New Trends in CFRP Treatment and Surface Monitoring for Automated Structural Adhesive Bonding

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SUMMARY

Peel plies, release films and mould release agents in the production of carbon fibre reinforced composites (CFRP) parts contaminate the surface with residues of release agents, which hinder durable adhesion to adhesives. For structural adhesive bonding surface treatments are mandatory to remove these residues. Treatments by plasma (AP, LPP), laser and blasting indicate a high potential for automation. Additionally new surface monitoring techniques like Infrared Spectroscopy and Aerosol Wetting enable the detection of those release agent residues before adhesive application and contribute to improved quality assurance.

Keywords: Structural Adhesive Bonding, CFRP, Surface Treatments, Plasma, , Laser, Grit Blasting, Surface Online Monitoring Methods, Near Infrared, Aerosol Wetting

Introduction

The use of peel plies, release films and mould release agents are state-of-the-art in the manufacturing of CFRP parts for easy de-moulding and surface consistence.
However it was very early noticed, already more than 30 years ago, that residues of release agents on such CFRP surfaces are responsible for bond line failures and insufficient mechanical performances. Therefore manual grinding processes were introduced in aerospace industry for surface treatment before bonding. These processes can remove different amounts of surface contamination and are still standard treatment procedures today.

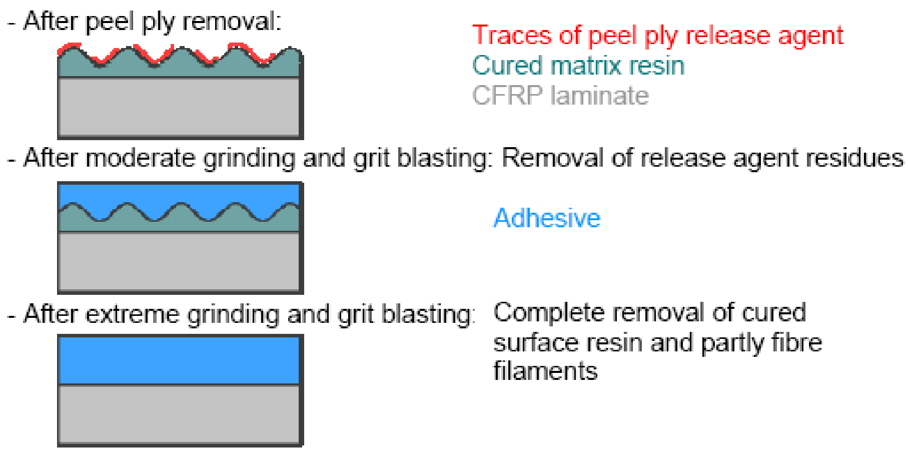

Fig .1 Illustration of adhesive bonding on CFRP with smooth and rough grinding / grit blasting conditions [1]

Manual grinding procedures depend to a high extend of the workers skills, are very difficult to control, particularly in case of shaped and curved parts, are very time consuming and creates a lot of grinding dust emissions in the bonding work shop.
For introduction of automated adhesive bonding processes alternative surface treatments are needed to enable a high, reproducible quality standard.

Alternative CFRP Surface Treatments

Therefore alternative CFRP surface treatments like atmospheric plasma, low pressure plasma, automated grit blasting and laser treatment are meanwhile available.
The first focus of this paper will be a comparison of these different treatment methods as alternatives for CFRP grinding. Atmospheric plasma treatments were intensively investigated and demonstrated a high potential in activating CFRP parts with different release agent residues on the surface.

- Atmospheric Plasma Treatment of CFRP:

The use of A-plasma as an alternative treatment method for adhesive bonding is meanwhile state-of-the-art for plastics and metals. For CFRP bonding the objective is to remove or activate surface contaminations coming from peel plies, release films and release agents, used in the fabrication for composites.

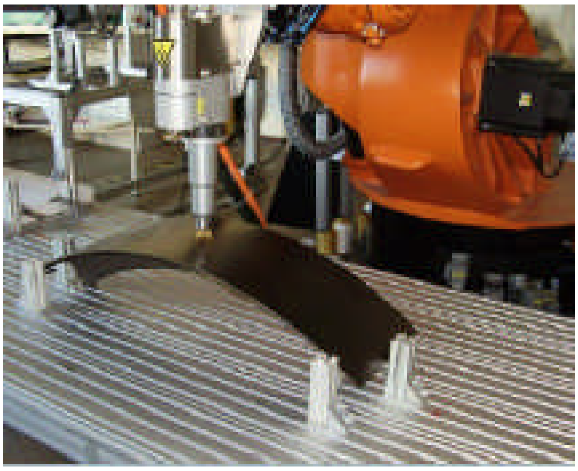

Fig. 2 Example of robot assisted A-plasma treatment on a single curved CFRP panel section

Almost all of these ancillaries are treated with de moulding agents based on hydro-carbons, siloxanes or fluorines. Meanwhile it could be demonstrated in different tests, that air / oxygen A-plasma removes or activate technical contents of such surface contaminations.

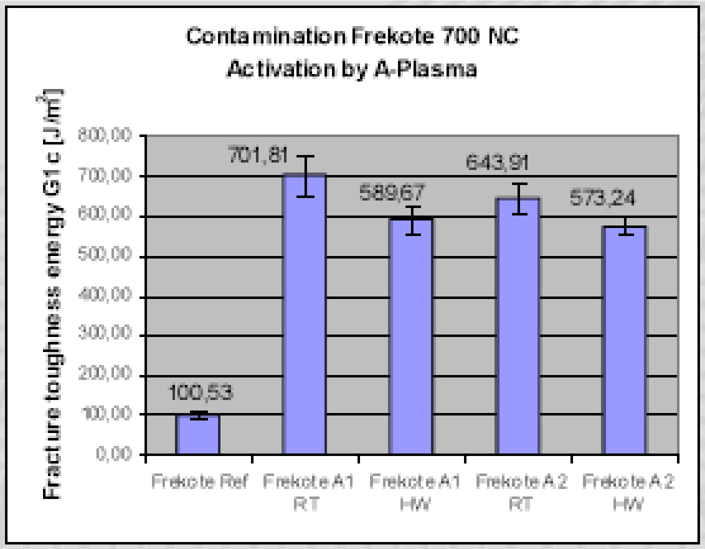

Fig. 3 Example of air-A-plasma (2 treatment conditions A1 and A2) on siloxane contaminated CFRP epoxy laminates. Comparison of G1C results in the non aged bonding status and after hot wet aging (1000 h – 70°C/85% r.H.).

Further on, A-plasma can be easily introduced in the bond shop (no dirt, no pollution) and has a high potential for automation. Disadvantages of A-plasma is the line treatment with the plasma nozzle, this means the treatment time for big bond areas is long or more nozzles have to mounted on the robot. Also the treatment of multi curved parts with the robot is quite difficult, because the nozzle distance to the part surface have to be constant. Therefore the programming of the robot can be complex.

- Low Pressure Plasma Treatment of CFRP:

Plasma as an ionized gas can be created thermally or by an electrical field, among others. In a Low Pressure Plasma (LPP) equipment the electrons are accelerated in an electrical field. The energy created inside the ionized gas can break any chemical bond of organic molecules. The temperature of the treated material however remains at room temperature.

The process is flexibly and can be configured through variation of the process parameters as gas flow, gas composition, pressure and power.

In contrast to atmospheric plasma, a plasma chamber and vacuum equipment are necessary. The advantages are that the whole composite part will be treated in one shot and geometrical inaccessible areas as slots, holes etc. will be activated. Disadvantages are that the size of CFRP parts is limited to the size of the plasma chamber and that the whole surface of the component will be always treated, even when only small regions are necessary for adhesive bonding.

In the framework of the European project MOJO (Modular Joints for composite aircraft components) 6^{th} framework program and peel-ply containing silicon investigations at Premium AEROTEC and EADS Military Air Systems, low pressure plasma evaluations where carried out. In this investigation the plasma is generated by means of microwave excitation. The frequency used was around 2 GHz (s. fig. 4). Super Release Blue (SRB) and WELA T0098 peel-ply were used on CFRP-specimens. The first was chosen to create silicon rest after peel-ply removal and the second one was used for process parameter investigations.

 

Fig. 4 Left: LPP equipment TEPLA300-5, right: chamber containing argon and oxygen excited gas

Oxygen is used to clean and to generate polar groups, Argon to introduce more energy to the gas and stabilise it and CF4 to react with silicon.
G1c-tests were carried out on specimens bonded CFRP laminates with a constant mixture of the paste adhesives EA9395 and EA9396 from Henkel. Fig. 5 compares the results obtained with both optimised parameters for LPP and test results using same specimens and test procedure but activating with atmospheric plasma. As can be seen the activation by means of atmospheric and low pressure plasma are equivalents.

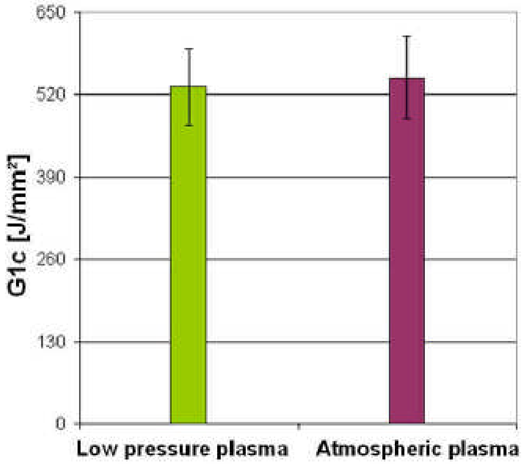

Fig. 5 G1C values obtained on adhesively bonded CFRP samples with LPP and AP

CFRP surfaces with relative thick contamination layers of e. g. siloxane, based on release agents, are difficult to prepare for a succeeding bonding step. Even the use of standard AP and LPP- plasma processes have difficulties to convert or remove thicker contaminations. Surface investigations have shown, that low pressure plasma activation (LPP) with oxygen/fluorine containing process gases are able to remove nearly all Si-content from the FRP surface. These analytical results were confirmed by mechanical tests. It is generally possible to use also such fluorine containing process gases in plasma chambers, but the generation of toxic hydrogen fluorides have to be avoided. In these cases the low pressure chambers have to be combined with attached gas washer equipment.

- **Laser Treatments of CFRP**

A meanwhile qualified procedure in the aerospace is the use of a carbon dioxide laser for the removal / activation of release agent residues on CFRP surfaces before painting. The application of the same laser technique, as a surface treatment method for structural adhesive bonding is still under investigation. The degree of treatment (removal of surface contaminations like siloxanes and hydrocarbons, removal of resin system layer like epoxies and attack of the carbon fibres depend very much on the laser systems and treatment conditions.

It is known, that the specific wave lengths of the different laser systems (e. g. CO2 – laser at 10,6 µm in the mid infrared range or the YAG laser at 1,06 µm in the near infrared range) react very different with the CFRP surface. Also the laser mode, continues wave (cw) or pulsed conditions influence interaction with the CFRP surface (e.g. surface heating, ablation and degradation.

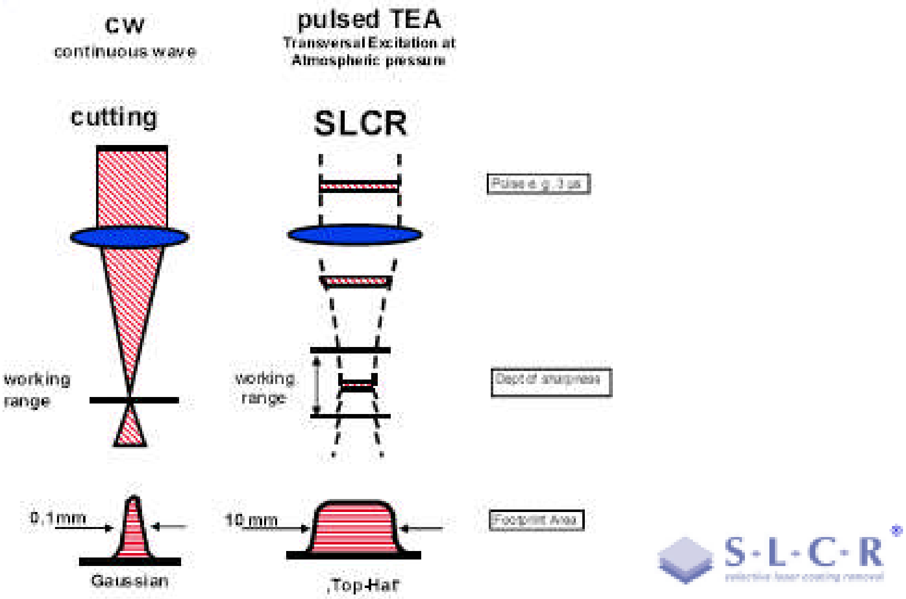

Fig. 6 Comparison and influence of continues wave and pulse mode CO2 laser conditions on surface preparation [2]

It is also known, that already laser ablated surface particles can again rearrange on the FRP surface and negatively influence the bonding properties. The efficiency of lasers for CFRP treatment seems to depend also on the specific composition of the CFRP resin systems and the embedded fibre types. The wave length of CO2 Laser remove very well the epoxy resin, but carbon fibre filaments remain on the surface.

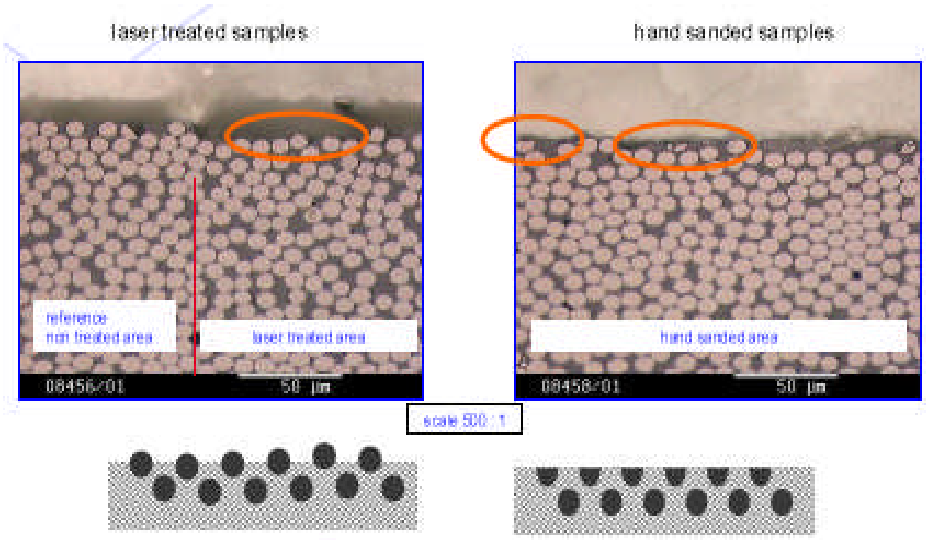

Fig. 7 Microscopic comparison of CO2 laser treated and hand sanded CFRP surface preparation [3]

Other mentioned techniques like automated grit blasting and fluorine containing plasma also demonstrate good results in CFRP surface treatment. These methods normally remove the release agent residues and also too a certain extend the resin from the surface.

Blasting techniques also can attack C-fibre filaments and brittle epoxy resins in the top laminate layer. This means they are more aggressive compared to plasma techniques. Compared to A-plasma and low pressure plasma higher amounts of contaminations of release agents can be easily removed.

- Automated grit blasting Treatment of CFRP:

Grit blasting applied as surface treatment of CFRP for subsequent structural adhesive bonding shall evenly abrade the surface comparable to the grinding (sanding) procedure on flat surfaces, thereby offering higher feasibility for automation and applicability on surfaces with considerable waviness in the sub millimeter range without severe damage of the composites fibres.

By this treatment contaminants such as residues of release agents are removed and the surface roughness can be adjusted to a range which is optimal for adhesive bonding. Standard grit blasting systems for removal of stains, paints and corroded layers from metals mostly apply aluminium oxide particles as abrasive media, which are forcefully accelerated by a comparatively high air pressure of above 3 bar. Such classic high pressure blasting onto CFRP can lead to excellent bond strength, but the development went to more mild abrasion characteristics obtained by low pressure blasting systems and less abrasive particles in order to enhance processing stability especially in manual operation. Meanwhile low pressure blasting systems found entry into aerospace industry for the removal of paints from CFRP as well for the surface treatment of CFRP for subsequent painting or adhesive bonding. Grit blasted CFRP surfaces require cleaning followed by a wetting test (water-break test) to assure surface quality as this is the case for the grinding based surface preparation.

Surface Online Monitoring Methods

The so-called water break test is introduced in aerospace industry. This water break test is a wetting test after CFRP grinding. Sometimes this test indicates problems on rough surfaces, needs a re-drying step of hours and has no real potential for introduction in an automated bonding process. There is a need for alternative and more reliable surface monitoring methods to check the surface status after treatment and before adhesive application and bonding.

Therefore the second part of this paper will focus on the selection and development of robust and reliable surface online monitoring methods, which are appropriate to inspect the whole bonding area within a short time period before adhesive application.

These monitoring methods need high identification sensitivities for CFRP surfaces, contaminated with siloxanes, flurocarbons and hydrocarbons, coming from peel plies, release films and release agents.

Within a still ongoing European research programme, called ABiTAS (Framework 6) different monitoring methods have been evaluated for the application on CFRP surfaces

After this pre-selection on CFRP surfaces with different release agent residues, two methods Near Infrared Spectroscopy (NIR) and Aerosol Wetting have been selected.

Near Infrared Spectroscopy

In the pre-selection of the research programme ABiTAS different NIR monitoring devices have been checked for the applicability on dark CFRP surfaces with different surface roughnesses [4]. After than, the NIR device (optic and lamp) was attached beside the atmospheric pressure plasma nozzle. The whole equipment (plasma nozzle together with the NIR device) was mounted on the robot arm.

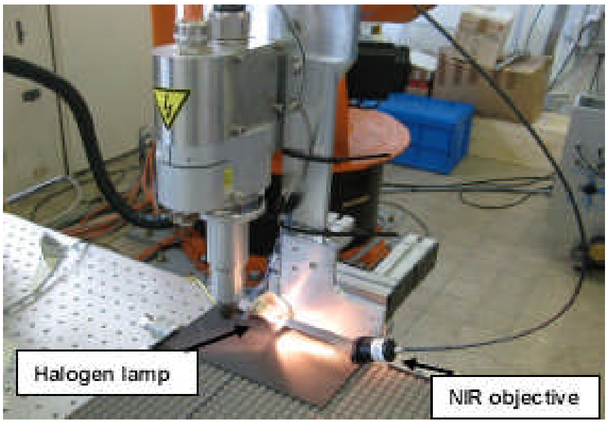

Fig. 8 NIR optic and illumination lamp attached beside the A-plasma nozzle on the robot arm

The whole NIR equipment consists of the FT-NIR process spectrometer, a power supply for the halogen lamp, the NIR optic and a PC for the data evaluation. [4]. The NIR monitoring device can easily be integrated in a robotic bonding process [see fig.7],

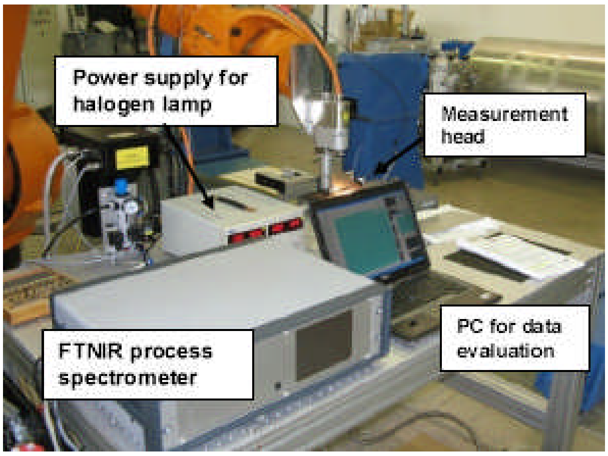

Fig. 9 Complete NIR test equipment (robot, A-Plasma, NIR optic and processor)

Different CFRP samples before and after plasma treatment have been investigated with the NIR online monitoring device with following preliminary results.

- The plasma treatment leads to changes in the NIR spectra. The differences in the spectra are caused by morphological changes on the CFRP surface due to the plasma treatment.
- The residue detection of surface contaminants on CFRP surfaces was in some cases indicated in the NIR spectra, in other cases not. This mean, not all of the relevant contamination residues could be identified with this NIR monitoring device
- Contamination residues, which were not detectable on CFRP surfaces, were detectable on metal reference samples, dipped with the some contamination. This mean, that the tested NIR reflection technique depend to a high degree on the substrate and on the surface reflection conditions
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- Aerosol Wetting

A further possible on-line monitoring method is the aerosol wetting test, developed by IFAM [5]. Depending on the surface energy liquids create droplets with different diameter on CFRP surfaces, due to remaining surface contaminations and due to the status of surface treatment. The drop size is the basic evaluation value of the aerosol wetting test. Water droplets with small diameters in the range of about 0,1 to 0,3 mm are sprayed on the CFRP surfaces. The wetting behaviour can be characterised by the mean droplet size and the droplet size distribution. Images of the surface are taken by a camera and evaluated with a software programme.

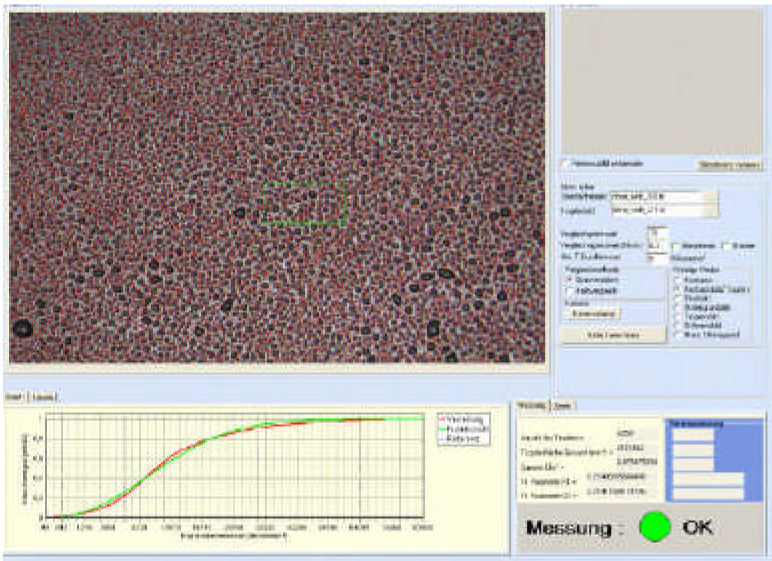

Fig. 10 Screenshot of the droplet size distribution on the CFRP surface (image above) and the droplet diameter distribution graph (below), [6]

Aerosol wetting showed better results in terms of surface sensitiveness after different CFRP treatment levels compared to the NIR on-line monitoring device:

- The aerosol wetting test is surface sensitive enough to detect surface contaminants on CFRP surfaces and effects of plasma treatment on CFRP surfaces
- So called thresholds of the mean droplet diameters are depend on topography and surface chemistry. The variances of the threshold values are still high. The accuracy of the threshold values have to be improved by better statistics and by application of mobile aerosol wetting tests

Based on these fundamentals a mobile aerosol wetting concept is under development for integration in industrial bonding applications [7].

Fig. 10: Illustration of mobile aerosol wetting on curved FRP parts [7]

The spray and imaging device of the wetting device will be mounted in the first stage of this development on a linear motor unit and later on a robot arm and moved over the part surface. The applicability of the mobile wetting device will be tested and compared with the results of already existing static wetting device.

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- MOJO (Modular Joints for composite aircraft components) EC-6th framework program
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