Pre-bond Quality Assurance of CFRP Surfaces Using Optically Stimulated Electron Emission

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ABSTRACT

Adhesive bonding reliably contributes to joining carbon fibre reinforced plastics (CFRP). Manufacturing and in-service effects may reduce the mechanical performance of these joints. Their reliability is governed by assuring the surface quality of CFRP material. Roughness of ready-to-bond CFRP surfaces affects in a complex way their wetting behaviour as determined with a water break test. Therefore, further in-line capable techniques are highly desirable for the assessment of surface quality prior to bonding.
In the present work, optically stimulated electron emission (OSEE) was investigated with this purpose. Sensitivity and accuracy of OSEE measurements allow to distinguish favourable surface states of CFRP adherends from surface states which are unfavourable for adhesive bonding. We show that OSEE may be applied in field and without electrically contacting CFRP surfaces for sensing moisture, thermal degradation or thin layers of contaminants.

Keywords: *surface quality assurance, pre-bond inspection, carbon fibre reinforced composite, aircraft structures, optically stimulated electron emission*

1 Introduction

With the quest for continuous decrease of air traffic-related fuel consumption and corresponding CO_2 emissions, the implementation of a structural material that combines light-weight design with superior mechanical properties is fundamental for airplanes. Nowadays, the comparatively low-weight metallic alloys (Al-Li, Al-Mg) are being replaced by new composite materials that better combine both characteristics[1] The use of composite materials in aircraft structures has increased considerably in the past decades[1,2]. CFRP structures have been widely used in several fields, as structural engineering materials and also in the automotive industry[3,4,5]. The material shows high energy absorption characteristic with a high strength-to-weight ratio[6,7].

In principle, adhesive bonding offers promising perspectives not only for joining CFRP light-weight structures in production but also in case of repair processes involving intact additional CFRP panels. However, CFRP surfaces are susceptible to various impacts during exposure to in-service environments and joining by adhesive bonding is sensitive to surface contamination which can compromise the bond strength. Cleaning before bonding needs to be adequate and sufficient to reduce the surface concentration of adverse substances to typically less than a monolayer. Moreover, moisture uptake into exposed CFRP or thermal impact may occur. Therefore, surface monitoring with an appropriate sensitivity is highly recommendable before manufacturing adhesively joint CFRP parts. A reliable quality assurance of the surface state is necessary to discriminate surfaces that are ‘ready-to-bond’ from those that are not ‘ready-to-bond’.

In order to ensure the performance of adhesively joined load-critical CFRP structures, technologies are required which can monitor the physico-chemical properties of adherents and adhesives or detect

adhesion properties of bonded components[8]. However, to date there are no reliable NDT methods available for the assessment of bond strength and therefore adhesive bonding is a special process. Anyhow, distinct properties of adherent surfaces may be assessed, and the only method established at the moment for pre-bond evaluation in field is the water break test. However, this is not a quantitative method for determining the CFRP surface wetting behaviour and results are inadequate for surfaces with a high roughness[9,10]. Therefore, further techniques need to be established for reliably assuring pre-bond surface quality. As a consequence of the manyfold potential impacts affecting CFRP surfaces, various rather specific monitoring techniques may be applied for detecting certain chemical substances like silicones or classes of possible contaminants like hydrophobic agents. However, the ideal technique should be sensitive to many of the common contaminants in order to indicate the appropriateness of the CFRP surface state for the bonding process.

For the investigation of optically stimulated electron emission (OSEE) with this purpose two factors must be considered: i) the intensity of electrons emitted from CFRP surfaces will be attenuated by air and ii) CFRP is a slightly electron conductive material. Electrically conductive carbon fibres may show a distinct photoionisation behaviour, but the electron emission behaviour of CFRP is influenced by the matrix resin and, often, by the presence of a sizing on the carbon fibres. Before bonding, however, CFRP panels are usually ground until a carbon fibre layer is exposed at the surface. Optically stimulated electron emission (OSEE) may be considered a non-destructive technique to detect contaminants on adherent surfaces due to the change of electron emission characteristics, e.g. the work function[11]. Modifications of the surface state of metals[12] or metals covered with self-assembled monolayers (SAM)[13], ceramics[14], polymers and also CFRP[15] may result in a change of the detected electron flow[16,17]. Instrumentation for investigating the surfaces of electrical insulators was developed and adapted exemplarily by NASA workers[18]. Despite such considerable performance for CFRP applications as detailed particularly by Parker and Waghorne[15], OSEE has not yet achieved a widespread use for investigating the surface state of CFRP samples exhibiting contaminations considered relevant, e.g., in aeronautical use.

The results presented in this contribution were obtained in the frame of the joint EU FP7 research project “Extended non-destructive testing of composite bonds – ENCOMB”. This project aims at identifying potentially suitable NDT techniques and adapting them to relevant aircraft manufacturing and in-service applications. As part of the work, the influence of various surface contaminants (hydraulic fluid, release agent, moisture) and of thermally damaged CRFP on the performance of adhesive bonds was quantified. It was shown that these factors result in a significant decrease of the mode-1 interlaminar fracture toughness (G_{IC}) of adhesively bonded joints of contaminated adherend as compared to clean reference samples[19]. For example, moisture uptake of 1.5 wt% and immersion in aqueous Skydrol® hydraulic oil reduced the G_{IC} by 20 %. Even more pronounced effects were obtained when annealing CFRP samples at 220 °C in air or when applying approximately 1 nm of a release agent, with a G_{IC} being lowered by nearly 70 %. Such huge influence of contaminants on bond strength clearly emphasizes the need to monitor adherend surfaces before bonding.

2 Experimental

In this section, the preparation of the carbon fibre reinforced composite (CFRP) material used for the investigations of the pre-bond quality and their characterisation are described.

2.1 Sample preparation

The CFRP material exhibited fibres arranged in unidriectional layers and a thermoset matrix (T700 low density carbon fibres and HexPly© M21 matrix from Hexcel). Clean untreated reference CFRP samples (further on denoted as UT) were ground until exposure of the top fibre layer and cleaned according to standards from aircraft manufacturers. Contaminated samples were produced containing release agent at the surface and moisture uptake by the CFRP bulk material (both relevant for manufacturing processes), as well as Skydrol hydraulic oil contamination and thermal degradation of CFRP panels, which may take place in service. In the four different scenarios investigated, the factors

were applied to the same extent that had been shown to result in a reduction of the mode-I fracture toughness of composite bonded joints[19]. In the first scenario, CFRP samples were dip-coated with release agent and a coverage characterised by a silicon surface concentration of 4 atom% according to XPS investigations was adjusted. For further investigations, films characterised by a silicon surface concentration of 8 atom% and 10atom%, respectively, were applied. Aiming at saturation moisture uptake, samples were exposed to demineralised water for 672 hours at 70 °C and a water uptake of 1.5 weight% was reached. Hydraulic oil contamination of CFRP surfaces was represented by samples immersed in a Skydrol®-water phase solution for 672 hours in an oven at 70 ºC. Finally, thermal degradation of CFRP was achieved by exposure of samples to a temperature of 220 °C for one hour in an air circulation oven.

Carbon fibres of type SIGRAFIL C30 T050 EPY with an epoxy sizing were supplied by SGL Technology GmbH, Meitingen, Germany. Glassy carbon (GC) of type SIGRADUR G was supplied by HTW Hochtemperatur-Werkstoffe GmbH, Thierhaupten, Germany. For grinding GC SiC emery paper with 800 mesh was used. A sample of an epoxy thermoset was prepared at Fraunhofer IFAM by using isophorone diamine for curing diglycidyl ether of bisphenol A.

2.2 Sample characterisation

Surfaces of CFRP panels were characterised using vacuum-bound instrumental analysis based on X-ray Photoelectron Spectroscopy (XPS), Scanning electron microscopy (SEM) and Transmission Electron Microscopy (TEM). XPS spectra were taken using a Kratos Ultra system using excitation of photoelectrons by monochromatic $Al_{K\alpha}$ radiation within an area of approximately 0.2 mm^2. SEM examinations were performed with a field emission scanning electron microscope (FESEM) of type FEI Helios 600 (DualBeam) and applying an Everhardt-Thornley detector for detection of secondary electrons. The Dual Beam instrument additionally is equipped with a liquid-metal ion source (LMIS) for facilitating Focussed Ion Beam (FIB) cutting of the sample surface with gallium ions. TEM investigations were made on a 200 kV field emission microscope of type FEI Tecnai F20 ST.

OSEE experiments were done under ambient conditions with a Surface Quality Monitor SQM200 (Photo Emission Tech., Inc. (PET), USA). During OSEE investigation the sample surface is exposed to ultra-violet light of a mercury vapour lamp with prominent emission maxima at 4.9 and 6.7 eV.

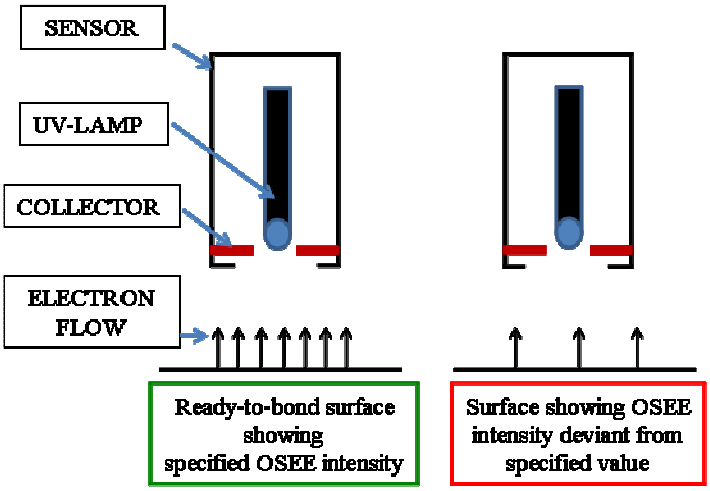

Figure 1: Functionality of OSEE device and scheme of applying OSEE for CFRP surface analysis

Based on the kinetic energies and escape depths of photoelectrons emitted by the investigated sample, OSEE is a surface-sensitive technique exhibiting an information depth in the range of 0.1 µm. Emitted photoelectrons may flow through the collector biased at 40 V and generate a current measured by a solid state electrometer. The measured current values reported are furtheron referred to as OSEE intensity, and they may be interpreted in terms of the integral band intensities of the underlying and contributing electronic spectra[14]. The OSEE device is operated in combination with a moving table for

surface scanning. OSEE measurements were done with the samples placed on the electrically conductive and earthed table and scanning the sample with the measuring spots being separated by 5 mm and, in case of electrically conducting analytes, by 2.5 mm. The CFRP panels investigated were typically 100 x 100 mm^2 wide and were scanned with 17 x 17 steps in orthogonal directions. A mean OSEE signal value was calculated by averaging over the whole sample surface area grasped, and the OSEE intensities are plotted along with the thus obtained standard deviation for each sample.

3 Results

In this section, results of characterising CFRP panels ground to the top carbon fibre layer are displayed. Such UT surfaces represent the surface state ready for adhesive bonding. Several factors affecting the OSEE signal of such surfaces are evaluated and discussed in comparison to results obtained with net polymer and carbon materials.

3.1 CFRP surfaces ready for bonding characterised by vacuum-bound analysis

CFRP surfaces of type UT were characterised using SEM, TEM, EDX and XPS as vacuum-bound surface sensitive microscopic and spectroscopic tools, respectively. Electron microscopic images of the UT surfaces are shown in figure 2. The SEM image on the left reveals remainders of the matrix on the sample surface aside from carbon fibres with a thickness of approximately 6 µm. The fibres are disrupted in places in longitudinal direction and prevailingly do not appear to be disintegrated in direction vertical to the surface. Investigating the bulk of the carbon fibres close to the fibre surface by EDX reveals 95 atom% ± 1 atom% of carbon and 5 atom% ± 1 atom% of nitrogen containing species. Probably a polyacrylonitrile precursor was used for C-fibre production. According to EDX investigations the matrix features oxygen, sulphur, nitrogen and carbon containing species. Based on a 0.1 µm thin FIB cut through the bulk of the CFRP sample in a direction perpendicular to the fibre axis, the TEM images displayed in the centre and on the right in figure 2 show sub-microscopic stacks of a few graphene layers within the carbon fibre. In proximity to the fibre surface the concentration of the stacks is slightly different from the one observed in the bulk of the fibre. Concerning the fibre surface, there do not seem to be topological differences between the topmost fibre surface region and regions which are several 10 nm closer to the bulk of the carbon fibres.

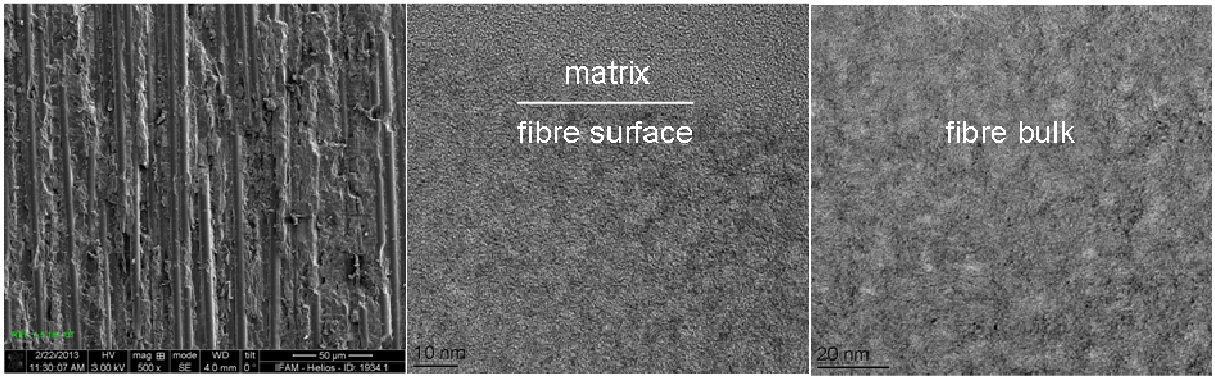

Figure 2: Electron microscopy investigation of CFRP samples of type UT:
left: topview SEM image of the surface;
center: TEM image of a FIB cut through the matrix/fibre interphase;
right: TEM image of a FIB cut through the bulk of a carbon fibre

For assessing the composition of the topmost region of the CFRP surface, XPS investigations yielding an information depth of approximately 10 nm were carried out. They indicate that the CFRP panel surface region exhibits 14.5 atom%± 0.2 atom% of oxygen besides 4.6 atom%± 0.2 atom% of nitrogen, 0.8 atom%± 0.2 atom% of sulphur and 79.6 atom%± 0.2 atom% of carbon containing species. Fitting the C1s signal smoothly works out using three Gausso-Lorentzian contributions with a width of 1.25 eV. In detail, the peak with the lowest binding energy comprises 65 % of the total C1s

intensity, the second peak with a 1.4 eV± 0.1 eV higher binding energy comprises 30 % of the C1s intensity, and the third peak appears at a 2.9 eV± 0.1 eV higher binding energy than the first peak. In particular the C1s detail spectrum is not governed by contributions of sp^2 hybridised carbon which would be characteristic for graphite-like constituents of the carbon fibre.

Concluding, the investigations using the vacuum-bound microscopic and spectroscopic techniques evidence aspects of the lateral surface structure and of the vertical composition within the surface region of the CFRP surfaces of UT samples. Basically, roughly equal parts of the surface region are composed of matrix system and of electrically conductive carbon fibres, respectively. The topmost region of the CFRP sample (comprising a thickness of some nanometres) is not dominated by graphite-like species which strongly contribute to the bulk structure of the fibres.

The thus structured surface region of CFRP UT samples is within the approximately 0.1 µm thin information range of OSEE measurements the results of which will be described subsequently.

3.2 CFRP surfaces ready for bonding characterised by OSEE in ambient atmosphere

CFRP samples of type UT were obtained by grinding a CFRP surface until exposure of a carbon fibre. The surface state of UT is characteristic for CFRP being ready to bond.

As shown in figure 3 in the plot on the left, the distance between the sample surface and the OSEE sensor strongly influences the OSEE intensity when investigating equally prepared CFRP samples. A strong decay of the OSEE signal intensity by 75% when increasing this distance by 50 % from 6 mm to 9 mm or from 7 mm to 10.5 mm was observed. This finding is attributed to an attenuation of electrons when travelling through the air between the sample and the sensor during the OSEE measurement. When the OSEE measurement was repeated once at the same position of the CFRP surface, an OSEE intensity decreased by approximately 10 % was observed. This finding is attributed to electrostatic charging building up on the CFRP surface which is not ideally electrically conductive.

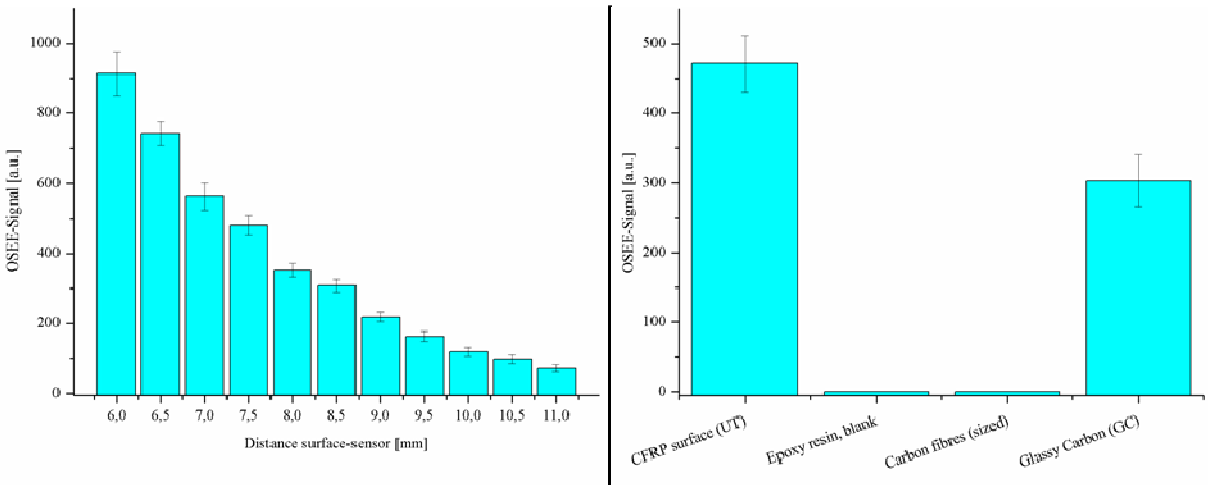

Figure 3: Results of OSEE measurements for composite and net sample surfaces:
left: CFRP samples UT, measured at different distance between sample surface and OSEE sensor;
right: UT sample, an amine-cured epoxy resin, sized carbon fibres, and a glassy carbon surface, measured at a fixed surface-sensor distance

Further investigations were performed in order to elucidate possible contributions of different constituents of fibre-reinforced plastics. For this purpose an epoxy resin without fibre-reinforcement and sized carbon fibres were investigated with OSEE. Surprisingly, both samples did not show a significant OSEE intensity when investigated at the same sample-sensor distance as a CFRP surface which showed a substantial OSEE intensity. In case of the electrically insulating epoxy resin this finding might result from electrostatic charging building up during the measurement. However, in case of the electrically conductive and earthed sized carbon fibres such finding may need to be attributed to

distinct effects. Indeed, the fibre structure and composition might play a particular role since the surface of an earthed and electrically conductive glassy carbon (GC) which is composed of a material relatively similar to the carbon fibres revealed a considerable OSEE intensity. Roughening the GC surface with an 800 mesh emery paper rather reduced the OSEE intensity by 15 %. These three latter findings show that the photoemission behaviour of distinct carbon materials and surface states deserves to be studied in more detail. This statement holds true to an even greater extent with respect to the CFRP surfaces the OSEE intensity of which was even 50 % higher than the OSEE intensity of the clean and smooth glassy carbon surface.

In summary, the CFRP surfaces of type UT show a remarkably high OSEE intensity. Therefore, the influence of factors reducing the bond quality of CFRP panels on the OSEE intensity was tested. The respective results are reported in the subsequent paragraph. The physical processes in the CFRP surface during an OSEE measurement seem to be rather complex. As CFRP is composed of an insulating matrix and electrically conductive carbon fibres connected through the fibre/matrix interphase, it might turn out that the electric contact in the interphase and the distribution of the dielectric matrix on the CFRP surface affect the photoemission and electrostatic charging behaviour during the OSEE measurement.

From the technological point of view, the described investigations show an important finding. The dependency of the OSEE intensity from the distance between the sample and the OSEE sensor indicates that the OSEE device needs to be placed and maintained in a controlled distance to the sample surface during a measurement. Therefore, on the one hand, in practice spacers proving a distance of some millimetres can be applied. On the other hand, in case of macroscopically uneven CFRP sample surfaces variations of the distance between sample surface and the OSEE probe by 1 mm may affect the measured OSEE intensity by not more than 20 % if the surface-sensor distance is higher than 6 mm. In any case, it is recommended to investigate the dependence of the OSEE intensity on the distance between the sample and the OSEE probe for each type of sample elaborately.

3.3 Identification of CFRP surface conditions unfavourable for adhesive bonding

In this paragraph, OSEE investigations of surface states of CFRP panels with controlled contaminations/degradation are reported. These contaminants/degradation were shown to result in a reduced bond strength[19]. We first investigated whether OSEE measurements allow to differentiate unfavourable surface states from the UT state and, secondly, if OSEE measurements allow to differentiate between distinct concentrations of surface contamination by release agent.

For the OSEE measurements, the distance between the sample surface and the OSEE sensor was set to permit a maximum sensitivity for possible changes of the OSEE intensity as compared to the UT state. As illustrated in figure 4 in the plot on the left, the thermally degraded CFRP sample TD shows a significantly smaller OSEE signal intensity than the UT sample. It is concluded, that OSEE is appropriate for detecting thermo-oxidative effects which were shown to reduce the strength of adhesive joints produced from correspondingly impacted CFRP adherends[19]. The moisture contaminated CFRP sample MO shows a significantly smaller OSEE intensity than the UT sample. From a sample covered by a several micrometer thick layer of liquid water no detectable OSEE signal was obtained. The CFRP SK sample covered with hydraulic oil shows a drastically smaller OSEE signal intensity than the UT sample. It may be extrapolated that OSEE may even permit the detection of smaller concentrations of hydraulic oil as compared to the concentrations present on sample SK. Finally, the CFRP sample RE covered with a silicone containing release agent was shown to yield a significantly smaller OSEE intensity than the UT sample. Based on the plot on the right of figure 4, it is concluded that the OSEE intensity strongly depends on the concentration of release agent. Silicone surface concentrations higher than in the case of sample RE result in a further decrease of the OSEE intensity. It may be extrapolated that OSEE may even be suitable for indicating smaller amounts of release agents than 4 atom% as applied to sample RE.

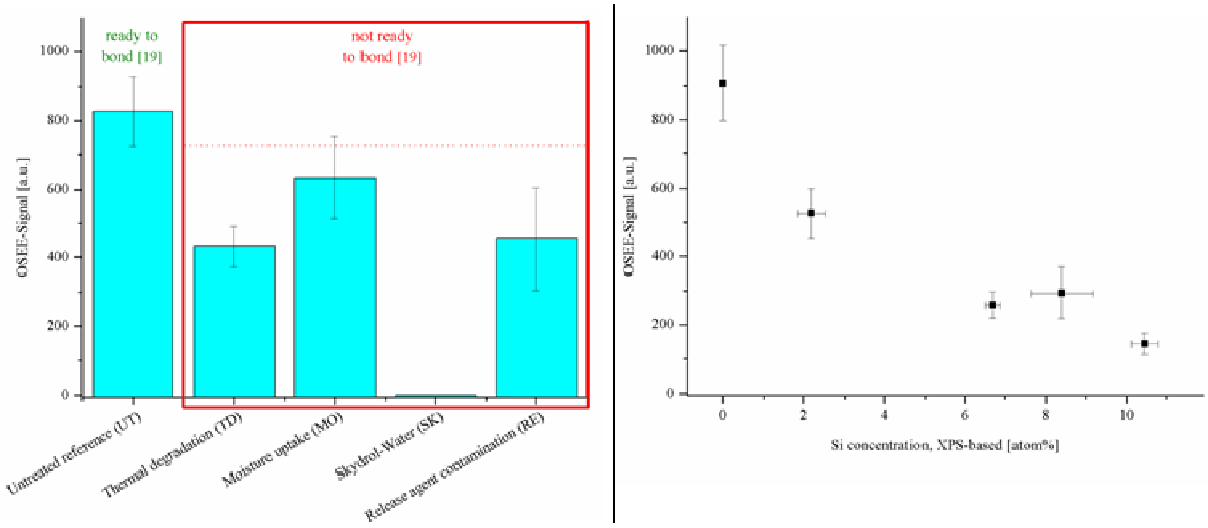

Figure 4: OSEE intensities obtained for distinct CFRP surface states:
left: untreated reference UT ready to bond[19] as compared to surface qualities not ready to bond[19],
right: distinct surface coverages of release agent, with Si concentrations from XPS investigations

These results show obtained that OSEE - even though not providing chemically-specific information - is an inline-capable tool facilitating versatile applicability for detecting contaminant layers such as water, Skydrol and release agent as well as effects of thermal degradation all of which significantly reduce the quality of adhesive bonds.

4 Summary

The implementation of CFRP as a structural material in the aircraft industry requires a reliable quality assurance of surface states for adhesive bonding techniques. Improper grinding during mechanical surface pre-treatment, contaminants on adherends, moisture uptake in the CFRP bulk or thermal impact can have a large negative influence on the mechanical properties of adhesive joints prepared in manufacturing or repair processes. Therefore, assurance of surface quality needs to be implemented in order to obtain the best conditions for an adhesive joint.

The optimum CFRP surface state before adhesive bonding denoted as UT had been obtained after grinding until exposure of a carbon fibre layer. It was characterised with respect to its structure and composition using vacuum-bound analyses. Applying optically stimulated electron emission (OSEE) as a surface-sensitive and inline-capable inspection tool operated in ambient atmosphere, these CFRP surfaces showed prominent OSEE signal intensities which were obtained without electrically contacting the CFRP material.

With OSEE signal intensities being sensitive to the presence of adsorbates on top of such photostimulated CFRP surfaces and possibly also to the electric properties of fibre/matrix interphases, monitoring by OSEE showed its capability to distinguish all the investigated surface states known to be unfavourable for adhesive bonding from the CFRP surface state UT. In detail, four types of unfavourable conditions of CFRP panel surfaces were considered. Thermally impacted adherends could be distinguished as well as moist adherends and adherends covered with release agent or hydraulic oil for aeronautical use.

In conclusion, the OSEE technique demonstrated its potential for surface state quality assurance of CFRP materials prior to adhesive bonding.

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