MOBILE NON-DESTRUCTIVE TESTING METHODS FOR SURFACE CHARACTERIZATION OF CFRP IN AEROSPACE

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Abstract

This paper presents Non-Destructive Testing (NDT) techniques for detecting thermal degradation of the polymer matrix and silicone based release agent residues on Carbon Fiber Reinforced Plastic (CFRP) surfaces. Thermal degradation can be successfully determined by mobile Fourier Transform Infrared spectroscopy (FTIR). The presence of oxygen during thermal degradation strongly influences the chemical changes of the matrix and therefore different degradation scenarios are investigated. For a differentiation of the multiple scenarios a Partial Least Squares Discriminant Analysis (PLS-DA) algorithm is used. Mobile X-Ray Fluorescence spectroscopy (XRF) is successfully applied to determine residues of silicone based release agents on the CFRP surface, which lead to problems for adhesive bonding or coating.

Additionally, a novel approach is investigated by combining a laser treatment of the surface with an analysis of the evaporated gas phase by a Gas Chromatograph coupled to an Ion Mobility Spectrometer (GC-IMS).

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1. Introduction

Lightweight materials in aerospace offer a high potential for saving fuel and protecting the environment. Carbon Fiber Reinforced Plastic (CFRP) materials meet the requirements for a lightweight design due to their specific mechanical properties. With the increasing usage of CFRP in aviation there is also an increasing demand for suitable Non-Destructive Testing (NDT) techniques. Currently there is a lack of available NDT technologies to characterize CFRP surfaces. In order to fill this gap, these investigations focus on technologies for the detection of thermal damage and silicone based release agents.

Fourier Transform Infrared spectroscopy (FTIR) is a technology that characterises the chemical condition of the CFRP Matrix on the surface [1] and is therefore predestined for the evaluation of thermal degradation processes. Oxidation processes during thermal degradation contribute intense to changes in the FTIR spectra. The resulting chemical constitution of the damaged material depends therefore strongly on the surrounding atmosphere (O_2 rich) and FTIR analysis is capable to differentiate these conditions. In the field of repair the main interest is to localise areas of reduced mechanical stability due to thermal degradation. After removing paint and primer the measurements are conducted on ground CFRP surfaces. Therefore, three different scenarios exist and are investigated in this work: Thermal degradation, thermal-oxidative degradation and a ground surface after a thermal degradation.

Another application that points at the lack of available NDT technologies is the detection of silicone based release agent residues. During production such residues may still cover the surface after demoulding, causing severe problems for bonding or coating [2–5], since bond quality depends on the condition of the joined surfaces. NDT methods are necessary as part of a quality assurance system, which allows measuring these very thin residue layers on the surface. In this work results are shown for the detection of silicones by Fourier Transform Infrared spectroscopy (FTIR) and X-ray fluorescence spectroscopy (XRF). Also a new approach is introduced based on a combination of a laser treatment of the surface and a Gas Chromatograph coupled to an Ion Mobility Spectrometer (GC-IMS).

2. Material

All tests were performed with the CFRP HexPly ® 8552/IM7 by Hexcel Corporation. A peel ply Richmond E 5555 from Richmond Aircraft Products Inc. was used to cover the surface during curing. In order to create samples without access to air, the peel ply was removed after the thermal loading. The samples were thermally degraded at temperatures ranging from 220°C to 300°C over a duration of 0.5 h to 240 h. The peel ply for these samples acted as a protection layer. For all other samples the peel ply was removed immediately after curing and cutting.

For the detection of silicone based release agents, samples were prepared with an A 6200 release foil from Richmond Aircraft Products Inc., whose separating effect is based on Fluor compounds. After curing the test panel was cut into 60 x 60 x 2 mm^3 coupons. The specimens were dip coated in different solutions of hexane and the silicone based release agent Marbocote TRE45 ECO from Marbo America Inc in the wt.% ratios of 99:1, 95:5, 20:80, 0:100 in order to deposit certain amounts of silicone on the surface. After dip coating the samples were stored in a vacuum oven for 150 min at 185°C and 25 mbar in order to simulate the curing procedure. The amount of Si atoms that correspond to the elementary composition of silicones on the surface was determined by X-ray photoelectron spectroscopy (XPS) at nine different positions and the mean value was calculated. The measurements were conducted in the middle of the samples in a rectangle area of 20 x 20 mm^2. The measured mean values and standard deviations of the Si amount on the surface of the different samples resulted in 1.3± 0.1, 2.5± 0.3, 7.1± 0.9 and 20.3± 1.6 at.% Si respectively.

3. Experimental

3.1. FTIR spectroscopy

FTIR spectra were recorded with the handheld device Exoscan 4100 from Agilent Technologies Inc. in diffuse reflection. All measurements were collected in the mid IR region between 4000- 650 cm^{-1} with a resolution of 8 cm^{-1} and 64 scans. The measurements were repeated at different locations 20 times and were equally separated into a calibration and validation set. The information in the collected FTIR spectra is complex due to the fact that changes appear in different regions. Multivariate analysis is an appropriate method to quantitatively evaluate the FTIR spectra. For the evaluation the software PLS Toolbox from Eigenvector Research Inc. was used to conduct predictions with the PLS algorithm for quantification and the PLS-DA algorithm for classification.

3.2. XRF spectroscopy

The X-ray fluorescence spectra were recorded with the handheld device XL3t from Analyticon Instruments GmbH. The measuring time was set to 90 seconds. For the evaluation the Si peak area at 1.75 keV was analysed. The measurements were repeated 5 times at different positions.

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3.3. Laser treatment coupled with GC-IMS

The technique is based on cleaning the surface by the laser Avia 266-3 from Coherent Inc. (266 nm, pulse width below 20 ns). The aim was to detect the amount of silicones, which are desorbed from the surface during the laser cleaning process. For this reason a desorber device was developed to gather the evaporated material and transfer it to a Gas Chromatograph coupled to an Ion Mobility Spectrometer (GC-IMS) from the company G.A.S. GmbH.

3.4. Mechanical testing

To quantitatively determine a value for the degree of thermal degradation, the interlaminar shear strength (ILSS) was measured. The tests were performed on 20 x 10 x 2 mm^3 dimensioned samples in the multi-purpose testing machine Instron 5566 in accordance to DIN EN 2565. The tests were repeated for five samples. Even though outliers were neglected, the mean ILSS value was determined from at least three measurements.

4. Results and discussion

4.1. Thermal degradation

For all three discussed degradation scenarios, increasing thermal degradation due to high temperatures and long thermal loads is indicated by a decrease of residual ILS strength. In Table 1 the interlaminar shear strength for „thermal oxidative degradation" is presented. Due to high variance some ILSS values can be recognized which do not fit into the trend (e.g. lower ILSS value after a thermal degradation at 240°C for 2 h than for 4 h and 8 h).

Table 1. Relative residual ILSS for the „thermal oxidative degradaded" samples.

Res. ILSS	25 °C	220 °C	240 °C	260 °C	280 °C	300 °C
0 h	1.0	-	-	-	-	-
0.5 h	-	-	0.77	0.81	0.66	0.59
0.75 h	-	0.84	-	0.75	-	0.60
1 h	-	0.82	0.78	0.75	0.64	0.04
1.5 h	-	-	0.81	-	0.58	-
2 h	-	0.82	0.74	0.73	0.64	-
3 h	-	0.80	-	0.75	-	-
4 h	-	0.78	0.77	0.73	-	-
6 h	-	-	0.77	-	-	-
8 h	-	0.84	0.76	0.73	-	-
16 h	-	0.77	-	-	-	-
24 h	-	0.81	0.75	-	-	-
48 h	-	0.75	0.73	-	-	-
72 h	-	0.79	0.76	-	-	-
120 h	-	0.76	0.68	-	-	-
240 h	-	0.74	0.15	-	-	-

FTIR spectra of thermal oxidatively degraded samples show intensive bands at about 1720 cm^{-1} characteristic for the formation of carbonyl groups, which indicate reactions with oxygen [6]. The presence of this band indicated that for samples thermally loaded over 72 h, 120 h and 240 h the peel ply did not sufficiently protect the surface from reactions with oxygen. These samples were excluded for the evaluation of the scenario „thermal degradation without oxygen". The FTIR spectra exhibit some scattering, mainly caused by variations of resin thickness above the top fiber layer. To diminish

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these influences for the PLS regression the FTIR spectra were baseline corrected, area normalized and smoothed over 3 points (Savitzky-Golay). The prediction in Figure 1 for the scenario „thermal degradation without oxygen” shows a good correlation with a root mean square error of prediction (RMSEP) of 3.7% for the residual ILSS. The RMSEP of 9.6% for a „thermal oxidative degradation” is worse, the reason can be found in the ILSS values below 0.2. They do not fit into the correlation and therefore contribute to high deviations in the regression result. This means that there is a high optimization potential by using a more accurate mechanical reference method or exclude untrusty values from the calibration set.

For the prediction of a „thermal damage after grinding” a RMSEP of 8.2% can be observed, which is similar to the thermal oxidative degradation. The reason is, that in both scenarios the same ILSS values were used. Once more, the high deviation of the ILSS values has a negative influence on the regression result.

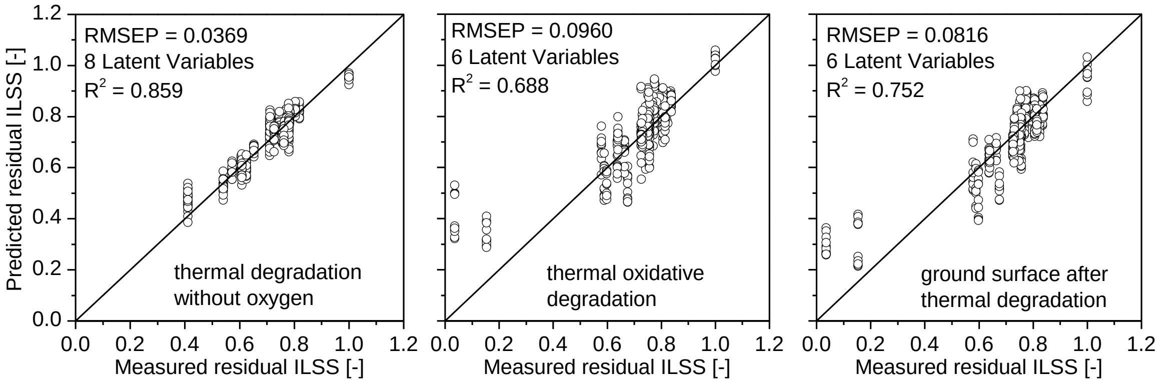

Figure 1. Measured vs. predicted normalized residual ILSS of thermally degraded CFRP surfaces, for the scenarios: „thermal degradation without oxygen”, „thermal oxidative degradation” and a „ground surface after thermal degradation”.

In order to verify, if there is a high risk for misinterpretation by using a regression model for a certain scenario and make predictions for other scenarios, all possible combinations were tested in Table 2. From this matrix it is obvious that the prediction quality is highly sensitive on the scenario. This is in accordance with former investigations on RTM 6 [7].

Therefore, a PLS-DA algorithm was used in order to differentiate the diverse scenarios automatically. The results in Table 2 show that this works perfectly. No false classifications were obtained, giving the opportunity to first determine the scenario and in a second step predict the residual ILSS.

Table 2. Results for the PLS and PLS-DA regression on the prediction of the ILSS with respect to the investigated scenario.

PLS: R^2 PLS: RMSEP PLS-DA: Accuracy		Prediction		
		Thermal degradation	Thermal oxidative degradation	Ground surface
Calibration	Thermal degradation	**R^2 0.899** **RMSEP 0.032** **100 %**	R^2 0.026 RMSEP 0.337 0 %	R^2 0.017 RMSEP 0.855 0 %
	Thermal oxidative degradation	R^2 0.177 RMSEP 0.170 0 %	**R^2 0.688** **RMSEP 0.096** **100 %**	R^2 0.064 RMSEP 1.395 0 %
	Ground surface	R^2 0.683 RMSEP 0.067 0 %	R^2 0.101 RMSEP 0.176 0 %	**R^2 0.752** **RMSEP 0.082** **100 %**

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4.2 Silicone contamination

4.2.1. FTIR spectroscopy

IR Spectra of silicones have strong bands at around 785, 1009 and 1259 cm^{-1}. In Figure 2 there is no obvious indication of these bands in the spectra of the CFRP samples with varying amounts of silicone on the surface.

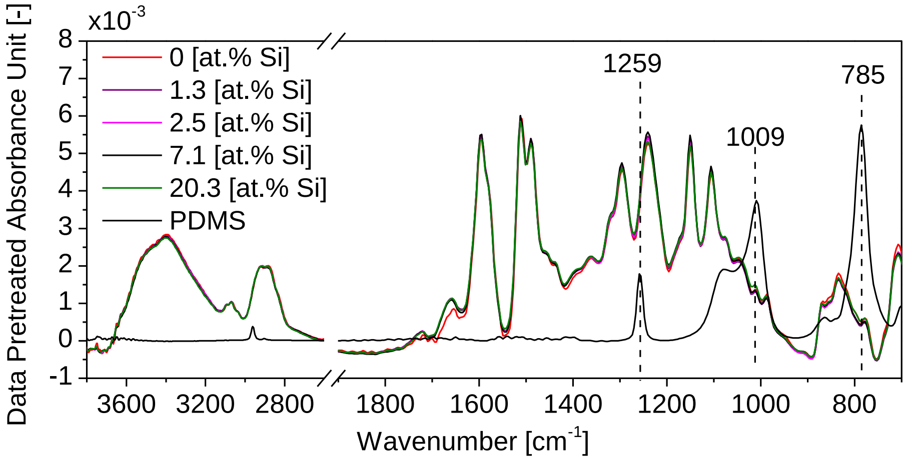

Figure 2. FTIR Spectra collected on CFRP samples with varying amounts of silicone residues determined by XPS measurements.

The evaluation of the spectra is performed by a PLS regression algorithm. In order to identify which variables, in this case the wavenumbers, are the most important for the prediction the selectivity ratio is calculated. The selectivity ratio can be calculated as the ratio between the explained and residual variance [8].

The selectivity ratio for the PLS model in Figure 3 shows some similarities with the silicone bands at 1262 cm^{-1}, 1016 cm^{-1}and 785 cm^{-1}. However, some selectivity ratio peaks are visible that do not correlate to silicone.

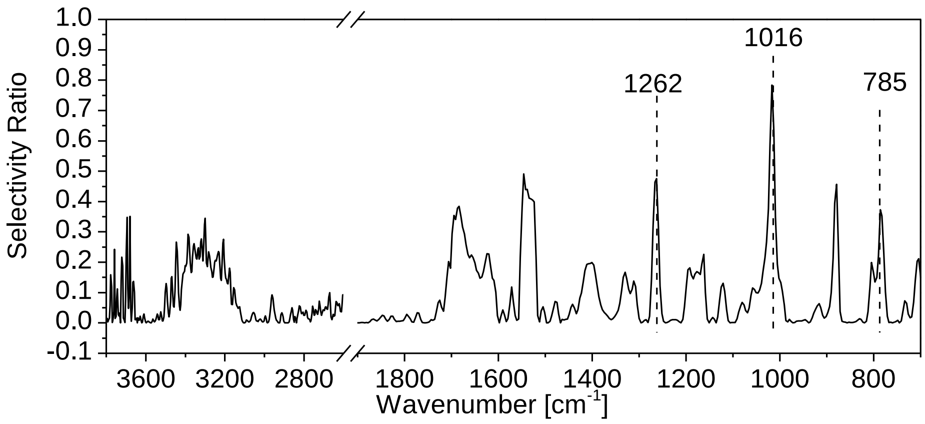

Figure 3. Selectivity ratio for a PLS regression model prediction silicone residues on the CFRP surface.

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These regions contribute to noise and lead to poor predictions in the PLS regression in Figure 4. In particular in the region of interest between 0 and 7.1 at.% Si, the predicted values are overlapping within standard deviations.

Former investigations at two different material systems show good adhesive bonding for a surface contamination with silicone below 2 at.% Si [2,9]. Above this assumed threshold an early stage of failure can be expected. Based on these observations the measuring technique must be able to predict contaminations below 2 at.% Si with a reasonable resolution.

The evaluated FTIR spectra only show a reliable distinction of high amounts of silicone residues (i.e. 7.1 and 20.3 at.% Si). A separation within the low amounts between 0 and 7.1 at.% Si is not seriously possible from Figure 4 and also not from Figure 2, as no change in the spectra can be recognized.

The problem of detecting small amounts of silicone residues with FTIR spectroscopy might be the fact that the information depth of IR spectroscopy is many orders of magnitude higher than the thickness of the silicone film on the surface.

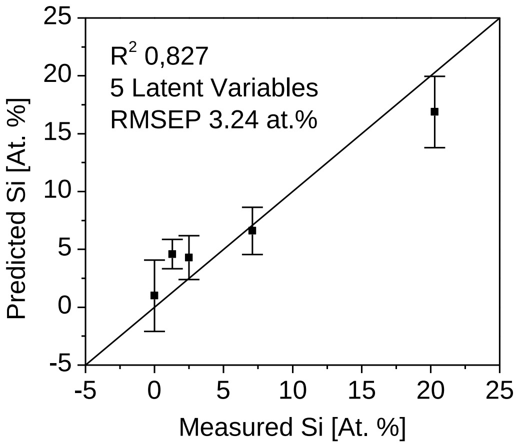

Figure 4. Prediction of silicone residues by FTIR spectra collected on CFRP samples with varying amounts of silicone residues.

4.2.2. XRF spectroscopy

With the same samples used for the detection of silicones by FTIR spectroscopy, XRF measurements were conducted. Figure 5 A shows that the Si peak at 1.75 eV allows a clear differentiation between high and low amounts of silicone.

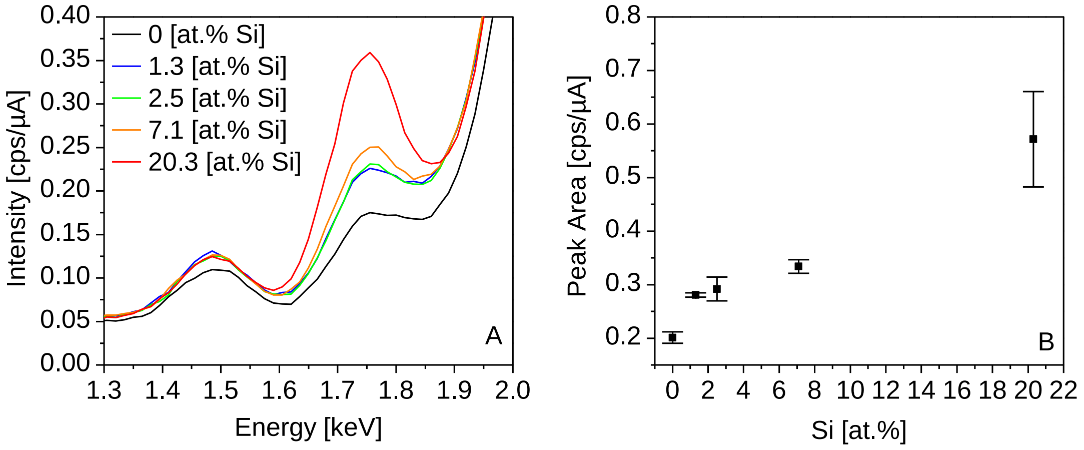

Figure 5. Mean spectra of XRF measurements on silicone contaminated CFRP samples (A). Evaluation of the peak area of the XRF measurements (B).

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Calculating the area under this peak, a good differentiation between the various amounts of silicone is possible in Figure 5 B. Only the sample of 2.5 at.% Si shows a small deviation. The obtained standard deviations are significantly lower than those for the FTIR spectroscopy and a clear differentiation between 0 and 1.3 at.% Si is possible. Due to a good repeatability and a high sensitivity already at low concentrations of silicone residues this technique provides a high potential for a quality assurance system.

4.2.3. Laser treatment coupled with GC-IMS

In published literature it is described that Polydimethylsiloxanes (PDMS) decompose predominantly into small (3-5) cyclic oligomers [10]. Hexamethylcyclotrisiloxane (D3) up to Decamethylcyclopentasiloxan (D5) can be distinguished by different retention times in the GC and different drifting times in the IMS. For the quantification of the GC-IMS signals the peak height was used. To prove the transformation into cyclic oligomers, by desorption through laser energy, Marbocote TRE 45 eco was dried on an aluminum foil which resulted in a 30 µm thick film.

No linear PDMS molecules were detected, but cyclic molecules ranging from D3 to D5. Higher molecular weights where not of interest as they appear at longer retention times and would lead to insufficient measurement cycles for in field applications.

In Figure 6 A it can be observed that the laser fluence has an influence on the desorbed amounts of D3-D5. Low laser fluence leads to the preferred detection of small molecules, while high laser fluence corresponds to longer chains. One observation during the experiments was that for a high laser fluence evaporated molecules interact with the following laser pulse, reducing its desorption efficiency.

To diminish this effect, several laser parameters were changed in order to decrease the processed area from 44.7% to 11.2% in Figure 6 B. Despite the decreased processed area an increase in signal intensity was observed.

This investigation shows that the interaction between the silicone and the laser energy is quite complex and a more fundamental understanding should be developed in order to improve the desorption process.

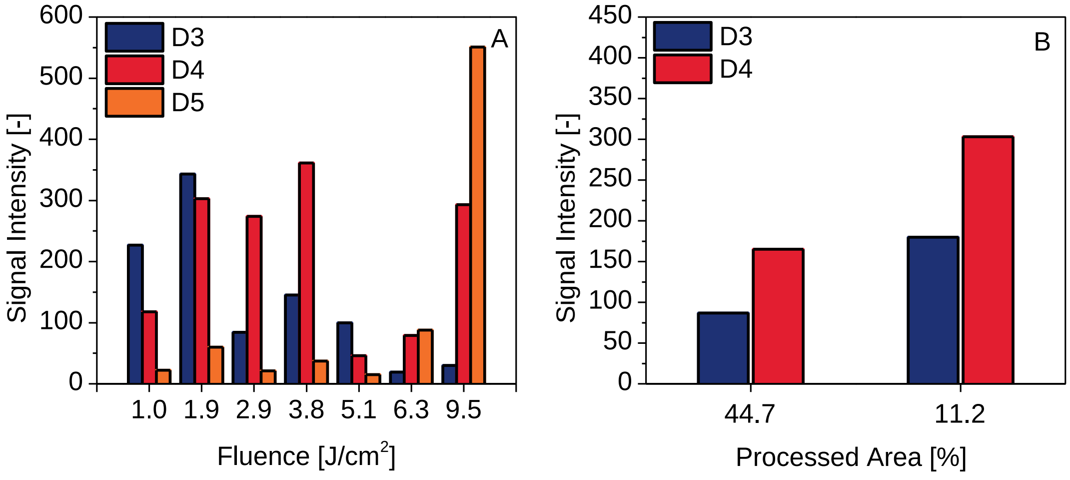

Figure 6. GC-IMS signal intensity of cyclic PDMS oligomers (D3-D5) in dependence of laser fluence (A) and laser scan speed (B).

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5. Conclusion

It has been shown that it is possible to characterize a thermally degraded CFRP surface by a handheld FTIR spectrometer. The presence of oxygen during thermal degradation influences the FTIR spectra and therefore the prediction of residual strength. A calibration only on a single scenario will lead to a high error of prediction when analysing a sample from a different scenario. Therefore, a PLS-DA algorithm was successfully used to automatically distinguish the different investigated scenarios with no false classification.

The detection of silicone based release agent residues is challenging due to the very thin film thickness. FTIR spectroscopy does not seem to be an appropriate method to determine critically low residue amounts characteristic for aviation applications. On the other hand, XRF spectroscopy shows a high potential of differentiating between contaminated and non-contaminated samples.

A novel approach for the detection of silicone residues on the surface by coupling a laser treatment with a GC-IMS shows that it is in principle possible to desorb the silicone and detect it with a GC-IMS. The interaction of the laser with the silicone and the resulting gas phase is complex and a fundamental understanding should be developed first.

Acknowledgments

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