DETECTION OF CONTAMINANTS – A KEY ASPECT FOR COMPOSITE ADHESIVE REPAIR BONDING

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Keywords: Composite Repair, Adhesive Bonding, Contaminants, Electronic Noses

Abstract

Detection methods are necessary for the assessment of the contamination source and for the determination of the degree of cleanliness of FRP adherents for bonded repairs. Developments are focused on research results primarily for electronics noses, along with visual sensor film and laser fluorescence. All three technologies fulfill the critical requirements: they are mobile detection methods and they are sufficiently robust for the use under repair shop conditions.

1 Introduction

Repairs of severe damages for load critical fiber reinforced polymer (FRP) composite parts by adhesive bonding are not allowed in the aerospace by the airworthiness authorities EASA and FAA. One main reason for this conservative attitude is that contaminants like water, kerosene and hydraulic fluids may alter the structural performance of composite bonded structures and of the composites themselves.
Further potential contaminations of composites under service conditions are media like mineral oils, solvents, anti-icing fluids, and aircraft washing agents. A general estimation of the behavior of commercial epoxy based composites by the different contaminations is currently not possible.
Therefore, detection methods are necessary for the assessment of the contamination species and for the degree of cleanliness of FRP adherents for bonded repairs. A number of different analytical methods are principally applicable, for example spectroscopy, ellipsometry, reflectometry, wetting tests, and electronic noses.

This paper will focus first on the definition and selection of FRP contaminants under aircraft relevant service conditions. Second, the applicability of three sensing techniques is investigated.

2 Definition of contaminants

Composites are influenced by different contaminants already during the manufacturing processes and afterwards under service conditions. In Table 1 the relevant FRP contaminants are summarized. The application of the testing methods described in section 3 refers to these contaminants, which can attack FRP structures during aircraft service life.

Contaminants	In or on laminate	Volatile (during curing)	Origin
Primer, Paint	On	No	Manufacturing
Release agents Hydrocarbons, Silicones, Fluorocarbons	On	No	Manufacturing Residues
Water	In	Yes	Manufacturing, Service
Kerosene	In/On	Yes	Service
Hydraulic Fluids Skydrol	In	Remaining Residues	Service
H-515 Oil Turbine Oil	In Mostly on On (?)	Remaining Residues No No (?)	Service
Methyl Ethyl Ketone	In	Yes	Service
Anti-Icing Fluid	Probably in	Yes?	Service
Runway de-icer	In?	Yes?	Service
Aircraft washing agent	?	?	Service

Table 1: Relevant FRP contaminants during manufacturing and aircraft service life. Highlighted in yellow are 3 species with the highest probability, as identified by the end-user partners in the research project.

3 Assessment of applicable detection methods

In this section, we report on our investigations on the applicability of 3 detection methods: Visual sensor film, a laser fluorescence device, and an electronic nose.

3.1 Visual sensor film

For this application a micro porous material within a thin film transducer, which produce changes in color upon exposure to a very wide range of volatile organic compounds (VOCs) was tested. Depending on the organic compound, a limit of detection down to 5 parts per million (ppm) is achievable. The sensor layout is depicted in Figure 1. A reflective interference filter is created by positioning of a microporous dielectric material between two reflective metallic layers. A metallic mirror provides partial light reflection while allowing a fraction of incident light to travel through the microporous layer. This light is reflected back through the stack by the permeable metallic mirror and interferes optically with the light reflected off of the partial mirror [1].

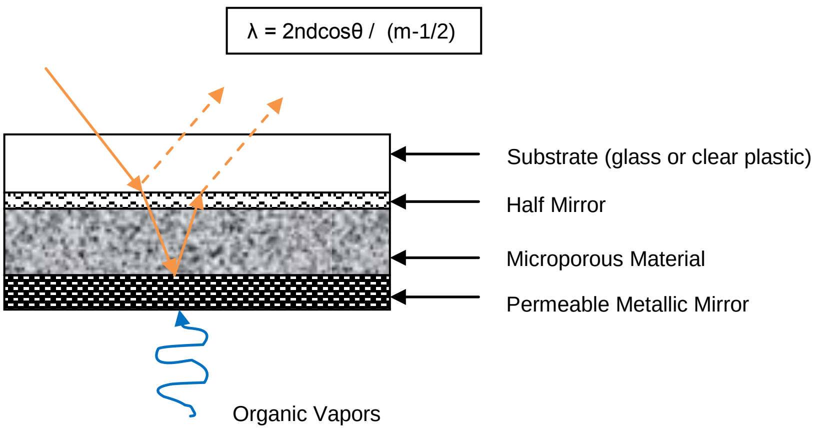

Figure 1: Visual indicator layout. color λ is the wavelength of the light, n the refractive index, d the microporous dielectric thickness, θ the incident angle of light, and m is the integer order number of the reflected peak [1].

For the tests two different epoxy laminates have been selected: one is a toughened prepreg resin, the other is an infusion resin. Both laminates have been contaminated under defined hot wet conditions, in kerosene, and in a hydraulic fluid based on phosphate esters. Beside the contaminated samples, non-contaminated reference samples were tested for both toughened and infusion laminates. Each laminate sample along with the sensor film was investigated in a separate clean and sealed glass vial. Tests were performed at room temperature and at 85°C. A qualitative ranking of the test results is shown in Table 2 with larger rating values being related to larger sensor responses [2].

Sample ID	**Conditioning**	**Test Condition**	**Qualitative Rating***
Toughened EP- CFRP	Reference	85 °C	1
Infusion EP-CFRP	Reference	85 °C	2
Toughened EP- CFRP	Hydraulic Fluid	Ambient	4
Infusion EP-CFRP	Hydraulic Fluid	Ambient	4
Toughened EP- CFRP	Kerosene	85 °C	3
Infusion EP-CFRP	Kerosene	85 °C	4
Toughened EP- CFRP	Humidity	85 °C	3
Infusion EP-CFRP	Humidity	85 °C	3
Aluminum	Packaging	85° C	0

* Wavelength shifts: 0 = 0 nm, 1 = 1-2 nm; 2 = 10-15 nm, 3 = 20-30 nm, 4 = 50-120 nm.

Table 2: Qualitative sensitivity rating of the film sensor, tested on different contaminated CFRP samples.

The results show that all tested FRP contaminations humidity, hydraulic fluid and kerosene) cause different wavelength changes up to 60 nm and lead to visually detectable color changes of the microporous film sensor. The highest sensitivity was measured for the hydraulic fluid. For kerosene and humidity, the samples had to be heated up to 85°C to increase the sensitivity. However, the wavelength shifts for the kerosene- and humidity-contaminated samples were sufficient for a clear differentiation from the reference samples. To exclude an influence of the aluminum packaging material, also the aluminum was tested separately and showed no wavelength shift.

3.2 Laser fluorescence detector

Fluorescence is the process of light emission from the substance to be measured, which is triggered by the absorption of exciting radiation. The fluorescence that is then emitted immediately after excitation of the molecule can be measured accurately even for very low concentrations [3].

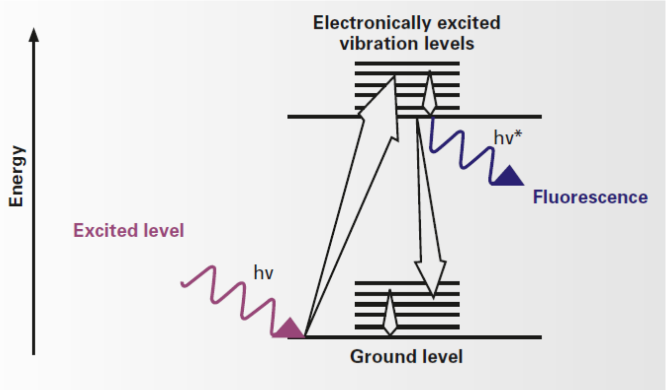

Figure 2: Principal sketch showing the process of fluorescence emission [3].

The measurement principle is based on the time-integrated laser-induced fluorescence detection [LIF(t)]. An in-situ fluorescence signal is induced in the process medium through ultrashort laser light pulses and detected with a fast single photon-counting photomultiplier unit. Signal evaluation is performed as intensity readings as well in transient analysis as a function of time (signal decay) [4].

The tested laser fluorescence detector is part of a process analyzer. Eight different positions on the CFRP surfaces were measured in a defined distance with a laser stimulation wave length of 266 nm. The test time of each measuring spot is on the order of seconds. The fluorescence signals of the samples were measured in the wavelength range of 300-400 nm. The test results are determined as relative fluorescence intensity counts, which were determined for hydraulic fluid and kerosene contaminated composite samples as well as for the reference samples. Differences in the relative fluorescence intensities between the CFRP samples are detectable. As shown in Figure 3, the residues of contaminants on the FRP surfaces are clearly detectable, variations in the “error bars” may be caused by the spatial resolution of contaminant inhomogeneity´s on the surface

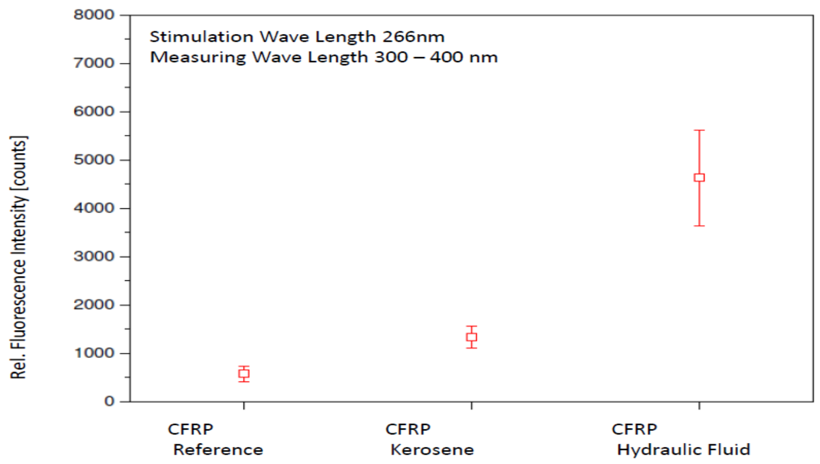

Figure 3: Evaluation of relative fluorescence intensity of different contaminated CFRP samples in comparison with the reference sample [5].

3.3 Electronic noses

In a German research program sponsored by the Federal Ministry of Economics and Technology [6], the suitability of so-called electronic noses was tested for the mentioned contaminants listed in Table 1. In this case the electronic nose consisted of a set of metal-oxide gas sensor arrays along with a humidity sensor. When gaseous contaminations are passing the sensors, they induce a change in their electrical resistance. The different responses of the metal-oxide sensors are evaluated via principle component analysis (PCA) [7]. With such a sensor array different contaminants on the FRP adherent surface can be qualitatively and quantitatively determined. The formation of gaseous contaminant species is generated by a specific heating device. Figure 4 illustrates the principal application of an electronic nose sensor array for the analysis on the FRP surface as well as for the analysis of FRP milling dust, already during milling operation [8].

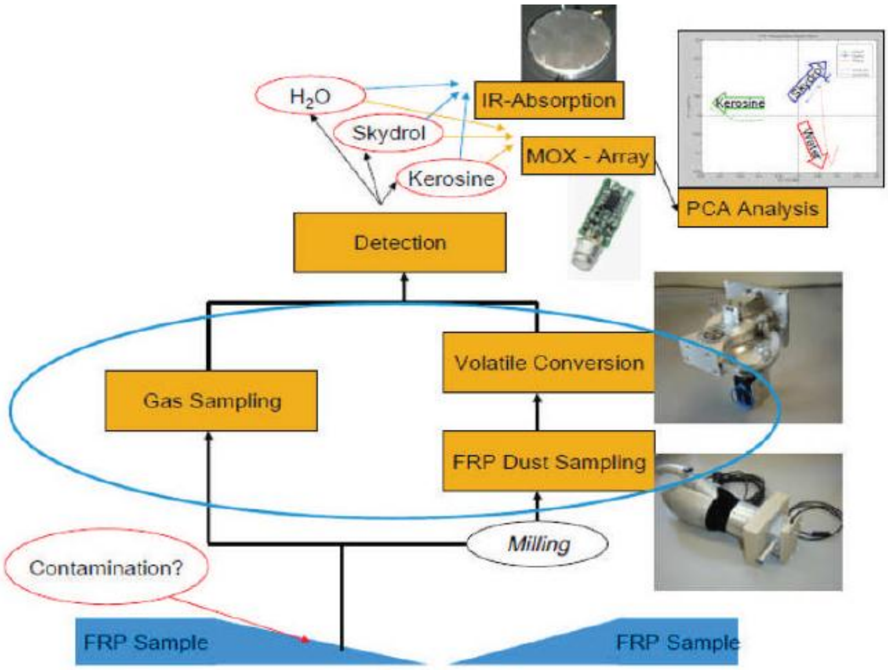

Figure 4: Principal application scenarios of an electronic nose detector, here in combination with an IR detector for the determination of CFRP contaminants, a) already during FRP milling; b) on the final milled surface [8].

For the electronic nose tests, the same two different epoxy laminates and three contaminants humidity, kerosene, and a hydraulic fluid (highlighted in Table 1) have been selected. Two probe sampling methods are possible: First, the dust generated during the FRP milling process may be analyzed. Second, contaminations species may be desorbed directly from the FRP surface.

Application for FRP milling dust

Here, particulate probes were collected during the milling process by suction of the milling dust through a filter pad. In a second step the filter pad with the particle dust on top was placed above the heating device. The contaminants are converted into the gas phase via thermal desorption, and the gaseous analytes are transported to the MOX sensor array for detection via a carrier gas stream. Figure 5 outlines this detection approach.

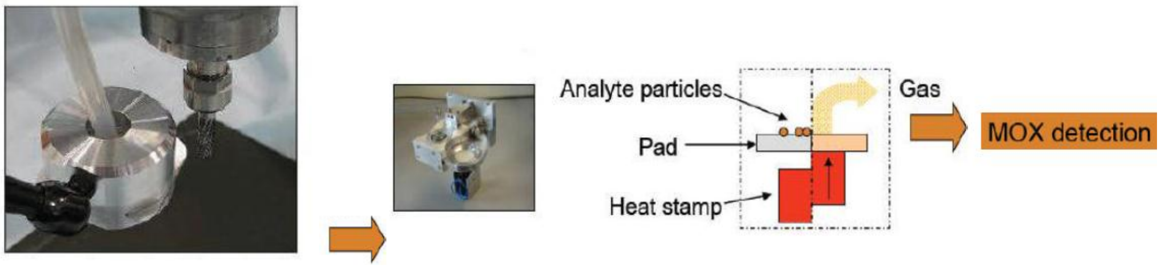

Figure 5: Electronic nose set up for the detection of CFRP milling dust [8].

Application on the FRP surface

In this case a temperature controlled heating device will be placed directly on the FRP surface. Contaminants are thermally desorbed from the probe, and passed to the MOX sensor array similarly to the method outlined above. Figure 6 shows the layout of this detection system.

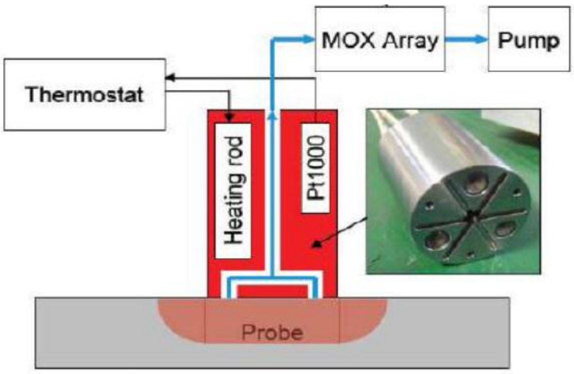

Figure 6: Electronic nose set up for the detection on the CFRP surface [8].

It could be demonstrated experimentally that electronic noses are generally sensitive to a variety of different contaminants relevant for an aircraft service life. This was demonstrated first by placing a liquid contaminant droplet on the FRP surface, sampling in the surface method described above and analyzing the MOX responses. In a second step the artificially contaminated probes described above, along with the corresponding reference samples, were analyzed. Both milling dust and surface sampling methods were applied. In Figure 7 experimental results are presented. On the left, responses of two sensors are plotted for the 4 probe types, using the surface desorption method. It can be seen that significant sensor responses are achieved. Due to the absorption of ambient humidity even in the reference sample, a response is induced. However, in the additional presence of the contaminants, the sensor responses are sufficiently different from the reference measurements, allowing for successful discrimination using PCA. This is demonstrated on the right side of Figure 7, showing a plot of the three most significant principal components, clearly separating the four probe measurements.

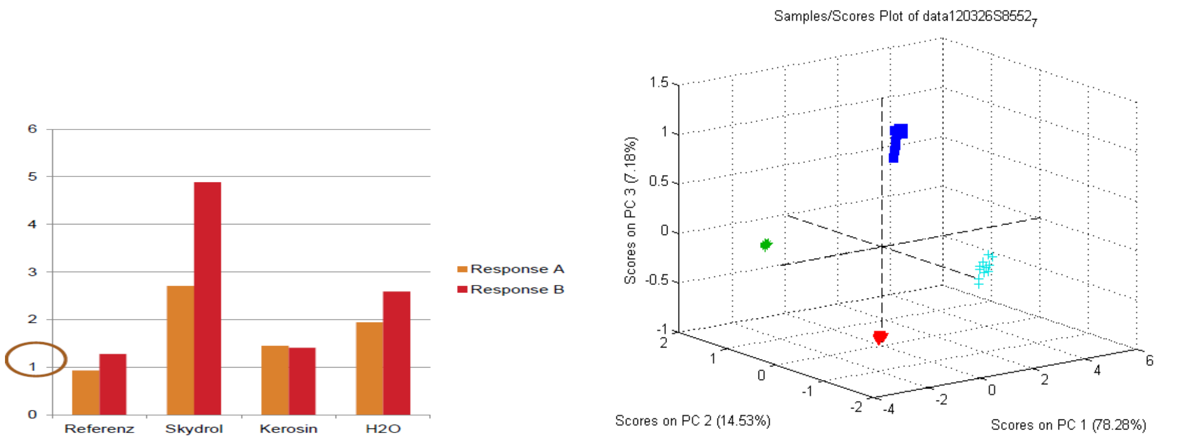

Figure 7: (Left) Responses of two different MOX sensors, tested on different contaminated epoxy CFRP laminates [9]; (right) PCA of the array responses for the four contaminants reference (red), humidity (green), kerosene (blue), and hydraulic fluid (teal).

4 Summary

In the presented results we identified the potential contaminations species critical for the adhesive bonding in FRP repairs. Our experimental results for three detection methods, visual sensor film, a laser fluorescence device, and an electronic nose, demonstrate their suitability for the development of a detection system. With such a system, contaminations on the FRP surface could be detected and identified. This allows for the implementation of countermeasures when contaminants are present, and it can confirm a contaminations-free surface to ensure a solid and safe adhesive bond.

Acknowledgement

The authors kindly acknowledge support for these results from the LuFo IV-2 research project "Rapid Repair", supported by the German Federal Ministry of Economics and Technology.

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