FTIR SPECTROSCOPY AS A NONDESTRUCTIVE TESTING METHOD FOR CFRP SURFACES IN AEROSPACE

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Abstract. Lightweight design is a key enabler to improve products in aerospace. Carbon fibre reinforced plastic (CFRP) is a material to meet the requirements for lightweight design, for example due to its specific strength. The favoured joining technology for CFRP parts is adhesive bonding. The bond strength is strongly influenced by the surface properties. Therefore there is a need for nondestructive testing (NDT) methods to characterise the CFRP surface properties.

In this work it was investigated, if Fourier Transform Infrared (FTIR) spectroscopy is a suitable NDT technology to characterize CFRP surfaces. A commercial handheld FTIR spectrometer was used. The information in the resulting FTIR spectra appears in different spectral regions, which leads to a complex interpretation of the spectra. For this reason, the collected spectra were used to build regression models with the Partial Least Squares (PLS) algorithm in order to predict material properties from the FTIR spectra.

The focus of the presented investigations is the detection of thermal damage, the detection of contaminations, such as hydraulic fluids, and the measurement of moisture uptake within the laminate. Especially for thermal damage it could be shown that there is a good prediction quality on the interlaminar shear strength (ILSS). Furthermore the moisture uptake at homogenously saturated samples could be successfully quantified and an indicator for samples stored in a hydraulic fluid could be identified.

Introduction

Carbon fibre reinforced plastic (CFRP) materials allow new opportunities in lightweight design, but they are also afflicted by a lack of nondestructive testing (NDT) methods. For traditional materials, such as metals other joining technologies are available. Especially for bonding of CFRP there is a need for NDT methods to characterise the surface before bonding for example with respect to surface contaminations [1]. In the European funded project ENCOMB several needs for the detection of surface properties before bonding have been identified and their influence on the bond strength has been investigated [2].

In this study the potential of FTIR spectroscopy as a nondestructive testing method is evaluated for the scenarios thermal degradation, hydraulic oil contamination and moisture uptake into the laminate.

In FTIR spectroscopy molecules close to the surface are vibrationally excited by infrared light. This excitement results in a partial absorption of the infrared radiation by the molecules. The absorbed infrared radiation is missing in the received infrared spectra and gives information about the chemical composition of the surface. The measured FTIR spectra have complex structures which can be interpreted by a Partial Least Squares (PLS) algorithm. The PLS algorithm correlates material properties with significant features in the IR-spectra. The advantage of this evaluation algorithm is that it can be interpreted qualitatively and quantitatively. One disadvantage of the algorithm is that the interpretation is only mathematically based what may lead to misinterpretation.

The main focus of this work is to provide a reliable tool for the prediction of material properties based on surface IR-spectra of samples with unknown history.

1 Experimental

1.1 Material

The trials for the detection of thermal degradation were performed on a CFRP with an IMA carbon fibre and an epoxy based RTM 6 resin both provided by Hexcel Corporation. The surface was covered with a fiberglass Richmond E 5555 peel ply. The unidirectional lay-up was build up with 16 layers which led in a vacuum assisted infusion process to a laminate thickness of about 2 mm.

For the detection of hydraulic fluid contaminations, Skydrol® 500B-4 was used. For the CFRP samples the epoxy based prepreg 8552/IM7 by Hexcel was used in a unidirectional lay up of 12 plys with an overall thickness of about 1.5 mm. The surface was covered with the peel ply Burlington Superlease Blue.

As samples for moisture uptake a unidirectional lay up of 16 plys of prepreg 8552/IM7, covered with the Richmond E 5555 peel ply was used, resulting in a thickness of about 2 mm. The curing of all samples in the autoclave was performed according to the manufacturer´s recommendation.

1.2 FTIR Spectroscopy

The task of this work is to proof the capabilities of a handheld FTIR spectrometer Exoscan 4100 by Agilent Incorporation.

The device measures in the mid-IR range from 4000 - 650 cm^{-1} and uses a temperature-stabilized DTGS detector. It weighs 3.18 kg.

For all FTIR measurements the parameters were kept constant. All measurements were performed in diffuse reflection mode. The resolution was set to 8 cm^{-1} and the number of scans per measurement was set to 64.

1.3 Mechanical testing

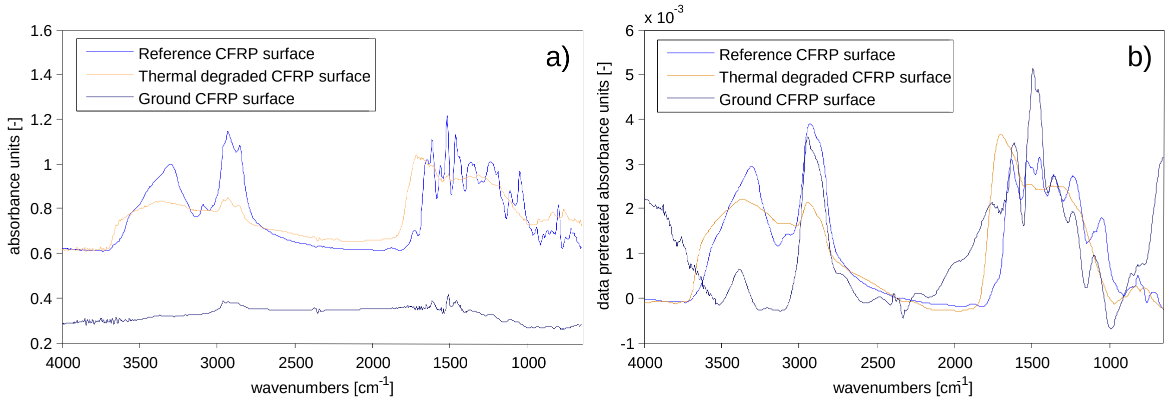
To characterise the mechanical properties the interlaminar shear strength (ILSS) was determined with the multi-purpose testing machine Instron 5566 in accordance to DIN EN 2565. The specimen dimension was set to 20x10x2 mm^3. Testing was performed on five samples for each set of parameters.

2 Contamination scenarios

2.1 Thermal degradation

For the evaluation of thermal degradation with IR-Spectroscopy it is important to consider the surface condition. After manufacturing the CFRP surface is rich in resin above the first fibre layer. When the degradation occurs in an environment with oxygen, a thermo-oxidative degradation takes place. This is clearly visible in the IR spectra. A strong band appears in Pic. 1 between 1670 - 1820 cm^{-1} which is characteristic for carbonyl groups.

In case of an overheating of a CFRP part there is the need to identify the affected area for repair. In order to inspect the CFRP the paint has to be removed by grinding. Through grinding the thickness of matrix above the top carbon fibre layer is reduced and due to a higher amount of carbon fibres in the measuring path more IR-light is absorbed. Therefore the measured reflected IR intensity is much lower than for a measurement on a resin rich surface as it is the case for not ground surfaces (reference and thermal degraded CFRP surface) (Pic. 1).



Pic. 1. IR Spectra of a reference, a thermally degraded CFRP and a thermally degraded surface after grinding. For the degradation the samples were stored in an air circulating oven at 280 °C for 1 hour. a) original data b) pretreated data.

The different surface conditions result in different IR-spectra. In order to compare the spectra a data pretreatment is used. Pic. 1 b) depicts the same spectra as Pic. 1 a) after a data pretreatment. For the data pretreatment a baseline correction with an automatic weighted least square algorithm with an order of 2 was used. Subsequently a Savitsky-Golay smoothing with a window of 15 points was used. Finally a normalisation over the area was applied. Even after a data pretreatment the variance between the spectra is quite high.

It has to be investigated if the different surface conditions have an influence on the prediction by the PLS algorithm.

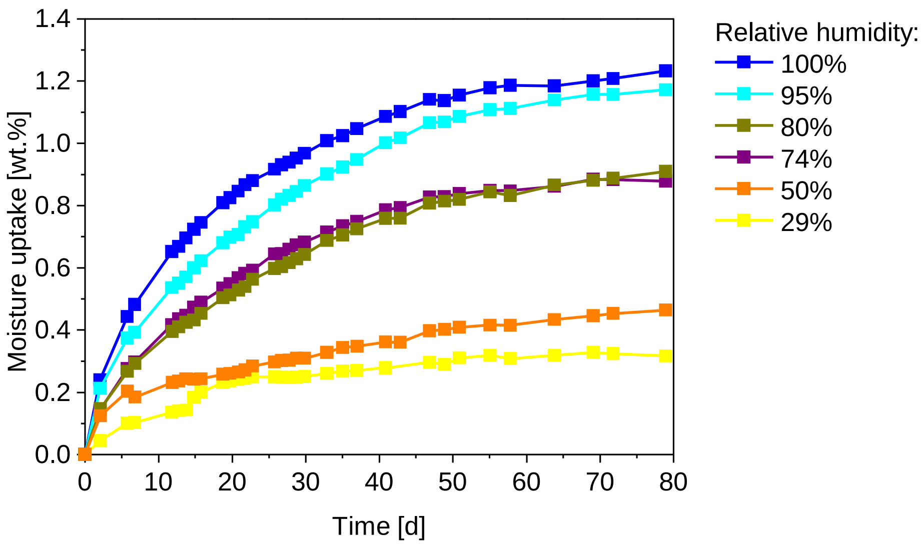
Samples were thermally degradated in an air circulating oven at 220°C - 300 °C for up to 8 hours as given in Table 1.

2.2 Moisture uptake

Cured CFRP laminates were stored at different relative humidity conditions. Pic. 2 presents the moisture uptake in dependence of the time at different relative humidity levels at 70 °C. To create different relative humidity conditions the samples were stored in closed boxes with different supersaturated saline solutions (K_2SO_4 RH 95%, KCl RH 80%, NaCl RH 74%, NaBr RH 50 %, $MgCl_2$ RH 29 %) in a closed vessel.

To determine the moisture uptake the weight increase of the samples was measured. The main problem for the detection of humidity is that diffusion takes place. This means that with a gravimetric method it is only possible to measure the average uptake. Therefore there is no possibility to measure the distribution of moisture inside the laminate. This can be a problem for the measurement with FTIR spectroscopy, because this method only allows to measure the matrix conditions on top of the first fibre layer.

The goal of these investigations is to only determine water uptake of homogeneously saturated samples. The problem of diffusion is not adressed yet.



Pic. 2. Moisture uptake into the CFRP laminates in dependence of different relative humidity levels and time at 70 °C.

2.3 Hydraulic fluid

Hydraulic fluids are used for several applications in aerospace such as flight controls, landing gear or breaking systems. After a leakage the phosphate ester based hydraulic fluid Skydrol® 500B-4 can get in contact with water and at elevated temperatures phosphoric acid is formed [3]. The phosphoric acid can etch the CFRP surface [2].

In order to simulate this contamination scenario Skydrol® 500B-4 was mixed in the ratio 50:50 with de-mineralised water and stirred for 14 days at 70 °C. Afterwards the water phase was separated with a separating funnel. The pH value of the water phase was about 2 and solutions of pH 3 and 4 were prepared by adding demineralised water. The CFRP samples were stored in the solutions for 30 days. This procedure is described by Markatos [2]. After storage the samples were cleaned with a dry cloth by wiping the surface and then measured by FTIR spectroscopy.

3 Results and discussion

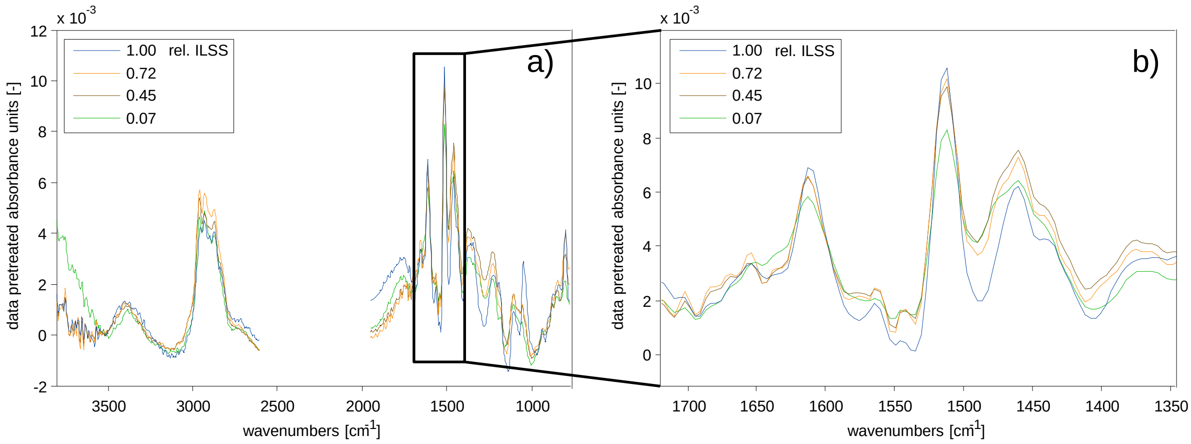
3.1 Thermal degradation

The normalized ILSS values in Table 1 show that with increasing time and temperature the ILSS value decreases. Furthermore the ILSS test shows some unreliable values especially for higher temperatures and longer periods of storage in the oven. For example after 4h at 260 °C and 1.5 h at 280 °C the ILSS values are increasing compared to the time steps before.

Table 1. Normalized ILSS values of thermally degraded CFRP samples in dependence of time and temperature.

Temperature/ Time	25 °C	220 °C	240 °C	260 °C	280 °C	300 °C
0h	1.00	-	-	-	-	-
0.5h	-	-	0.92	0.87	0.57	0.10
0.75h	-	0.95	-	0.86	-	0.07
1h	-	0.97	0.94	0.83	0.17	0.09
1.5h	-	-	0.94	-	0.28	-
2h	-	1.00	0.89	0.56	0.05	-
3h	-	1.00	-	0.45	-	-
4h	-	0.96	0.89	0.66	-	-
6h	-	-	0.88	-	-	-
8h	-	0.92	0.72	0.16	-	-

The IR spectra consist of 900 measurement points between 4000 cm^{-1} and 651 cm^{-1}. For the chemometric evaluation of the spectra the wavenumbers above 3800 cm^{-1}, between 2603 cm^{-1} and 1951 cm^{-1} and below 774 cm^{-1} were not taken into account, as it is depicted in Pic. 3 (a). These spectral ranges do not provide significant information concerning the expected changes and would therefore increase the noise in the data. The spectra in picture 3 (b) show that with an increasing thermal degradation of the ground surface and a decreasing ILSS value the IR band intensity at 1510 cm^{-1} (which is characteristic for the degradation of the epoxy resin) decreases [4].

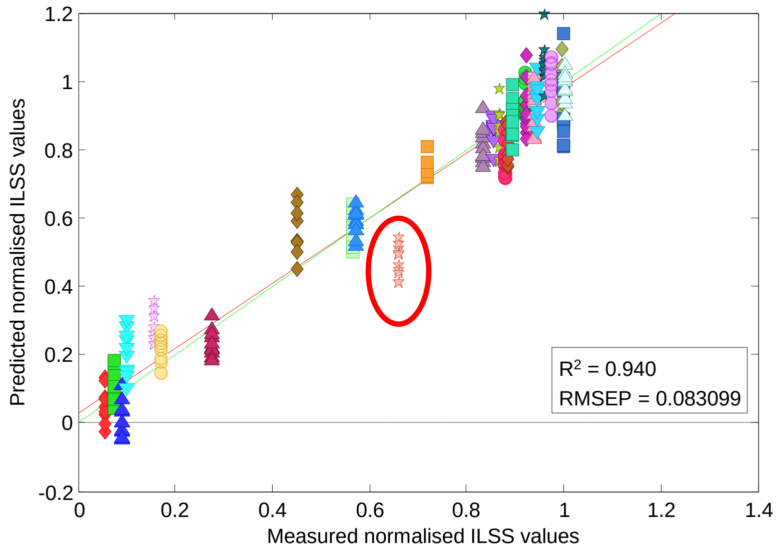


Pic. 3. Spectra of thermally degraded CFRP surfaces after grinding in relation to the ILSS value.

In order to quantitatively evaluate a thermal degradation the IR spectra were used to predict ILSS values with a PLS algorithm.

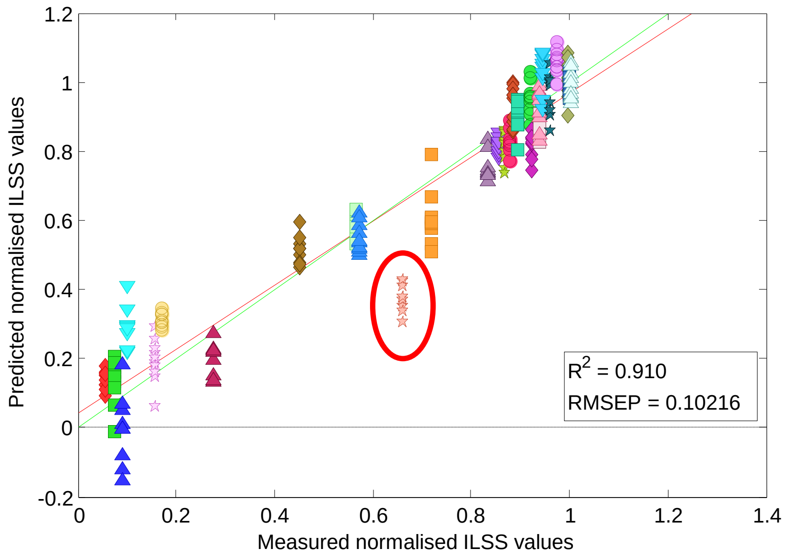
For calibration and validation 10 spectra were used. Pic. 4 shows the prediction of the ILSS values from the IR spectra. The predicted values show a good correlation and give the opportunity to define thresholds for a decision whether a part is still useable or has to be repaired.

The prediction quality of the ILSS values is highly depending on the measuring accuracy of the ILSS value. In Table 1 the ILSS value for 4 h at 260 °C show an unreliable ILSS value that is therefore badly predicted by the PLS algorithm (red circle (Pic. 4)).



Pic. 4. Prediction of normalised ILSS values from IR spectra recorded on ground thermally degraded RTM 6 CFRP samples. The red circle indicates poorly predicted ILSS values due to an unreliable ILSS value from the mechanical testing at 260 °C for 4 hours.

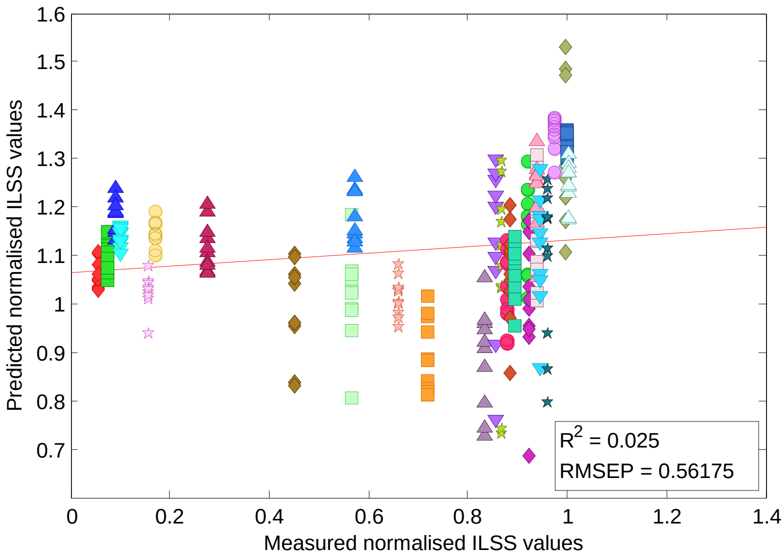
When non-ground surfaces are analysed (Pic. 5) the same outlier is visible. The root mean square error of the prediction (RMSEP) received for the ground surface (0.08) is slightly better compared to the non-ground surface (0.10).



Pic. 5. Prediction of normalised ILSS values from IR spectra recorded on the surface of thermal-oxidative degraded RTM 6 CFRP samples. The red circle indicates poorly predicted ILSS values due to an unreliable ILSS value from the mechanical testing at 260 °C for 4 hours.

In order to prove if there is a risk to misinterpret the prediction of residual mechanical strength a calibration for non-ground specimen was established and applied to ground specimens. The results in Pic. 6 show that it is not possible to make predictions in this way.

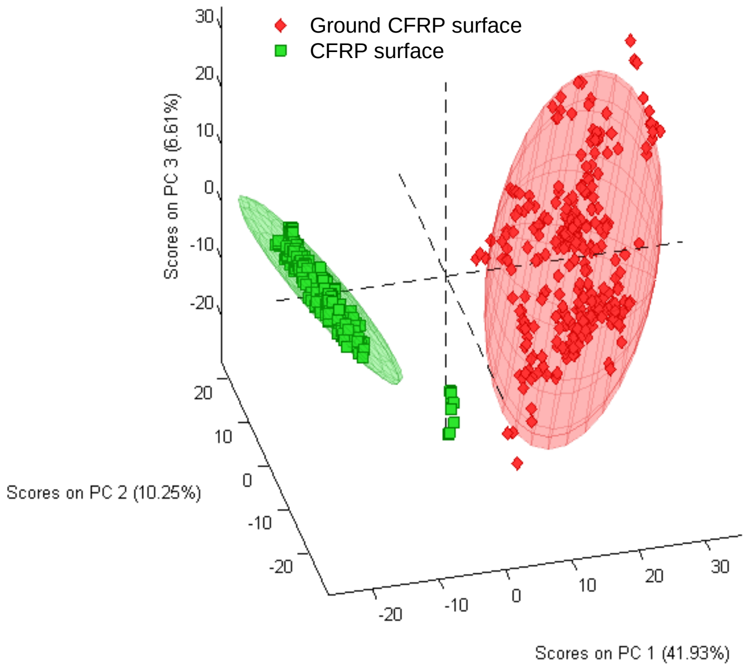
Furthermore the ILSS values are predicted to higher values as they were measured. This leads to a high risk of misinterpretation.



Pic. 6. Prediction of normalised ILSS values from IR spectra recorded on the surface of thermally degraded RTM 6 CFRP samples. The calibration for this prediction was made with spectra on a surface without grinding. The validation was done with spectra collected on ground CFRP surfaces after thermal degradation.

It is investigated if there is a possibility to differentiate the surface status (ground or not) with a Principal Component Analysis (PCA) algorithm. Pic. 7 shows that the different surfaces can be distinguished.

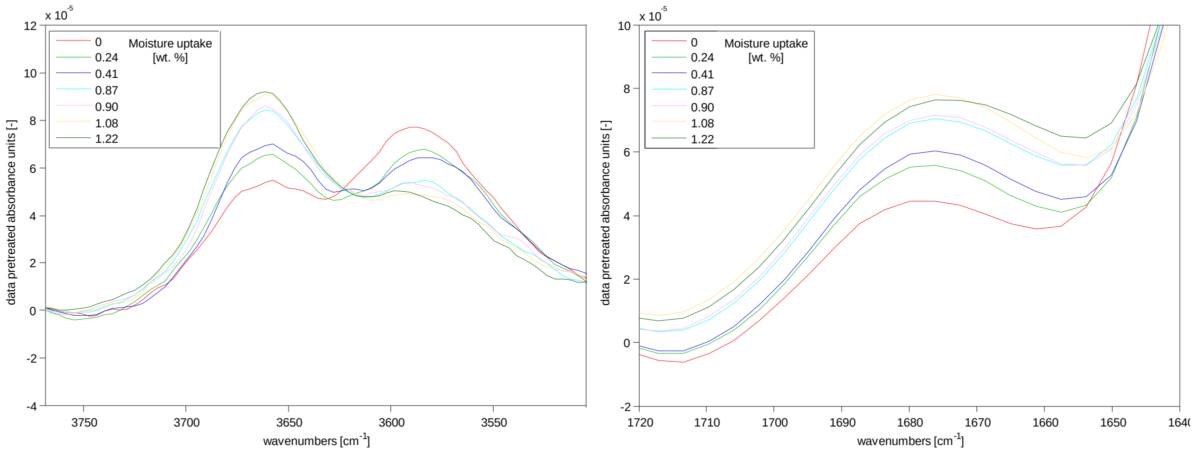
This gives the opportunity to combine different algorithms, which first predict the surface status and in a second step predict the properties of the surface status concerning the thermal degradation.



Pic. 7. PCA analysis of the spectra collected on thermally degraded CFRP surfaces and thermally degraded CFRP surfaces after grinding. The different surface conditions can be distinguished from each other.

3.2 Moisture uptake

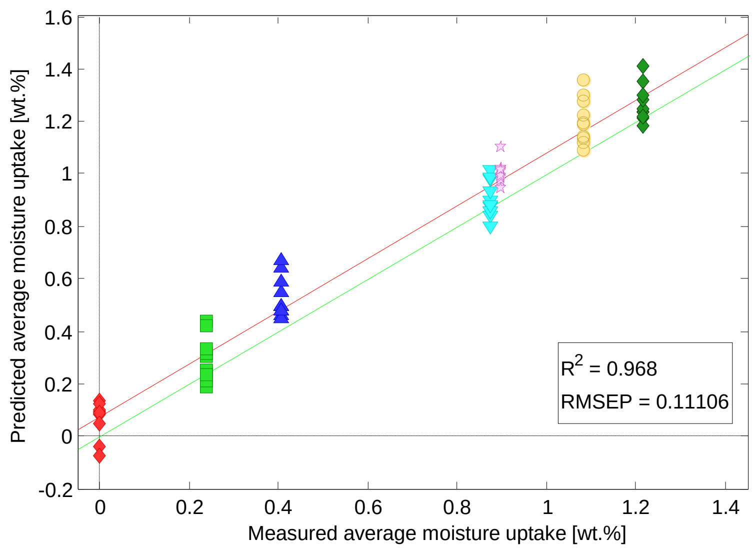
Pic. 8 shows sections of IR-spectra recorded on CFRP samples differently saturated with moisture. The IR spectra were pretreated with a baseline correction, normalization of the area and the 1st derivative Savitsky- Golay with a window of 15 points.



Pic. 8. Sections of spectra (which are characteristic for moisture uptake) recorded for differently saturated moisture CFRP samples. The moisture uptake was determined gravimetrically.

The intensity of IR-bands characteristic for water at 3660 cm^{-1} and 1670 cm^{-1} shows a good correlation with the amount of moisture uptake. Pic. 9 shows the result for the prediction of the average moisture uptake with a PLS algorithm. The mean values give a good prediction quality with a small RMSEP (0.11) and would be sufficient for predictions. This may allow the use for a real application.

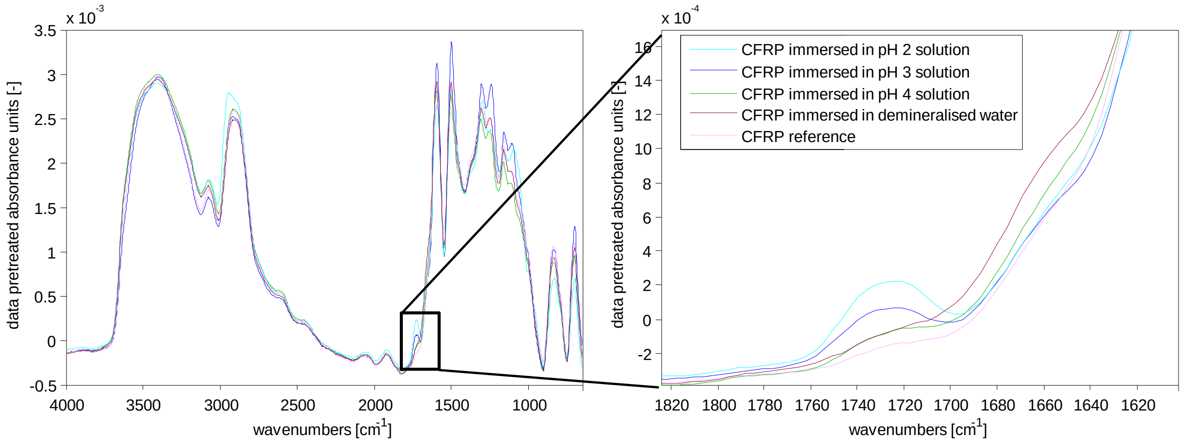
Further investigations are necessary to prevent misinterpretations due to diffusion processes inside the laminate, as it is considered in the contamination scenario for moisture uptake.



Pic. 9. Prediction of average moisture uptake into the CFRP laminate from IR spectra on the surface with a PLS algorithm.

3.3 Hydraulic fluid detection

After exposure of the CFRP samples in the liquid acid phase of the hydraulic oil an absorption band in the region between 1760 cm^{-1} and 1700 cm^{-1} appears. The band intensity in Pic. 10 correlates with the pH value. This gives the opportunity to develop algorithms that can predict the resulting bond strength of a Skydrol® 500B-4 contaminated CFRP surface. Furthermore it can be verified that the changes in the FTIR region between 1760 cm^{-1} and 1700 cm^{-1} are not caused by water uptake (CFRP immersed in demineralised water), as water bands do not appear in this spectral region. Further investigations are necessary to identify the origin of the changes in the IR spectra.



Pic. 10. Pretreated spectra of different 8552/IM7 CFRP samples stored in the acid phase of Skydrol® 500B-4, demineralised water and an untreated reference.

4. Summary and Outlook

FTIR spectroscopy has proven to be a valuable tool for a significant characterisation of CFRP surfaces. The benefit of the FTIR spectrometer used within the investigations is that it is handheld and has a high technical readiness level. It is therefore suitable to be used in a manufacturing or a repair environment. It has been proven in this work that thermal degradation can be measured with this technology quite accurate. It has been shown that there is a strong influence on the prediction by the surface condition. But it is possible to differentiate the different surface status by a PCA algorithm. The first steps to quantify the humidity uptake of CFRP laminates can be successfully done. Further investigations are necessary to solve the problem of measuring the distribution of moisture inside the laminate. For the detection of hydraulic fluids it was shown that there is a region that indicates the storage of the CFRP in the acid water solution of the hydraulic fluid.
Based on the results of these investigations the FTIR technology seems to be promising as a nondestructive testing method in aerospace for the scenarios thermal degradation, moisture uptake and hydraulic fluid contamination.

References

[1] Ehrhart B, Bockenheimer C, Chobaut N, Gendard A, Sarambé M, Valeske B. Preliminary Tests for the Development of New NDT Techniques for the Quality of Adhesive Bond Assessment: DGZfP-Jahrestagung: 2011.

[2] Markatos DN, Tserpes KI, Rau E, Markus S, Ehrhart B, Pantelakis S. The effects of manufacturing-induced and in-service related bonding quality reduction on the mode-I fracture toughness of composite bonded joints for aeronautical use. Composites Part B: Engineering: 2013;45(1):556–64.

[3] Helwig A, Maier K, Müller G, Bley T, Steffensky J, Mannebach H. An Optoelectronic Monitoring System for Aviation Hydraulic Fluids. Procedia Engineering: 2015;120:233–6.

[4] Eibl S, Wolfrum J. Prospects to separately estimate temperature and duration of a thermal pre-load on a polymer matrix composite. Journal of Composite Materials: 2013; 47(24): 3011-3025.