UV-Laser Treatment of Thermoplastic CFRP Parts for Paint Applications

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The surface pre-treatment of a high performance thermoplastic CFRP for improved paint adhesion was investigated with a 30 W KrF UV-excimer laser (248 nm). Surface analysis showed no fiber release or visible removal of the thermoplastic matrix but an effective removal of silicon organic release agent residues. The ablation on nanoscale led to a cleaning effect, which improved the paint adhesion. Paint adhesion tests with a solvent-reduced paint system showed good results even after long-term ageing in water or under warm and humid conditions. After UV-laser treatment the adhesion of industrial polysulfide sealants could be achieved even without adhesion promoter. Large scale application concepts based on a compact UV-excimer laser system showed high potential for robotic guided applications with high treatment rates.

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1. Introduction

Lightweight structures in aerospace industries are becoming more and more important to remain competitive and economically successful. Since thermoset matrix materials for carbon fiber reinforced plastics (CFRP) are already applied, e.g. for the fuselage in recent aircraft generations, the interest in high performance thermoplastics is constantly increasing. Like FRP thermoset materials, they exhibit a high specific strength at low weight with high thermal and chemical stability. Due to their thermoplastic properties, multiple reforming and welding processes are possible during production [1]. Besides shorter processing times and a more cost-effective production, the avoidance of fasteners leads to more space and weight saving combined with an improved design flexibility.

However, paint adhesion on typical thermoplastics like Polyphenylene sulfide (PPS) or Polyaryletherketones (PAEK) is poor due to their hydrophobic chemical character resulting in a bad surface wettability. Additionally, the use of release agents in manufacturing processes leads to contaminations by e.g. silicon-organic residues on the surface. The formation of this weak boundary layer causes insufficient adhesion properties of applied paints, adhesives or sealants. To improve adhesion of subsequently applied materials, an appropriate surface pre-treatment technology is required.

The typical surface pre-treatment of small thermoplastic CFRP components is manual pressure blasting within a chamber combined with cleaning and drying before and after the blasting process [2,3]. This causes high recurring costs due to the use of blasting material and low automation potential, as well as a process limitation to a rather small component size. Furthermore, so far only solvent-based paint systems exhibited sufficient paint adhesion.

Laser ablation is discussed as a reproducible, automatable and environmentally friendly alternative. Previous literature has investigated the effects of laser surface treatment of composites and polymers on the adhesion between substrates of similar types during adhesive bonding. These include GFRP- and CFRP-materials [4,5] and thermoplastic composites [6,7]. However, with few exceptions [8], no work has been published on improving paint adhesion of CFRP, especially PAEK-CFRP by laser treatment.

As described in literature, the wavelength specific absorption and ablation threshold of individual materials play an important role for gentle laser CFRP component cleaning. The PAEK material applied in this work absorbs radiation < 600 nm very well, especially within the UV wavelength range, so that a UV laser appears quite suitable for cleaning and pre-treatment of the surface [9]. Due to the good absorption of the PAEK matrix material and low ablation threshold [7,10], in combination with the high ablation threshold of the embedded carbon fibers [4], a "top-down process" is possible. This means that material, e.g. topmost resin as well as covering contaminations, is selectively removed from the surface with a low ablation depth and without a significant thermal input. Due to the high ablation threshold of the carbon fibers, damage to them can be avoided if the laser parameters are chosen appropriately.

In the past, e.g., Rotel et. al demonstrated that UV laser treatment of PEEK carbon composite material leads to a significant increase in bond strength compared to untreated and SiC abraded samples [7].

In the present investigation, the application of an excimer UV laser (248 nm) was studied for the treatment of PAEK carbon fiber composites before paint application. The aim was to evaluate the effects of laser radiation on the surface topography and chemistry of the composite with a special focus to cleaning and subsequent paint application. Different analytical methods as well as paint adhesion tests were used for evaluation.

2. Material and Methods

2.1 Materials and sample preparation

A high performance CF/PAEK composite (sample size 500 mm x 500 mm x 4 mm), manufactured with an external liquid silicon-organic release agent in an autoclave process, was used for the experiments. The specimen were cut with a wet saw and purged with demineralized water.

The reference pre-treatment by pressure blasting was performed using a polymeric blasting media (urea resin) in a common blasting cabin with pressurized air. Afterwards, to remove dust and remaining blasting media samples were purged with demineralized water and dried for 12 hours at 23 °C.

The samples for laser pre-treatment were used directly for the experiments without any pre- or post-treatment.

A solvent-reduced internal primer qualified for CFRP in aircraft production was applied according to its specification.

2.2 Laser

The majority of laser treatments of CFRP samples were performed under ambient conditions using a COMPexPro 205F excimer laser system (Coherent, Göttingen, Germany). The laser was operated with a commercial KrF-premix gas mixture (Linde, München, Germany), leading to an emitted wavelength of 248 nm. The pulse duration of the beam was 25 ns with a maximum average output power of 30 W. The original flattop beam profile (10 mm x 24 mm) has been limited to 5 mm x 15 mm by an aperture in order to use only the homogeneous fluence part. For laser fluences below 50 mJ/cm², an attenuator module (Coherent GmbH, Göttingen, Germany) was used, enabling a better pulse-to-pulse stability. The rectangularly shaped laser beam was applied directly onto the sample surface without the use of additional optics. Samples have been mounted on a two axis LES5 system with an iMC-S8 Controller (isel Germany AG, Eichenzell, Germany). The pulse overlap of individual laser pulses was adjusted via the speed of the positioning system in combination with laser spot size and repetition rate. A constant repetition rate of 10 Hz was used for all experiments.

Additionally, some experiments were performed with a compact 10 W UV-laser type ExciStar 500 (Coherent GmbH, Göttingen, Germany). The system enables the emission of radiation with a wavelength of 248 nm at a pulse duration of 7 ns and a repetition frequency of 500 Hz.

Due to the developed scanning procedures and the chosen laser parameter, the achieved material removal did not lead to a relevant re-deposition of ablated polymer material and the removed contamination so that no post-cleaning after the laser process was needed.

2.3 Scanning electron microscopy

The sample surface morphology was further characterized using a Phenom XL (Thermo Fisher Scientific, Waltham, USA) scanning electron microscope (SEM). The electronic beam acceleration voltage during measurement was 10 kV. Imaging was done with a backscattering electron detector. In order to avoid charging effects, samples were sputtered with approx. 5 nm of carbon.

2.4 Analytical Surface Testing Methods

X-ray photoelectron spectroscopy (XPS) was used to measure the surface chemical composition of PAEK before and after surface pre-treatment on samples of approx. 1 x 2 cm² size (3 measurements per specimen). XPS spectra were acquired using a Quantum 2000 scan (Physical Electronics, Minneapolis, USA). An argon ion beam at 2 kV with a sputtering rate of 10 nm/min were used for the measurement. Monochromatic Al Kα radiation ($h\nu$ = 1486.6 eV) with a beam diameter of 200 µm was used to excite the photoelectrons which were measured at an exit angle of 45°, calibrated to SiO_2.

To measure the arithmetic mean height S_a of the surfaces before and after the pre-treatment, laser confocal scanning microscopy was done with a VK 9700 (Keyence, Osaka, Japan) by using a 408 nm laser beam.

2.5 Paint adhesion

The samples were painted directly (within 12 h) after the respective pre-treatment, and handled only with gloves. Paint adhesion of the applied paint system was tested with the cross cut method according to DIN EN ISO 2409. According to the paint thickness, the distance between individual cuts was set to 1 mm. The lattice was cut with six parallel cuts and six additional cuts shifted by 90° with a scalpel and a template. Detached particles were removed with a soft brush. The adhesive tape Tesa 4651 was placed onto the cross cut, pressured with finger nail and pulled off quickly in a 60° angle. The resulting surface was classified in GT0 to GT5. At a classification of GT0 the edges of the cuts are completely smooth which indicates full paint adhesion. GT1 means a detachment of small flakes of the coating at the intersections of cuts, where less than 5% of the coating is affected. A cross cut area with less than 15% is classified in GT2, if less than 35% is affected the classification is GT3. Detachments between 35% and 60% are classified as GT4 and any degree of flaking that can not even be classified is GT5.

The adhesion was tested at the initial state 7 days after application (requires GT0), after ageing for 14 days in demineralized water at 23 °C (requires ≤ GT1) and after 500 and 2000 hours storage in a climate chamber (Liebisch, Bielefeld, Germany) at 40 °C and 100% relative humidity (requires ≤ GT1).

3. Results and Discussion

3.1 Surface topographical and chemical characteristics

To investigate a possible fiber exposure and damage after the surface pre-treatment, SEM images were taken from the CF/PAEK surfaces (Figure 1). The untreated CF/PAEK (a-b) shows the polymeric matrices with fibers embedded in matrix material and minor particle residues on the surface. Due to the electron beam energy of 10 kV used and the resulting high depth of information, the embedded carbon fibers can be seen in the SEM image. After a reference process by pressure blasting (c-d), the fibers are partly exposed out of the PAEK matrix in specific areas. Furthermore, blasting media residues are visible. The abrasive removal of the first surface layer does not only remove the contaminations but also higher amounts of the polymeric matrix material. Due to the small cover layer of the matrix material, the fibers are exposed for more intensively treated areas or areas with a

thinner matrix cover layer. A constant laser fluence of 100 mJ/cm², a pulse overlap of 90% (10 pulses/area) and a frequency of 10 Hz were chosen for the laser cleaning. The laser fluence was selected above the material-specific ablation threshold to ensure cleaning of the surface contaminations by ablation. UV-Laser pre-treated SEM images show no detectable fiber exposure or residues on the surface. The carbon fibers are still fully embedded and no fiber damage could be detected. The SEM images show that the UV laser process is a "top-down" process, which does not lead to a critical, unwanted removal of the matrix material. It rather results in a selective layer by layer removal.

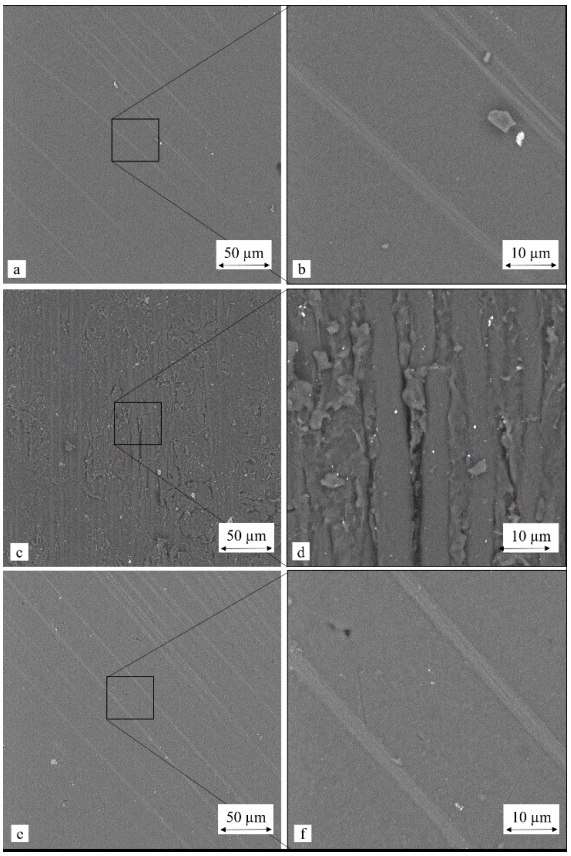

Fig. 1 SEM images of a CF/PAEK surface at untreated state (a) and (b), after surface pre-treatment with reference blasting (c) and (d) and UV-laser (e) and (f) in different magnifications.

Roughness measurements show an arithmetic mean height S_a of 0.58 µm on an untreated CF/PAEK surface. After surface treatment with the reference blasting process the roughness is increased to a S_a of 6.32 µm due to the abrasion of the surface by the blasting particles and the exposed fibers. The UV-laser treatment shows a micro structured surface (S_a = 0.81 µm) compared to the untreated sample, which leads to a higher effective surface for adhesion.

Furthermore, XPS measurements were performed to analyze the chemical composition of the CF/PAEK surface. Thereby, the cleaning efficiency of the surface pre-treatment via reference blasting or UV-laser should be validated.

Table 1 XPS-measured surface composition of CF/PAEK samples as delivered and after surface pre-treatment with reference blasting and UV-laser. For the "As delivered" and "Reference blasting" sample state also some minor S, Ca and Zn contaminations were detected (not listed).

Sample	Atomic percentage [at.%]			
	C1s	N1s	O1s	Si2p
As delivered				
Pos. 1	52.6		29.6	17.5
Pos. 2	63.1		24.1	12.0
Pos. 3	52.3		29.2	18.1
Reference blasting				
Pos. 1	77.6	1.7	16.7	2.5
Pos. 2	80.8	1.4	14.4	1.4
Pos. 3	78.7	1.9	15.7	2.2
UV-laser				
Pos. 1	89.7		9.4	0.9
Pos. 2	91.7		7.3	1.0
Pos. 3	88.8		9.6	1.7

Table 1 summarizes the surface composition at three measuring points (Pos. 1-3) of the samples. The untreated sample ("as delivered") shows silicon organic contaminations, which could be identified by their peak position at 102.6 eV. The Si signal reveals significant variation between 12.0 and 18.1 at.% and is a good correlation with the used type of release agent for the sample production. Besides the silicon content, carbon (52.3 – 63.1 at.%) and oxygen (24.1 – 29.6 at.%) were detected which can be assigned to the composition of the silicon-organic release agent, and in minor contribution to the PAEK matrix material covered by the release agent.

Surface pre-treatment with reference blasting shows a reduction of the silicon-organic amount to 1.4 – 2.5 at.%, but blasting media transfer could also be detected by an increased nitrogen concentration (1.4 – 1.9 at.%), which is in good correlation with the used abrasive media. Chemical composition of the laser pre-treated surface shows lowest content of silicon-organic residues between 0.9 and 1.7 at.%. The carbon (88.8 – 91.7 at.%) and oxygen (7.3 – 9.6 at.%) concentrations are in the stoichiometric ratio as specified for the used PAEK matrix material. In the XPS measurements, no functional oxygen-containing groups were detected on the PAEK surface after surface pretreatment by UV laser, so that an activation effect of the surface by the laser treatment is not to be expected. Furthermore, no residues from the fabrication process left on the surface after laser treatment.

3.2 Paint adhesion

The effectiveness of the surface pre-treatment with reference blasting and UV-laser on the paint adhesion of an epoxy-based paint with reduced-solvent content was tested by the cross cut test method according to DIN EN ISO 2409. The results are shown in Table 2 listed according to the ageing condition of the respective samples. In case of untreated PAEK samples paint adhesion failed even in the delivery state with GT5, therefore these results are not shown here.

Table 2 Paint adhesion results of solvent-reduced paint system on surface pre-treated CF/PAEK after different ageing conditions.

	(1)*	(2)*	(3)*	(4)*	Passed/ not passed
Reference blasting					
Sample a	GT 2	GT 5	GT 5	GT 5	Not passed
Sample b	GT 2	GT 5	GT 5	GT 5	Not passed
Sample c	GT 1	GT 5	GT 5	GT 5	Not passed
UV-laser					
Sample d	GT 0	GT 0	GT 0	GT 0	Passed
Sample e	GT 0	GT 0	GT 1	GT 1	Passed
Sample f	GT 0	GT 0	GT 0	GT 0	Passed

* (1): testing at delivery, (2): testing after 14 days ageing in demineralized water, (3): testing after 500 hours in 100% relative humidity at 35 °C, (4): testing after 1000 hours in 100% relative humidity at 35 °C

All samples pre-treated by the reference process blasting showed moderate to insufficient paint adhesion properties with up to 15% detachments of the coating (GT 1 – GT 2) at delivery, which already could not pass the requirement of paint adhesion for this application. However, paint adhesion after different ageing conditions in water and long-term humidity is extremely poor. Furthermore, blisters and large flaking outside the testing area were detected. This is caused by an instable interface layer, prone to water intake, as a result from release agent or blasting media residues. The ageing is caused by osmotic effects, leading to a water accumulation in the interface between the CF/PAEK surface and internal primer. Since solvent-reduced paint systems have higher demands on the wettability of a surface to create adhesion, the generated roughness of the reference blasting process is not sufficient for long-term adhesion.

Compared to the reference blasting process, surface pretreatment with UV-excimer laser showed excellent paint adhesion, as depicted on the lower side in Figure 2. For all tested ageing conditions and samples, the paint adhesion passed the requirements. As shown in 3.1 the reference process abrasive blasting shows a higher surface roughness compared to the UV-laser treatment. However, an UV-laser treatment leads to strong paint adhesion, due to an almost residue-free and micro structured surface.

Additionally to paint adhesion, bead peel tests with industrial polysulfide sealants have been performed. In combination with a belonging solvent based adhesion promoter the sealant showed cohesive failure after surface pretreatment with reference process blasting and also after UV-laser processing. However, without use of the adhesion promoter, the sealant failed to adhere on the blasted PAEK and revealed an adhesive failure to the substrate.

In contrast to that, the PAEK samples pre-treated with the UV-laser showed again a cohesive failure of the sealant material even without additional use of the solvent based adhesion promoter. Beside the excellent cleaning effect and nearly complete removal of the silicon-organic residues of the release agent, a sub-micrometer surface structuring is assumed as a possible explanation for the improved adhesion.

For applications on complex, large scale structures one typical drawback of the UV-laser is a high effort for beam guidance. To demonstrate transferability of the process to more compact systems, also a commercial 10 W KrF excimer laser was tested in combination with Kuka robotic system. Again the paint adhesion results showed GT 0 for all tested samples at all ageing conditions, confirming the results with the CompexPro laser system and verifying the process transferability to other Excimer based lasers. Via the given repetition frequency of up to 500 Hz a treatment rate of up to 12 m²/h can be achieved and due to the much lower weight of the system also a direct movement on the simple rail and lifting equipment is possible.

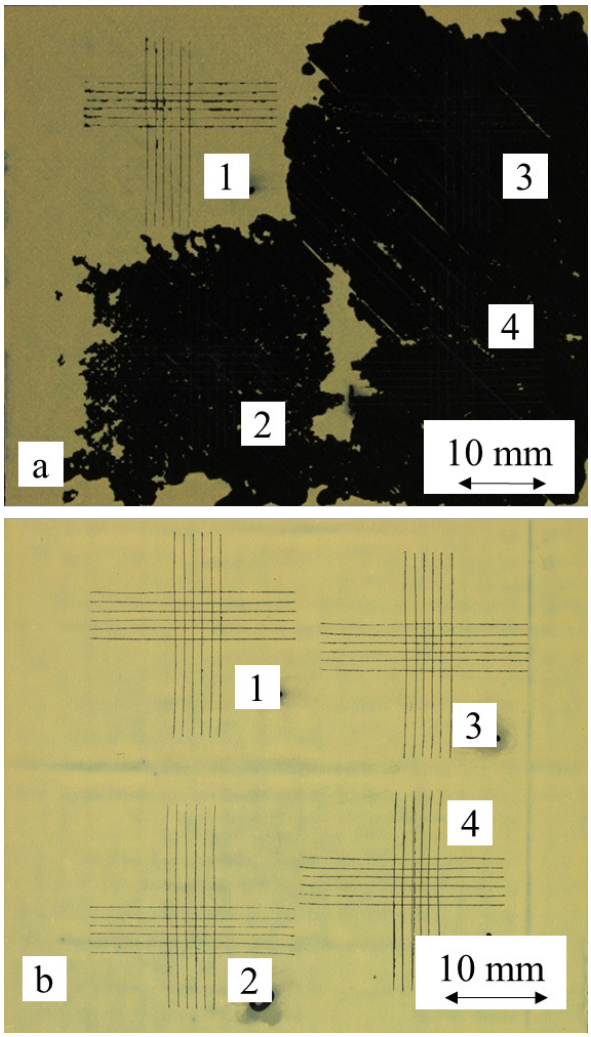

Fig. 2 Paint adhesion results of solvent-reduced paint system on CF/PAEK pre-treated with reference blasting (a) and UV-laser (b) tested with cross cut method according to DIN EN ISO 2409 after different ageing conditions. (1) at delivery, (2) after 14 days water immersion, (3) after 500h 100% relative humidity at 35 °C and (4) after 1000h 100% relative humidity at 35 °C.

4. Conclusions

Investigations of UV-laser surface pre-treatment before paint and sealant applications on thermoplastic CF/ PAEK showed good adhesion results with solvent-reduced paint systems and also for sealants which have been applied without an additional adhesion promoter. UV-laser with 248 nm could successfully remove silicon-organic contaminations

caused by used release agent from the PAEK substrate. Due to the developed process parameters, the PAEK could be cleaned and prepared for improved adhesion without the risk of material deterioration or the unwanted release of carbon fibers out of the PAEK matrix material.

Acknowledgments and Appendices
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