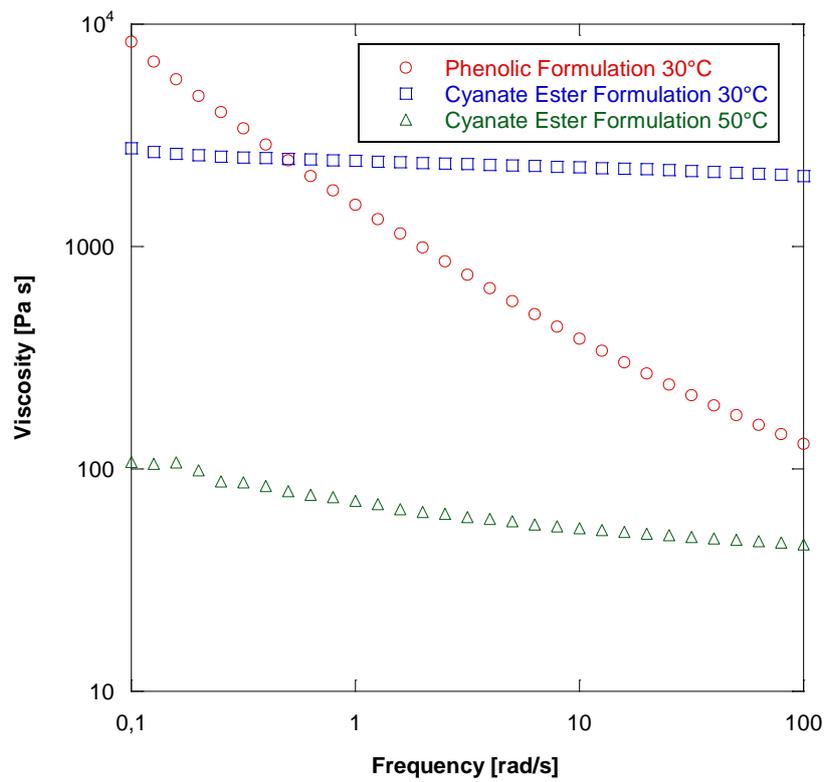


Figure 3 . Viscosity curves versus rotation frequency of the as prepared selected phenolic and cyanate ester-based adhesives at 30°C; (but also at 50°C for the cyanate ester adhesive, to show its viscosity behaviour at a higher temperature).

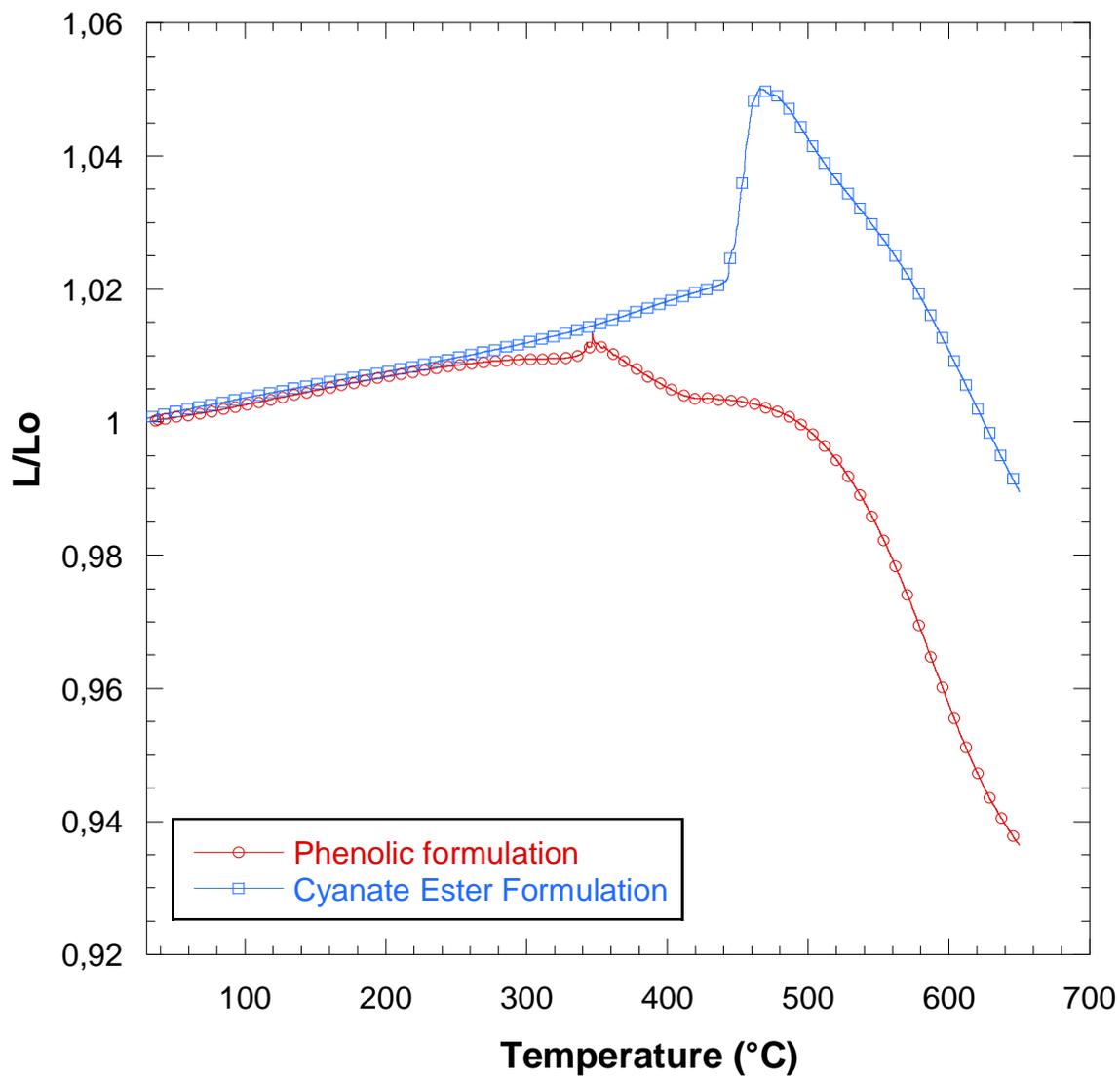


Figure 4 . Dilatometry curves of the selected cured phenolic and cyanate ester-based adhesives

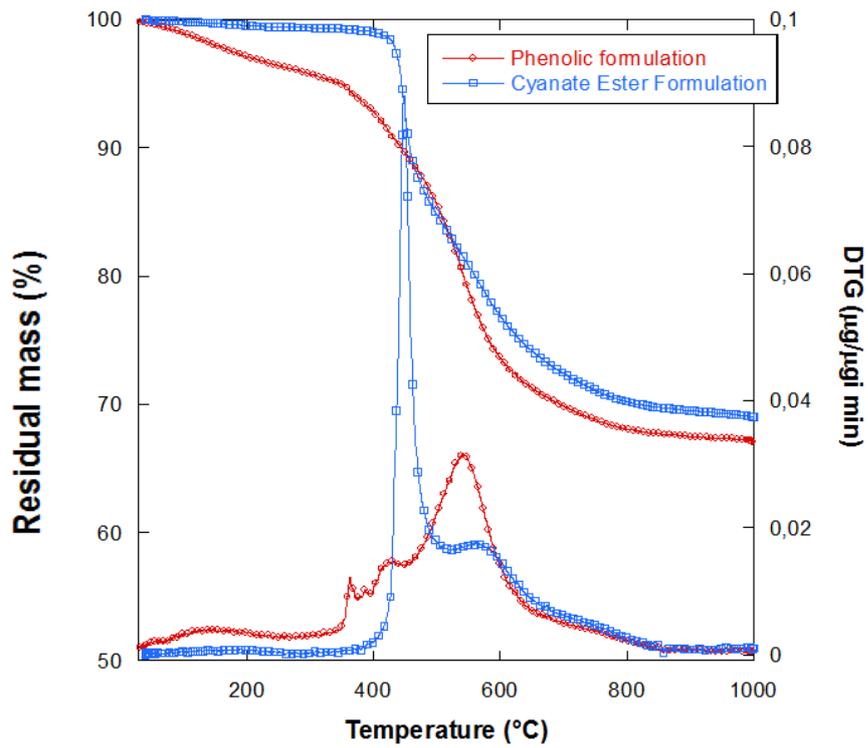


Figure 5 . Thermo-gravimetry and differential (DTG) curves of the selected, cured phenolic and cyanate ester-based adhesives (heating rate of $10^{\circ}\text{C min}^{-1}$)

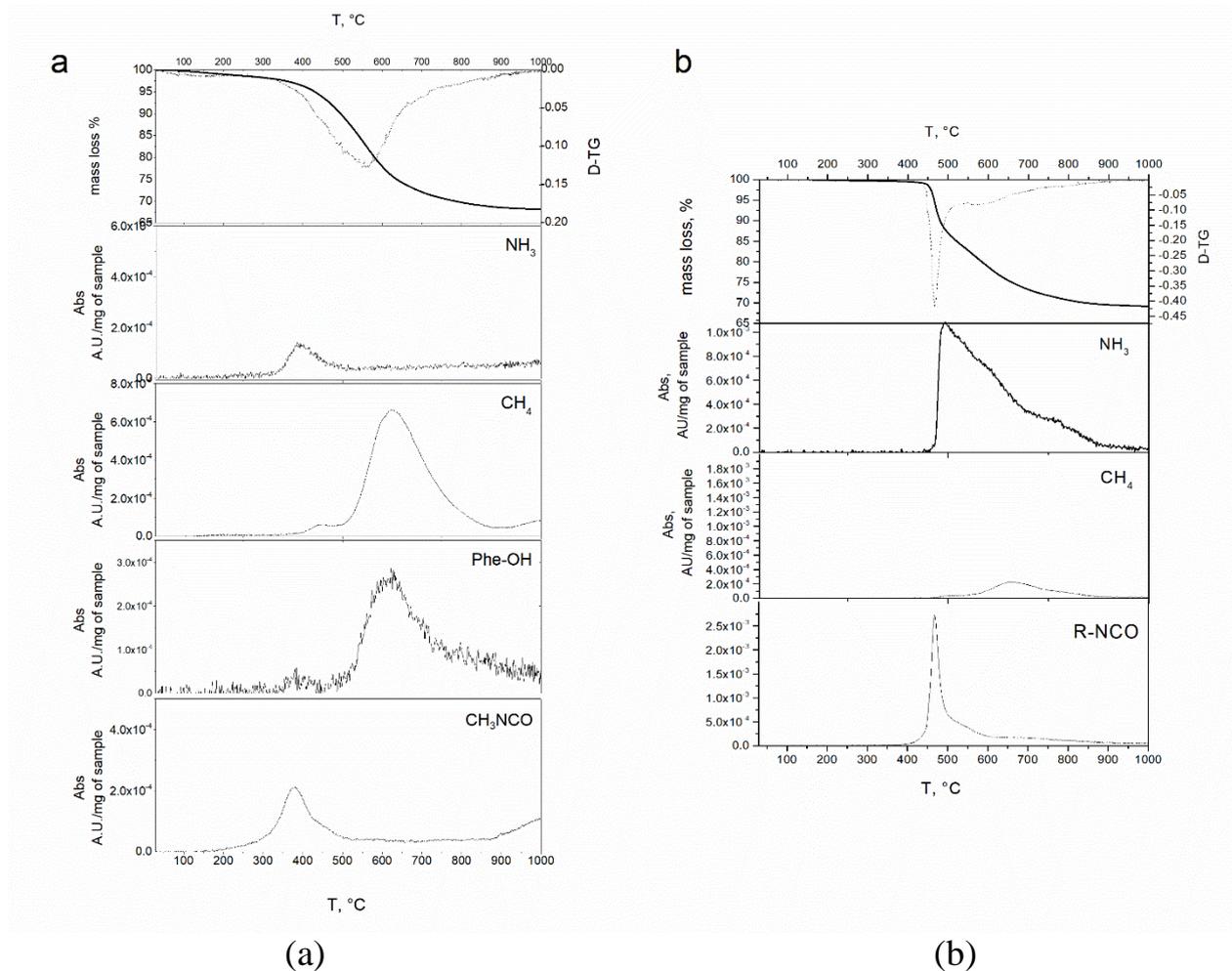


Figure 6 . Thermograms (TG, solid line) and derivative curves (D-TG, dotted line) recorded for the heating of the cured phenolic-based adhesive (a) and the cured cyanate ester-based adhesive (b), under an N_2 dynamic atmosphere from 35 to 1000 $^{\circ}\text{C}$ ($20^{\circ}\text{C min}^{-1}$). FTIR profiles of NH_3 , CH_4 , phenol and methyl and alkyl isocyanate release as a function of the temperature are also reported.

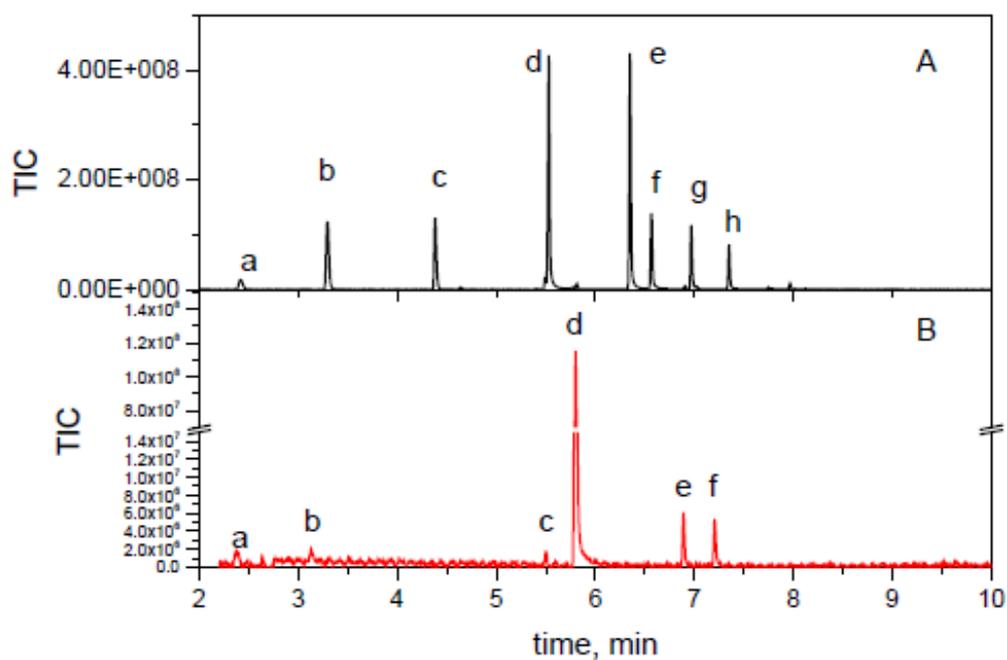


Figure 7 . (A) Gas chromatogram of the gases that evolved from the cured phenolic adhesive during the TGA analysis at $T = 570\text{ }^{\circ}\text{C}$ under an N_2 flow. Benzene (a); toluene (b); 1,3-dimethylbenzene (c) ; phenol (d), 2-methylphenol (e); 4-methylphenol (f); 2,6-dimethylphenol (g); 2,3-dimethylphenol or 2,4-dimethylphenol (h).
 (B) Gas chromatogram of the gases that evolved from the cured cyanate ester adhesive during the TGA analysis at $T = 465\text{ }^{\circ}\text{C}$ under an N_2 flow. Benzene (a), toluene (b), phenylisocyanate (c); phenol (d); 2-methylphenol (e); 4-methylphenol (f)

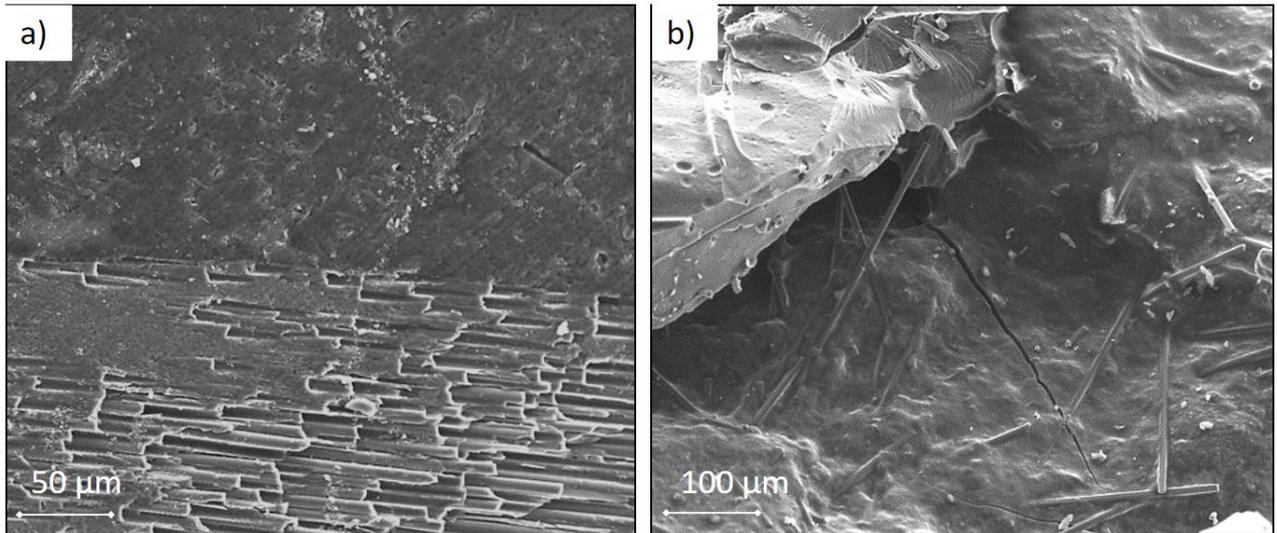


Figure 8 . (a) Cross-section of a C/C - phenolic resin adhesive, continuous and crack free interface; (b) details of the adhesive fracture surface after a mechanical test, showing the presence of well dispersed carbon fibres in the adhesive.

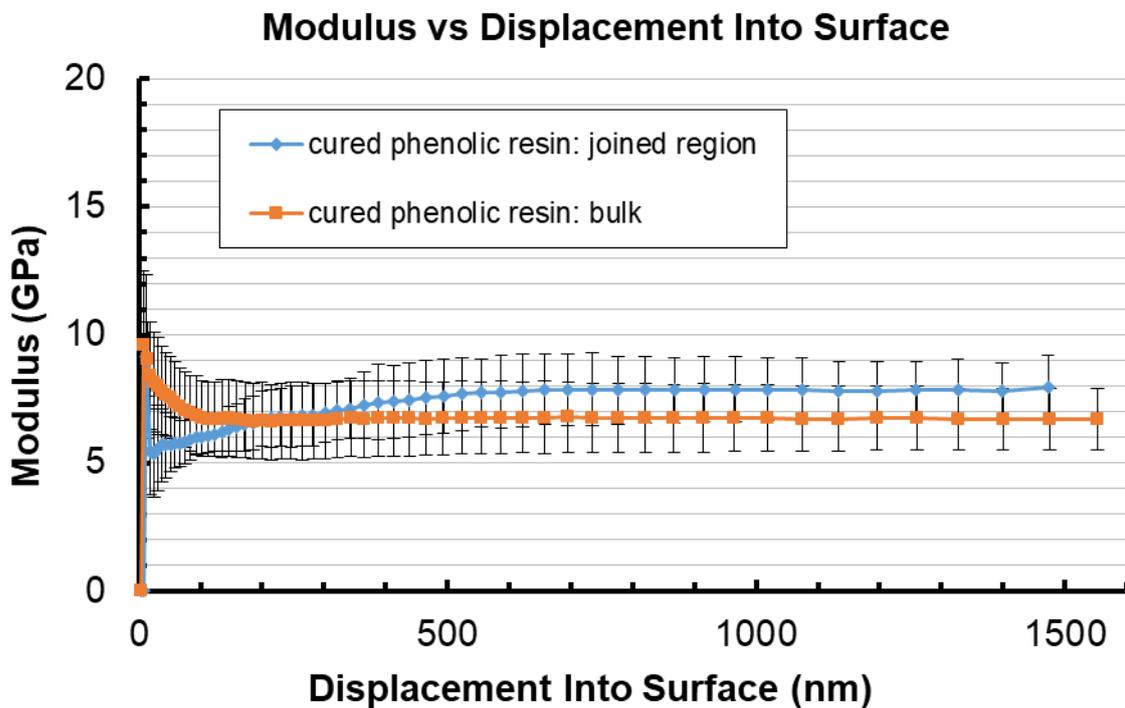


Figure 9 . Results of indentation elastic modulus measurements by means of a nano-indentation test: comparison between the adhesive inside the joined sample and the bulk cured adhesive .

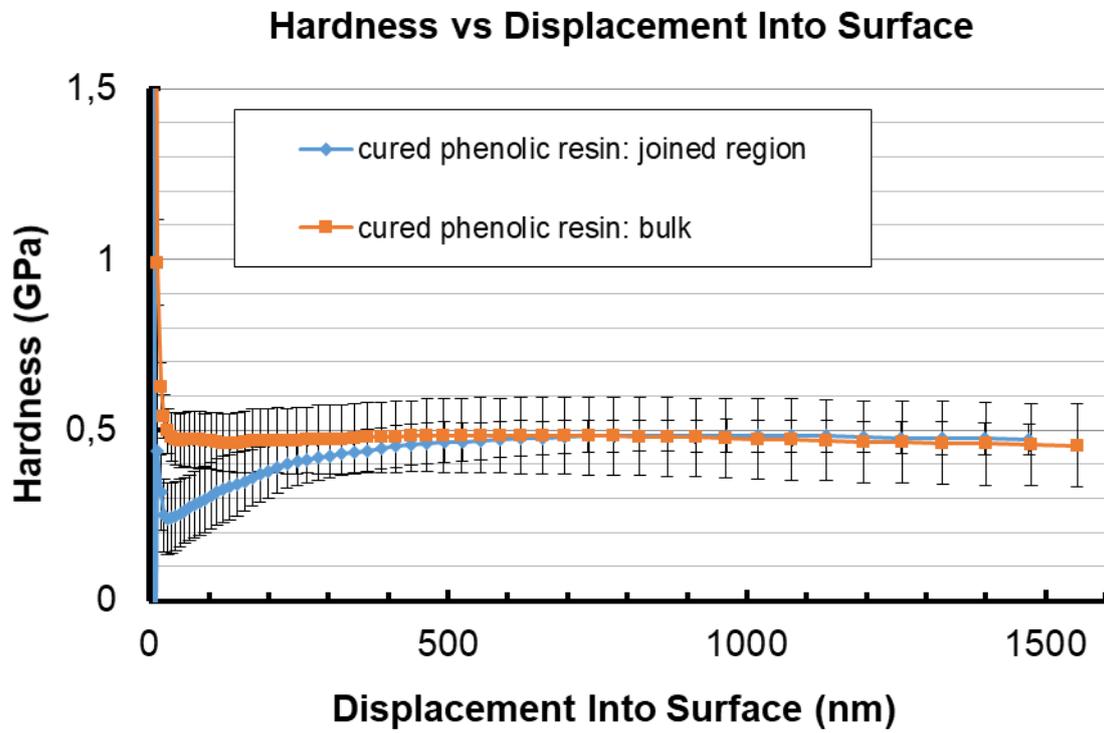


Figure 10 . Results of Martens hardness measurements by means of a nano-indentation test: comparison between the adhesive inside the joined sample and the bulk cured adhesive .

Table 1. Requirements for the adhesives discussed in this work (Thales Alenia Space, private communication).

Maximum joining process temperature [°C]	< 300
Operating T range [°C]	-50 / +250
CTE [$10^{-6} \text{ } ^\circ\text{C}^{-1}$] [-50°C/+ 50°C]	≤ 5
Lap shear strength at Room Temperature [MPa]	≥ 12
Young's Modulus (E) [GPa]	1-30
Joint thickness [μm]	100-200

Table 2. Indentation elastic modulus and Martens hardness obtained from nano-indentation: comparison between the adhesive inside the joined sample and the bulk adhesive; average values calculated over an indentation depth range of 900-1000 nm.

phenolic resin-based adhesive	Indentation elastic modulus [GPa]	St.Dev. [GPa]	Martens hardness	St.Dev. [GPa]
inside the joint	7,9	1,3	0,48	0,05
bulk	6,8	1,3	0,48	0,12

Table of contents

The design of high performance adhesives for the joining of carbon fibre reinforced composites (C/C) is presented for ultra-stable applications in the aerospace field. The performance of formulations based on phenolic and on cyanate-ester resins (charged with carbon based fillers) is analysed in terms of mechanical strength, low coefficient of thermal expansion and ease of application on large components.

Keyword : joining

V. Casalegno* , S. De la Pierre des Ambrois, I. Corazzari , F. Turci , P. Tatarko, O. Damiano, L. Cornillon, A. Terenzi , M. Natali , D. Puglia, L. Torre, M. Ferraris.

Design, realization and characterization of advanced adhesives for joining ultra-stable C/C based components

