EXTENDED NDT FOR THE QUALITY ASSESSMENT OF ADHESIVE BONDED CFRP STRUCTURES

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ABSTRACT

Due to the increased use of carbon fibre reinforced plastics (CFRP) and the constant urge for lighter structures, adhesive bonding as an assembly technology has a great potential for high-loaded structures in the aeronautic industry. A prerequisite for such an application is that the bond quality of the adhesive joint can be controlled in a non-destructive way. Non-destructive testing (NDT) methods exist for the characterisation of defects like pores, delamination or debonding in adhesive bonds. However, these NDT methods for conventional “defectoscopy” do not allow the control of selected physic-chemical properties of the adherend surface and the adhesive joint, which are decisive for the mechanical performance of the adhesive bonds. This lack is an obstacle to a wider deployment of adhesive bonding technology. For this reason, the scope of NDT methods has been widened by Airbus and Fraunhofer IZFP towards “propertyscopy” as new field of technology that has been named ‘Extended NDT’.

This presentation highlights the most important use cases and requirements for Extended NDT in the field of adhesive bonding of CFRP structures. Moreover, on these bases recent results from research and development and feasibility studies of Extended NDT are presented. Among these methods, the approach of proof test methods including laser adhesion test, based on high intensity short laser pulse will be presented. These laser adhesion tests generate an elastic shock wave that disbands the weak adhesive bonds, making the defect visible for other NDT techniques (thermography, US scan, etc...) and so, aim at ensuring the quality of optimal adhesive bonds.

Keywords: Adhesive bond, adhesive joint, NDT, quality, aerospace, CFRP, composite, adherend surface, contamination, chemical-physical properties, Laser, Shock, LASAT
INTRODUCTION

Due to the increased use of carbon fibre reinforced plastics (CFRP) and the constant urge for lighter structures, adhesive bonding as an assembly technology has a great potential for high-loaded structures in the aeronautic industry. A prerequisite for such an application is that the bond quality of the adhesive joint can be controlled in a non-destructive way. Non-destructive testing (NDT) methods exist for the characterisation of defects like pores, delamination or debonding in adhesive bonds. However, these NDT methods for conventional “defectoscopy” do not allow the control of selected physic-chemical properties of the adherend surface and the adhesive joint, which are decisive for the mechanical performance of the adhesive bonds. This lack is an obstacle to a wider deployment of adhesive bonding technology. For this reason, the scope of NDT methods has been widened by Airbus and Fraunhofer IZFP towards “propertyscopy” as new field of technology that has been named ‘Extended NDT’. Different Extended NDT methods are being developed for both the characterisation of the adherend surface and for the characterisation of the adhesive bond. This paper aim at presenting the potential future Extended NDT methods and their first experimental results.

USE CASES

Use cases of contaminations from CFRP adherend surface of adhesive joint raise a need of E-NDT methods for the characterisation of the CFRP specimen to ensure its quality.

Use cases for the characterisation of adherend surface

Skydrol & water contamination in CFRP in case of bonded-repair: Skydrol is a fire-resistant hydraulic fluid based on phosphate ester which is used to convey power via pressure in order to command flaps, slats, rudder, etc. In each part of the aircraft made of CFRP and in the presence of Skydrol, a contamination due to a leakage of the hydraulic system can occur. Skydrol and water react to form a phosphoric acid that can etch the CFRP. After the standard cleaning and drying processes, Skydrol traces may remain on the surface and diffuse into the interface of the adhesive bond and weaken any bonded repair or even prevent its adhesion completely. The E-NDT methods were tested once directly after the cleaning procedures and also once again 48 hours after in order to evaluate any possible retro-diffusion of the contaminant from the inner core to the near surface.

Mould release agent contamination in CFRP: During the moulding process of composite panels, release agents containing silicon are used. After the moulding process, the silicon concentration on the CFRP surface can be typically in the range of 5 to 20 at.% Si depending on the number of moulding cycles and the concentration of the mould release agent. Silicone can penetrate up to hundreds of nm into the matrix of the CFRP panel. The silicone contamination, which prevents any further adhesive bonding, is not homogeneous on the surface and the distribution is to be determined by the measuring device. For this reason, pre-treatments to clean and activate the surface are used. After these processes, the Water Break Test (WBT) is used to confirm the absence of Si-contamination and test if the surface is ready for paint application. Although the WBT provides satisfying results, this test is too laborious for large parts.
alternative process needs to be developed to ensure optimum surface state without resorting to the WBT anymore.

**Moisture contamination in CFRP:** during the manufacturing process, CFRP panels undergo several pre-treatment steps such as wet abrasion and water break test to make sure the surface is clean and ready for further use. In some cases, due to water remaining on panels or storage in a humid atmosphere for example, the surface is contaminated by moisture with a concentration up to a few wt.%. Moisture however, is to be avoided because it lowers the quality of the adhesion and leads to a loss of performance in the CFRP. Large CFRP parts whose exposure is in an uncontrolled state are by default dried-out. This step is yet mandatory and costly in time and money. Typically, moisture concentrates in the resin and its amount does not exceed about 2 wt.%. Extended-NDT methods shall be able to detect quantitatively the moisture rate in the CFRP panels which can reach up to several m² over different geometries.

**Heat Damage in CFRP:** Thermal degradation can occur in several parts of the aircraft (e.g. Rudder), due to local overheating/lightning strike and many more other accidental damage. High temperature ranges on short periods or lower temperature ranges on longer periods can cause damages in the (resin) matrix of the CFRP and thus, lead to a loss of its mechanical properties through a loss of its own integrity. The focus is made on the detection of heat damage in composite matrix. As heat alters the chemical composition of the degraded element, characteristic molecular groups are expected to form in the material and shall be detected by the Extended NDT technologies.

Use cases for the characterisation of adhesive joints

The same uses cases as for the adherend surface cases apply in the frame of the characterisation of the adhesive joint; contaminated or adhesive joints are produced by performing a bonding process on a contaminated CFRP adherend surface. In the same way, defective or weakened adhesive bonds can be produced by changing critical parameters (e.g. curing cycle temperature, time of curing cycle, etc.) from the adhesive bonding process. As a result, the quality of the adhesive joint is deteriorated and its performance is expected to be low.

**CHARACTERISATION OF THE ADHEREND SURFACE**

Extended NDT Technologies for surface characterisation

Among the potential E-NDT methods referenced by Airbus for the characterisation of the adherend surface, few techniques have been selected for feasibility studies. The most promising methods and their parameters are hereby introduced.

**IR Spectroscopy - portable spectrometer FT-IR Exoscan®:** Infrared (IR) spectroscopy is based on the detection of molecule vibrations caused by absorption of infrared radiation. This technique is used to identify chemical compounds/sample compositions. The spectrometer Exoscan® was alternatively equipped with the Attenuated Total reflectance (ATR), the diffuse reflectance, or the 45° external reflectance sampling probes. The Exoscan also involves a Michelson interferometer (8 cm⁻¹ resolution) and a TGS detector. Five measurements at
different spots were done on each specimen. For each measurement, the device compiled 128 spectra.

**X-Ray Fluorescence:** an X-Ray wavelength is used to dislodge a tightly-held inner electron of an atom. The atom becomes thus unstable and an outer electron replaces the missing inner electron while emitting itself an X-ray, the so-called fluorescence. Each element has a precise electronic arrangement so that this mechanism can be used to identify the elemental composition of a specimen. The device used is a NITON XL3t GOLD from the company Analyticon Instruments. It has 30 seconds integration time and is calibrated to focus only on relevant light chemical elements (P, Si, S...).

**Active Pulse Thermography:** The Active Pulse Thermography set up involved the use of two flash lamps of 3200 J as excitation sources. The light pulse duration was set at 20 ms. Some part of the IR radiation incident on the object surface is absorbed and transformed into a thermal energy, which propagates by thermal diffusion from surface inside the object. An infrared Silver 480 M camera from Cedip Infrared System, operating in the 3-5 µm spectral range was used. A sequence of 150 images was recorded over a period of three seconds after the flash impulse.

**Experimental Results from feasibility studies**

The best results from the numerous feasibility studies run are described in the following part. The results published are not exhaustive here.

**Skydrol traces detection with IR Spectroscopy and X-Ray Fluorescence:**
For the purpose of the skydrol contamination, a mix of skydrol 500-B4 and de-ionised water (50/50) was prepared according to Airbus specifications. CFRP specimens with unidirectional fibres were available at the clean reference state and at 850 h contaminated state. Both sets of specimens underwent the mandatory cleaning process defined by Airbus, including solvent wipe, sandpapering, water break test and its compulsory dry-out.

The feasibility study led with IR spectroscopy revealed a significant difference in the absorbance between the reference (black spectrum) and contaminated (red and blue spectra) specimens, despite the cleaning process (Fig. 1a). Two important peaks corresponding to the bands of phosphoric ester C-O around 1000 and 1100 cm$^{-1}$ can be detected. The presence of contaminant traces is thus qualitatively assessed.

This diagnostic is confirmed by the use X-Ray Fluorescence. of Fig. 1b displays the spectra from the XRF measurements. A difference in intensity at 2 keV corresponding to phosphorus is observed, illustrating the presence of phosphorus either from the phosphoric ester or phosphoric acid. The difference is however only to be seen between the reference clean specimen and the contaminated one. With both methods, no significant changes are however visible between the IR-spectra at 0 hour and 48 hours after the cleaning process, that suggesting that no retro-diffusion takes place.
Moisture detection with IR Spectroscopy and with Active Pulse Thermography:
Specimens were stored over more than 3 months in a climatic chamber (80 °C / 85 % r.H.) to simulate the moisture contamination and obtain a complete saturation. To design specimens with a reference dry state, specimens were also stored over days in an oven with air circulation at 60 °C. After a demonstration of the repeatability of the measurements on the faces of the CFRP, tests were done on 4 coupons. Two were moisture saturated and two dry. **Fig. 2** shows all 4 averaged spectra.

The wave number regions of 3100-3600 cm\(^{-1}\) and 1600-1800 cm\(^{-1}\) show the greatest differences between dry and wet conditions:
- 3100-3600 cm\(^{-1}\) is the OH Stretching vibration region, influenced by the presence of water. The peak height (absorbance) increases with the moisture content while the peak width remains unaffected;
- 1600-1800 cm\(^{-1}\) is the OH bending mode vibration of the hydroxyl of the water and shows highly different intensities in the spectra whether the specimen is dry or wet: as visible in the enlargement (Fig. 2 right) a new peak appears at ~1666 cm\(^{-1}\) while a significant decrease of the peak at ~1566 cm\(^{-1}\) is visible for wet specimens. A small shoulder between ~1744 cm\(^{-1}\) and ~1729 cm\(^{-1}\) can also be attributed to changes in the chemical environment of carbonyl groups. A correlation between the moisture content and the IR absorption could successfully be shown thanks to the Exoscan.

With active pulse thermography (Fig. 3), it can be observed that the wet specimen (green curve) decreases faster than the dry specimen (blue one). This characterizes a higher effusivity (capacity of an object to exchange thermal energy with its environment) meaning also a faster outcome of the thermal energy absorbed, possibly because of the moisture absorbed. The difference measured is however still too sensitive yet and thermography requires a higher resolution for further experiments on this field.

![Fig. 3: Thermographic image (a) and Time-temperature curve (b) of saturated and dry CFRP specimens (Source: Fraunhofer IZFP)](image)

Detection of heat damage with IR Spectroscopy:
CFRP specimens were exposed to heat in an oven with air circulation at a range of temperatures between the curing temperature of the composite (180 °C) and the limit temperature at which the delaminations in the monolithic material appeared (250 °C). Six specimens were scanned and their absorption spectrum was plotted on the same graph for comparison purpose (Fig. 4). Qualitatively, some differences in shape and intensity are observable between the individual spectra.

Two bands around 3000 cm\(^{-1}\) (see Fig. 4a) change in intensity depending on the overheating temperature: the band labelled A around 3100 cm\(^{-1}\) accounts for a stretch vibration of C-H bond in aromatics functional groups. The higher the overheating temperature is, the higher the absorbance is and hence the more C-H bonds are excited in stretching mode. The band labelled B around 2900 cm\(^{-1}\) accounts for a stretch vibration of C-H bond in alkanes. One large band labelled C around 1680 cm\(^{-1}\) (see Fig. 4b) changes in shape and intensity with thermal degradation. It accounts for a stretch vibration of C=O bonds. These results show that the higher the overheating temperature, the higher the infrared absorbance.
CHARACTERISATION OF THE ADHESIVE BOND

Extended NDT Technologies for adhesive joint characterisation

Numerous technologies for the characterisation of the adhesive joint quality are being developed for a better detection capability but up to date, no method can reliably and with a good reproducibility detect any weak adhesive bond, neither on metal nor on composite substrate. [1] Among all the available methods such as alternative ultrasonic methods (US spectroscopy; Nonlinear US; Guided Waves; Oblique incidence; Shear Wave Resonance; etc.), shearography or thermography, one method called Laser Adhesion Test (LASAT) has shown a great potential on its path to test the performances of all kind of bonded structures.

Principle of the Laser Adhesion Test (LASAT): The Laser Adhesion Test (LASAT) is based on a high power laser irradiation (GW/cm²) of a given target resulting in a controlled traction load [2]. When focused on a target, this laser irradiation leads to a high pressure plasma (GPa) generation near to the target surface, whose expansion is inducing a mechanical shock wave inside the target by reaction. The tension is generated thanks to the superposition of the released wave and the reflected wave propagating in the target. The first one is due to the reflection of the laser induced incident shock wave at the rear free surface. The second one follows this incident shock wave as the maximum pressure is brought back to the ambient pressure at the end of the load duration (Fig. 5). Depending on the laser shock parameters, the interface between two materials can be subjected to a strong tensile stress. The stress level varies according to the laser intensity, and can exceed the bond strength. This could lead to a damaged interface if the shock wave propagation parameters (shock duration and amplitude, materials nature and thicknesses) allow locating both shock and reflected waves crossing at the interface in order to generate the high tensile stress there. During the test, the rear free surface velocity can be measured using non intrusive diagnostics like a Velocity Interferometric System for Any Reflector (VISAR) or heterodyne probe (Fig. 5). These diagnostics can give direct information to compare with the shock propagation theories and

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provide a clear evidence of the debonding or integrity by very different velocity time. The LASAT resulting damage can also be observed thanks to several post shock diagnostics (e.g., ultrasonic testing, microscopy) since the shortness of laser impact enables a soft recovery of shocked samples. Coupled with numerical simulation of shock wave propagation and damage modelling, experiments give a quantitative evaluation of the adhesion threshold of coatings or assembly systems [3].

![Diagram of LASAT principle](image)

Fig. 5: Sketch of the LASAT principle on a three layer (A,B,C) target

The LASAT principle was demonstrated for the first time by Vossen [4] and then patented by Gupta et al. [5] to be applied to a wide variety of systems [6]. Even if the technique is now mature for the adhesion test of metallic coatings or metallic assembly (Cu/Al systems [3]), it remains to be improved for more complex systems, especially thick targets, and new high technology materials (like CFRP). The main challenges come from the shock parameters, particularly from the shortness of the load duration which can lead to a strong attenuation of the shock amplitude inside the target, limiting thereby the induced traction levels. This short irradiation also restricts the area where the crossing of the release can occur; it is meaning the location of the high tensile stress that is used to test the interface of the adhesive joint.

First results on monolithic composite specimen:

In this context, LASAT has recently been performed on carbon fibre epoxy composites [7-9]. Experiments demonstrated the suitability of the technique for these new complex materials. Different composite assembly interfaces have been tested by varying the laser pulse duration. The capacity to discriminate two adhesion levels at the interface adhesive/composite with the LASAT has been demonstrated [9] on given systems whose dimensions were matching the laser shock conditions used (duration and amplitude). Even if the feasibility of this test under defined conditions has not to be proven anymore, its development requires reaching the adequate shock test conditions for any given structural assembly. For that, a better comprehension of the shock wave propagation inside composite targets is still missing in order to fully understand the influence of each shock wave parameter. This could be achieved through a certified numerical optimization tool based on shock waves propagation studies in each component of the composite.
structure to be tested in order to get the suitable shock parameters to locate first traction events at the interfaces.

As a first step, the composite material behaviour under laser induced shock has been studied because its response can deeply influence the way of performing laser shock test on composite assemblies. The laser shocks were used as a laboratory tool able to produce different levels of damage inside a classic CFRP composite, a T800/M21 (Hexcel composite) made of several oriented plies. Its particularity is a non-conventional matrix, mixed from a thermoset epoxy resin and thermoplastic nodules whose elasticity should enhance the composite shock resistance. Several diagnostics providing complementary information on the damage produced or not into the samples have been tested. Microographies (Fig. 6) have revealed a cone-shaped damage through the sample thickness. Moreover, a clear correlation has been made between the laser intensity and the damage dimensions. Thus, different levels of damage were produced and observed. The delamination profiles have been observed by microographies showing that the cracks leading to delamination were following the thermoplastic nodule shapes.

![Damage on a 1.5 mm thick T800/M21 composite sample with an example of delamination position](image)

**Fig. 6:** a) Damage on a 1.5 mm thick T800/M21 composite sample with an example of delamination position - Water confined laser intensity (duration: \( \Delta t = 30 \) ns) and b) Referred delamination with a ply ejection on the back face; the remaining ply and the coating resin replacing the ejected ply are separated by the delamination profile

X-Ray radiographies of thin slice T800/M21 samples have been taken to confirm the main damage dimensions and their link to laser intensity. This different diagnostic has also revealed the anisotropic characteristics of the damage in spite of an axy-symmetric loading (laser shock). For thick T800/M21 composite sample, the LASAT results in small blisters on the target back face as laser shock wave is more decayed through the material thickness. Interferometric Confocale Microscopy (ICM) appeared as an efficient diagnostic to measure this kind of damage. The anisotropic characteristics of the defect were traduce by an elliptical shape of the blisters observed. Once more, the geometries measured have been linked to the laser shock intensity and allow forecasting that a damage threshold could be found for this material using this non-intrusive method with more investigation. Preliminary numerical simulations of these experiments evidence all the possibilities for validating constitutive laws and damage criterion used in predictive models. The conformity of the shock wave characteristic between numerical simulation and experimental data is sought in order to optimize the shock loading parameters according to the geometry of the composites bonded systems.

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CONCLUSION

The approach of Extended NDT is demonstrated through the results of previously mentioned test campaigns shown in this paper. For the characterisation of the adherend surface, the FT-IR Exoscan and the X-Ray Fluorescence techniques are so far the only portable and commercialised technologies. Other methods are still under development and shall be improved. The implementation of E-NDT methods shall be possible in manufacturing and in-service environment.

Concerning the characterisation of the adhesive joint performances, the first observations of the LASAT effects on monolithic composite provide information about the composite behaviour under laser shock wave, which improve the comprehension of the main LASAT parameters. Following the optimisation of the shock loading parameters, The LASAT experiments on adhesive bonded CFRP assemblies could be performed with a precise control on the traction load position at the interface to be tested. By iterative experiments, the debonding threshold could be determined for a given system using the post-shocked diagnostics as well as the numerical modelling. Therefore, the quality of an adhesive joint system can be evaluated provided the phenomena are understood and controlled.

Further general development will involve more detailed application scenarios (e.g. measuring task, limit values, substrate type, surface treatments, environment requirements, etc.) and a larger range of specimens to characterise. The specimens shall also cover the complete issue addressed in the application scenario in order for the technology to show its complete potential and be optimised for the required measuring tasks.

REFERENCES


