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Published in:
The Journal of Adhesion

DOI:
10.1080/00218464.2021.1938004

Publication date:
2022

Document Version
Author accepted manuscript

Link to publication in ResearchOnline

Citation for published version (Harvard):

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Download date: 15. Sep. 2023
Comprehensive Study on the Influence of Different Pretreatment Methods and Structural Adhesives on the Shear Strength of Hybrid CFRP/Aluminum Joints

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Comprehensive Study on the Influence of Different Pretreatment Methods and Structural Adhesives on the Shear Strength of Hybrid CFRP/Aluminum Joints

The aim of this study was to investigate the influence of laser treatments with varying energy density and wavelength on the surface structure, shear strength and fracture behavior of hybrid compounds of thermoset carbon fiber reinforced polymer (CFRP) and aluminum (Al) bonded with three different structural adhesives. The CFRP was pretreated by laser with near-infrared (NIR) and ultraviolet (UV) wavelengths and applying different energy densities. Aluminum surfaces were structured with NIR. Reference CFRP/Al-specimens were prepared by acetone cleaning, low pressure oxygen/argon plasma or sand blasting. The surfaces were investigated microscopically before bonding and after mechanical testing. In addition, the surfaces were examined with white light interferometer and sessile droplet test methods. The bonded compounds were characterized in standardized single lap shear tests to reveal the influence of the pretreatment strategies on the joint strength. Suitable process windows for laser pretreatments were identified, including NIR-pretreatment methods that can compete with an UV-laser source. For every adhesive, a suitable pretreatment method was found.

Keywords: hybrid joint; adhesion; mechanical testing; surface treatment; laser; ablation

1. Introduction and state of the art

The increasing interest in lightweight construction solutions in recent years, particularly for automotive and aerospace applications, is the driving force for new approaches to lightweight structures, materials and thus joining processes \[^1\]. The direct correlation between fuel-saving emissions and vehicle weight is the main reason for car manufacturers to make targeted use of thinner and stronger materials. Consequently, fiber-reinforced polymer composites (FRPs) in combination with new steel grades like ultra-high strength steels, the AA5/6/7xxx series aluminum or magnesium become more popular \[^2\]. Carbon fiber reinforced polymers (CFRPs) are convincing through their low density, high corrosion resistance and excellent mechanical properties, which is decisive for highly stressed components. If the focus is on joining of CFRP with aluminum alloys the variety of methods are mechanical interlocking between both substrates (i.e. clinching, substrate pins), adding elements (i.e. nails, rivets, screws and
friction/resistance welds), adhesive bonding with additional adhesives as well as fusing thermoplastic substrates. Beside the adhesive joining methods, all methods have in common that the carbon fiber reinforcement is discontinuous in the area of the drilling. Furthermore, galvanic corrosion, between the substrates and/or the inserted rivet/nail, can appear. Concerning the metallic substrate, the choice of the joining method must be chosen regarding the physical properties i.e. hardness, deformability of the substrate \[^3\]. In contrast, with adhesive bonding the stress is distributed more evenly and is therefore a more appropriate technology for hybrid joints based on composites \[^{1,4}\]. The polymer as well as metal surfaces are contaminated with moisture, lubricants, dust and, in the case of CFRP, release agents during manufacturing and handling \[^5\]. Therefore, prior to bonding hybrid joints, surface pretreatment is the most important factor influencing their mechanical strength. Different pretreatment methods are under investigation and the most relevant are briefly reviewed in the following. All of them are aimed to improve the wetting behavior, generating functional groups and/or to enhance the surface area of the adherends and therefore, gain an optimal mechanical performance of the joint.

The laser surface treatment is one method where the wavelength of a laser source defines the ablation mechanism in the matrix of the CFRP. Most common and available solid-state laser sources emit in a wavelength range of \(\lambda = 1000 - 1100\) nm within the near infrared (NIR) region of \(\lambda = 780 - 3000\) nm according to ISO 20473. However, a deficiency of NIR-laser sources is the low absorption of the laser intensity by the epoxy resin whereas it is completely absorbed by the underlying carbon fibers \[^6\]. Despite that the absorption takes place on the carbon fibers, the matrix can be removed due to pyrolysis in the transition zone between carbon fibers and the epoxy matrix itself resulting in a recoil pressure removing the surrounding materials \[^6\]. Investigations revealed that evaporations, broken carbon fibers as well as delamination in the CFRP laminate due to combustions \[^{7,8}\] and voids could not be completely filled by adhesive \[^9\]. However, the surface composition is affected positively, Li et al. increased the amount of functional groups (carbonyl and carboxyl) on the surface with a NIR-laser wavelength \[^{10}\]. Liu et al. revealed a reduction of single, non-polar carbon-carbon bond and an increased amount of hydroxyl, carbonyl as well as aldehyde and carboxyl polar bond content. Contact angle measurements show an improvement of the surface free energy \[^{5,11-13}\].

Different studies on significant and expedient laser process parameters were published in the past years. Li et al. applied different single pulse energies on woven CFRP. They found out that a single pulse energy of 40 mJ is necessary to ablate the matrix
and receive the maximum shear strength \cite{14}. Leone et al.\cite{15} revealed that a rising emitted energy, pulse energy and pulse power have an positive influence on the matrix removal. Additionally to Leone et al.\cite{15}, Sun et al.\cite{16} as well as Genna et al.\cite{17} showed that the applied laser energy density in relation to the processed area is a promising value for describing the processing strength. The consideration of the total amount of released energy shows that a lower pulse frequency and thus higher single pulse power is to be preferred \cite{15}. The latest investigations by Xie et al. revealed that a periodic structure / grooves in the exposed carbon fiber surface by NIR-laser treatment can improve the mechanical shear strength due to interlocking between the carbon fibers and the adhesive \cite{18}. This effect can also be used to increase the fiber-matrix-adhesion by creating saw-tooth-like profile on the carbon fibers \cite{19}. The nano- and microscale roughness of the exposed carbon fibers by NIR laser treatment also lead to improved mechanical shear strengths \cite{9,11}.

The usage of ultraviolet (UV)-laser systems significantly improves the absorption in the matrix \cite{8} and extends the ablation by a photolysis process \cite{20} depending on the matrix material. Several investigations showed that the UV-light enables a damage free exposure of carbon fibers \cite{7,8,21–23} or a slight ablation of the surface of the matrix \cite{8,24,25}. Moreover, the superficial chemical composition of the CFRP is affected due to the UV-pretreatment. Rotel et al. published the modification of the surface chemistry by imposing polar groups on CFRP with a UV-laser system \cite{22}. Akman et al. reported that the amount of hydroxyl functional groups and thus, the mechanical shear strength is increased with UV-treatment. According Liu et al.\cite{11}, the UV-laser surface treatment also increased the carbonyl and carboxyl functional group concentration which improved the surface free energy. In contrast, a CO\textsubscript{2}-laser treatment has a reducing effect on both since the predominant photo-thermal ablation process leaves re-solidified residues on the surface lowering the adhesion to the surface and carbon fibers \cite{26}. However, Sorrentino et al used a CO\textsubscript{2} laser for selective laser structuring of the CFRP matrix surface. The shear strength could be increased until the mechanical properties of the substrate material were limiting \cite{27}.

The aluminum substrate also requires a pretreatment to achieve a high mechanical joint strength. In some of our previous work we could show that for a given set of laser parameters, the laser treatment of the aluminum counterpart does not significantly affect the shear strength of the hybrid single-lap joints \cite{7}. The relatively strong structuring on aluminum has proven successful, and in the latest investigations by Özgür et al. this is
confirmed by varying the laser structure on aluminum [28]. Liu et al. showed that the surface roughness may have an influence on the achievable shear strength. Here, the result depended on the viscosity of the applied adhesive, where a lower viscosity can fill the rougher surface and ensure high shear strength [29].

The number of investigations dealing with laser-based pretreatment strategies prior to bonding of hybrid CFRP/Al-joints is limited. A review [3] and a small amount of studies correlates the surface state after pretreatment to the shear strength of hybrid single-lap joints. Galantucci et al. studied the laser pretreatment of aluminum and CFRP for hybrid material single-lap joints. They repeatedly showed that they could set the average shear strength in a narrow range of 11.8 - 14.3 MPa. In comparison, neither the strength nor the reproducibility could be achieved in reference measurements for sandblasted specimens [21]. Finally, a number of publications investigated the laser pretreatment of different aluminum alloys. The applied energy ensures either the cleaning of the surface [22,30] or, with increased energy, structuring of the surface takes place [31]. The roughness and structure depth have a positive influence on the shear strength [30,31]. Morini et al. showed that a crossed plane laser structure generate a 80% higher G1C rate in double cantilever beam tests compared to sand blasted surfaces. However, the roughness should not be excessive, otherwise, air pockets may trapped in the structures [32] [33] or the wettability is reduced due to oversized single structured hatches [34]. Another way to increase the interlock between adhesive and aluminum substrate by generating area ablated sections was shown by Liu et al. [29].

**Alternative surface treatment methods:** As the number of available publications and therefore key findings on hybrid single-lap joints is limited, results for alternative surface pretreatment on homologous samples based on CFRP or aluminum are also taken into account in the following. Abrasive methods (blasting, grinding) are applied to remove contaminants on aluminum [35] or to increase the surface roughness of CFRP [36] or hybrid joints [37]. Both effects promote the shear strength. Kim and Lee [37] as well as Boutar et al. [38] found out that an optimal roughness is necessary, to improve the wettability and shear strength on homologous CFRP [37] as well as aluminum [38] joints, respectively. Both publications also revealed that an excessively rough surface deteriorates the strength. In another study, it was shown that increasing the roughness by sandblasting, which generated by crevices on the surface, improves the adhesion of polyphenylene sulfide to aluminum [39]. Harris and Beevers recognized, that grit blasting may contaminate the surface due to residual abrasive media [40]. Thus, the combination of
‘sand blasting’ and subsequent removal of contaminants and dust with solvents promotes a high shear strength of homologous aluminum or hybrid CFRP/Al single-lap joints \([7,41]\). Plasma techniques enable a good shear strength by introducing functional groups which improve the wettability and hydrophilicity of CFRP \([42–44]\). However, latest findings by Arikan et al., showed contrary findings, where the surface of thermoset and thermoplastic material were pretreated by a vacuum UV or plasma treatment and subsequent cleaned afterwards with water or ethanol. Thereby, the removal of chemical functionalization and macroscopic polarization was realized. After the washing process, the adhesive bonding strength remained constant high which indicate that the topography on molecular scale is the most important factor to achieve a high strength. Combined methods i.e. sand blasting with a subsequent plasma treatment showed high shear strength \([35]\). A comparable investigation was conducted with peel ply and subsequent plasma treatment \([45]\).

The study presented here is based on our previous work \([7]\), in which we investigated the influence of a limited number of laser parameters on the shear strength of hybrid Al/CFRP joints. However, only one adhesive was used here. In doing so, two contradicting effects on the mechanical strength induced by the laser treatment became obvious. It was shown that a strength increasing surface activation and a strength-reducing damages of fiber-matrix adhesion due to fiber matrix debonding takes place. In the present work, the effects of different pretreatment methods on three different adhesives are to be investigated and demonstrated in more detail. To do so, we (i) systematically extended the variation of laser parameters, (ii) introduced further structural adhesives and (iii) evaluated cause-effect relationships between laser pretreatment, surface properties and the respective mechanical strength. In detail, we compared (i) two laser wavelengths (NIR and UV) and eight different parameter sets (six NIR, two UV) that resulted in different energy densities with (ii) sandblasting, plasma treatment, and acetone cleaning as alternative methods applied to the thermoset CFRP surfaces prior to bonding. For all hybrid joints with laser pretreated CFRP, the aluminum part was exclusively treated with one constant NIR-laser parameter. If the CFRP adherend was treated with acetone, sand blasting or plasma, the aluminum part was pretreated in the same way.
2. Experimental Design

2.1 Material

The quasi-isotropic thermoset CFRP laminate with epoxy matrix is made of eight unidirectional pre-preg plies lay-up made of Hexcel HexPly® M21 toughened epoxy matrix and reinforced with 24k tow TORAYCA® fibers T800S. The fibers have a diameter of about 5 µm. The stacking sequence of [0/45/90/-45], results in a final thickness of 2.0 mm and is cured for two hours in a hot press process at 180 °C and 7 bar. As the second joining part, the aluminum alloy AlMg3 (EN AW-5754, H22, work-hardened by rolling and then annealed to quarter hardness) of 2.0 mm thickness was milled to the corresponding size in accordance with the standards. Based on manufacturer specifications, a cathodic electro-deposited coated EN AW 6082 metal sheet was used for the polyurethane adhesive (see below). Mechanical specification of the CFRP and both aluminum materials is given in the following Table 1.

To meet the dimensions for SLJ-samples (DIN EN 1465:2009), the CFRP was cut from 200 x 300 mm plates with a diamond-coated cutting wheel on a water cooled cutting machine. Three different adhesives were used in this study: Firstly, HP-E60K (HP-Textiles), a two component (2-C) epoxy-based adhesive colored red with approximately 1.2 wt.-% pigments of the HP-FD series with the aim of facilitating the evaluation of the fracture patterns. Secondly, TEROSON® EP 5065 (Henkel), a 2-C epoxy-based and amine-based adhesive1. Thirdly, LOCTITE® UK 2015 (Henkel), a 2-C polyurethane adhesive1. The resin component is based on organic compounds containing hydroxyl groups1. The hardener component is based on isocyanates1. Whereas EP 5065 and HP-E60K were applied manually, LOCTITE® UK 2015 was applied by a robot KR30 HA (KUKA) connected to an automated adhesive dispenser system due to its high viscosity (see Table 2 line 4). The specifications of the adhesives including the curing conditions and the adhesive thickness for the SLJ-joint geometry are shown in Table 2. All three adhesives used are suitable for bonding CFRP as well as hybrid material combinations and are recommended by the manufacturers1.

1 The chemical composition has not been disclosed by the manufacturers, as these are a trade secret. For the user, therefore, only safety-relevant information is given, which describes the acute and chronic toxicity of the components, but is intended to prevent the user from synthesizing the adhesive himself.
2.2 Pretreatment of surfaces

Laser pretreatment

Both material surfaces (CFRP and Al) were pretreated in an area of 25 x 12.5 mm, see Figure 2 b), with a NIR-wavelength laser system, a TRUMPF TruMark 5020 nanosecond short pulse laser system with a wavelength of 1062 nm and an average laser power of 20 W. Two different types of focal optics were used. The first focal optic with an optical length of 254 mm and a resulting spot diameter of 114 µm was used for the CFRP pretreatment. A second one with 160 mm optical length respectively 72 µm diameter was used for the laser structuring of the aluminum surface, Table 3.

In addition, a UV-laser source, TRUMPF TruMark 6350, was used to modify the CFRP-surfaces (note, that also in this case the Al-part were structured using the NIR-laser). The emitting average power is 5 W with a wavelength of 355 nm. The laser beam had a focal length of 160 mm and a laser spot diameter of 36 µm, Table 3.

A comparison of different laser settings requires suitable values. A solution is given by Genna et al. [17], where the "energy input per area", the energy density $ED_{\text{Area}}$, is used for the comparison of different laser pretreatment parameters. Thereby, the average laser power $P_{\text{avg}}$, the scanning speed $v_{\text{scan}}$ and the hatch distance are used, (1).

$$ED_{\text{Area}} = \frac{P_{\text{avg}}}{v_{\text{scan}} \cdot d_{\text{hatch}}}$$  \hspace{1cm} (1)

Other publications such as [15–17] show that the applied laser energy $ED$ in relation to the areas is a promising value for describing the processing strength. For this reason, in the following, the different laser parameters are named after the energy density and laser wavelength, e.g. $ED_{\text{Area}} = 2.3 \text{ J/cm}^2$ with near-infrared (NIR) wavelength are named with NIR02.3, ultraviolet (UV) with UV.

Moreover, the pulse overlap $PO$ (2) and track overlap $TO$ (3) have to be considered in order to compare the chosen velocity $v_{\text{scan}}$ and hatch distance $d_{\text{hatch}}$ in combination with different pulse repetition rates $f_{\text{rep}}$ and spot diameter $d_o$.

$$PO = (1 - \frac{v_{\text{scan}}}{f_{\text{rep}} \cdot d_o}) \cdot 100$$  \hspace{1cm} (2)

$$TO = (1 - \frac{d_{\text{hatch}}}{d_o}) \cdot 100$$  \hspace{1cm} (3)
The chosen laser process parameter, which based on preliminary investigations and on previous investigations, are given in Table 4. Note, that the energy densities and peak power between NIR and UV laser systems are not directly comparable due to the different absorption behavior of the epoxy matrix and the differences in the ablation mechanism.

All laser pretreatment parameters were applied with the same process strategy. Thereby, the laser beam was guided perpendicular to the top layer of the CRFP (Figure 1).

The aluminum samples were structured perpendicular to the applied load direction, i.e. comparable to the CFRP-samples. The processing took place under ambient atmosphere. Ablated matrix and aerosols were removed by a suction during the laser processing.

Reference pretreatments: Plasma, sand blasting and acetone cleaning

Three different reference pretreatments were applied: i) manual acetone cleaning and drying afterwards, ii) low-pressure plasma treatment for 30 seconds with oxygen and argon (volumetric ratio: 1:1) used as the process gas (laboratory system Zepto by Diener Electronic), iii) sand blasting in a normal finishing cabinet type DP14 with the chilled cast granulate WIWOX HG 005 (matches the DIN EN ISO 11124-2 M/CI/G and the standard grain size G05 of 0.16 to 0.30 mm according to BS 2451:1963) for five seconds with 1.2 bar from a 200 mm distance in an angle of 90° to the surface. Due to the spray radius of the sand blasting nozzle, no movement of the nozzle was necessary. After sand blasting, the surface was cleaned with compressed air.

2.3 Surface analyzation, Mechanical testing and fractographic investigations

The surfaces before / after pretreatment and the fracture analysis, see Figure 2 c) according to DIN EN ISO 10365:2020 [46] were carried out with the digital microscope Carl Zeiss SmartZoom 5 and a scanning electron microscope (SEM) Carl Zeiss Sigma 300 VP. The average matrix thickness of the untreated surface and the average carbon fiber depth was measured in cross sections in direction to the top layer fiber direction on a length of approximately 8 mm. The average surface roughness was measured with a white light interferometer Zygo NewView 8300 on an area of 4x4 mm on five individual surfaces. In addition, the surface free energies (SFEs) were determined in a sessile droplet test – at a Kruess DSA 100 Goniometer – using the Owens-Kaelbe-Wendt-Rabel
Thereby, the SFE of the initial and all pretreated surfaces were measured five times on an individual and dry surface.

The joined SLJ samples were tested at normal temperature and pressure according to DIN EN 1465:2009 with a traverse speed of 1.5 mm/min using a Schenck RSA100 testing machine. Rectangular aluminum cap strips with the dimension of 45x25x2 mm³ were applied with a 2-C adhesive (Typ UHU® Endfest 300) on both sides of the SLJ sample 24 hours before the mechanical testing. The cap strips compensate the individual CFRP and aluminum thicknesses and ensure that the SLJ specimens fail under shear. The deflection during the mechanical testing was reduced by a frame, comparable to those used in DIN 65 148:1986, which was manually bolted on the test specimens, Figure 2 a). The background to this is that the substrates used with a material thickness of 2 mm in combination with the adhesives, some of which adhere very well, cause the substrate to rotate or deform, resulting in peel stresses. With this tool, the deformation under load was minimized in order to perform the test under pure shear stress. The samples were positioned in the clamping jaws and a pre-load of 100 N was applied. The testing was stopped after a 90% decrease of the maximal detected shear force. Each adhesive-pretreatment combination was conducted five times. The average shear strength and standard deviation was calculated.

3. Results

3.1 Pretreated CFRP and Aluminum substrate

In Figure 3 a), the original surface, acetone (AC), plasma (P), sand blasted (SB) and UV-laser-pretreated surfaces are depicted. The first two surface treatments did not result in visible ablation and therefore show the same appearance and surface microstructure as the material in its original state. The slight irregularities and small particles on the surface are assigned to the original surface. In comparison, sand blasting produces a bright appearance on the light microscopic image. The SEM images show a wavy surface structure of the matrix with loose matrix residues and particles on the surface but no exposed fibers. The UV-laser with an energy density of 40 J/cm² produces a rough, crater-like surface with partially exposed carbon fibers. If the energy density is doubled to 80 J/cm² the fibers are almost completely exposed and matrix particles remain loose on the surface.
In Figure 3 b) the influence of different NIR laser parameters are depicted. According to Table 4, a variation of laser and process parameters took place. At a NIR-energy density of 2.3 J/cm², the surface is still completely covered with matrix except for a few spots. The SEM image confirms that no fiber damage has occurred. In a range of 16.8 J/cm² to 28.6 J/cm², residual matrix particles and stripes are still on the surface. Increasing the energy input to 37.7 J/cm², the fibers are entirely exposed. A further increase of the laser energy density causes a higher fiber removal. The high-resolution SEM images show the transition between untreated and irradiated material and the increase in ablation can be seen in the step height. The effects of the NIR-laser pretreatment can be categorized as follows. With an almost full ablation of matrix, the SEM image reveal a rising fiber damage (≥NIR16.8). As a result, a fiber damage free ablation process of the matrix is not possible due to the necessary energy input.

In addition, the surface of the initial Aluminum and laser threated respectively sand blasted surface is given, Figure 4. The initial Al surface exhibit a grinded surface. With the sand blasting, the surface appear dull. The laser structuring generate a rough surface with linear deepenings.

To quantify the pretreatment, the surfaces were measured with a white light interferometer. The average arithmetic roughness Sₐ and the standard deviation were calculated in the following Figure 5, the results are given. The measurements reveal that the initial surface roughness can be increased from Sₐ = 3.16 µm to 8.38 µm with sandblasting, 5.77-6.97 µm when the carbon fiber are fully exposed with NIR28.6-71.2. NIR16.8 generate a high surface roughness of Sₐ = 8.26 µm and have an increased standard deviation. With the UV pretreatment, the surfaces is after the UV40.0 processing is less rough than with the full ablation (UV80.0) of the matrix.

In Figure 5 b), the average depth of the exposed carbon fibers is given. The initial carbon fiber depth is 24.4 µm, rising NIR laser treatment led with the partial ablation of the matrix by applying NIR02.3 to a lower average exposed fiber depth. With NIR≥16.8, the average exposed fiber depth is in the increasing range of 30.9 µm to 50.2 µm. The measurements after the UV radiation show a reduced average exposed fiber depth with UV40.0 (22.3 µm) and a comparable depth with UV80.0 (25.7 µm). The initial Aluminum roughness is with Sₐ = 0.34 µm relatively smooth, after sandblasting, the roughness increases to 3.98 µm. The highest roughness is achieved with the laser structuring NIR273 with a roughness of 17.55 µm.
The determination of free surface energy was realized by sessile drop shape measurements. Measurement of the surface free energy (SFE) of the CFRP were only successful at low energy densities due to critical changes in the surface state after structuring. In the initial state, the SFE is at $\gamma = 40$ mN/m and cannot be changed by reference pretreatment processes. A low energy density of 2.3 J/cm² is also not sufficient to change the SFE. At an energy density of NIR16.8 J/cm² respectively UV40.0 and higher, the fibers are exposed over a large area. This meant that no measurement was possible because the drop immediately infiltrated the fibers.

3.2 Shear strength of adhesively bonded CFRP/Al-Joints

The results of the SLJ-shear strength are given in Figure 6, Table 5 and Table 6 in dependence of the pretreatment method as average mean values and their range of variation based on five measurements.

In general, Figure 6 shows that the shear strength $\tau$ for all three applied adhesives variate in dependence of the pretreatment method, however some correlations are available.

Teroson EP 5065: According to the technical data sheet, the expected shear strength $\tau_{\text{EP5065}}$ is 25 MPa (Table 2). It is noteworthy that all reference pretreatment methods reached the expected shear strength specified by the manufacturer ($\tau_{\text{AC}} = 26.1^{+3.6}_{-1.2}$, $\tau_{\text{P}} = 24.2^{+3.1}_{-2.7}$ and $\tau_{\text{SB}} = 26.1^{+1.5}_{-2.4}$). Also, the scatter range remains in the same interval from 3.9 to 5.8 MPa as the following laser-based pretreatments.

Comparing all laser-pretreatment processes, an average $\tau$ in a range of $\tau_{\text{NIR71.2}}$ 19.2$^{+2.0}_{-3.1}$ MPa (77%) to $\tau_{\text{NIR02.3}}$ 25.5$^{+2.2}_{-1.1}$ MPa (102%) was achieved. Increasing ED$_{\text{Area}}$ stepwise up to 48.6 J/cm², $\tau$ remained on a high level above 90 % of the expected value. With a further increase of the energy input we observed a decrease of the shear strength to $\tau_{\text{NIR71.2}}$ 19.2$^{+2.0}_{-3.1}$ MPa (77%). As is to be expected, the scatter range of the shear strength shows an opposite trend and assumes a maximum of 5.1 MPa at an ED$_{\text{Area}}$ of 71.2 J/cm². For the UV-laser pretreatment exhibit a similar correlation, that the UV40.0 pretreatment generates a higher shear strength in comparison with UV80.0 (22.5 MPa vs. 20.7 MPa). However, $\tau_{\text{UV80.0}}$ 20.7$^{+1.4}_{-1.5}$ MPa remains higher compared to the NIR-pretreatment on a higher level overall compared to the NIR-pretreatment with ED$_{\text{Area}}$ of 71.2 J/cm².

Loctite UK 2015: Overall we observed shear strength in range of 77% and 93% of the data sheet value for all different types of pretreatment ($\geq$ 20 MPa). The polyurethane-based adhesive achieved on an acetone cleaned and sand blasted specimen
(τ_{AC} = 19.1^{+0.3}_{-1.7} \text{ MPa}, \quad τ_{SB} = 18.2^{+0.9}_{-0.7} \text{ MPa}) an high shear strength. However, the plasma treatment has reached only τ_p 14.8^{+4.3}_{-1.9} \text{ MPa or approximately. 74 % of the other reference processes. For laser-treated specimen a shear strength at an ED_{Area} between 2.3 and 16.8 of 15.1^{+0.8}_{-0.7} \text{ MPa and } 12.9^{+0.6}_{-2.8} \text{ MPa, respectively, was found. With further ED_{Area} increase the highest shear strength appeared at NIR28.6, NIR37.3 (τ_{NIR28.6} = 18.7^{+1.5}_{-1.6} \text{ MPa, } τ_{NIR37.3} = 18.3^{+2.5}_{-2.4} \text{ MPa}) as well as UV40.0 (τ_{UV40.0} = 19.2^{+1.1}_{-1.3} \text{ MPa). Comparable to EP 5065, the shear strength of laser treated samples decreases significantly with high energy input to τ_{NIR71.2} = 16.8^{+1.4}_{-1.4} \text{ MPa and } τ_{UV80.0} = 15.5^{+3.2}_{-2.9} \text{ MPa.}

HP-E60K: We already investigated the performance of HP-E60K for hybrid joints of Hexcel HexPly® and aluminum for acetone cleaning and the laser pretreatment [7]. With a total range of 52 to 124 %. Therefore, the adhesive is much more sensitive to the different types of pretreatment compared to the other two species mentioned above. For the reference process a solely sand blasted treated specimen showed the performance maximum of 17.4^{+4.5}_{-1.8} \text{ MPa. Distinctive drops of the shear strength occurred with acetone cleaning } 7.2^{+0.5}_{-0.8} \text{ MPa and plasma treatment } 9.1^{+0.9}_{-0.8} \text{ MPa. However, the spread of the measured values shows the opposite trend and is reduced by a factor of approximately four making the treatment process more stable.}

With a CFPR pretreatment in between ED_{Area} of 2.3 to 28.6 J/cm² the shear strengths are steadily located around 11.8 MPa and then jump to 16.2^{+4.1}_{-5.3} \text{ MPa at } 37.3 \text{ J/cm². With further increasing ED_{Area} of 48.1 J/cm² and 71.2 J/cm² the shear strength decreases again but stays at approximately. } τ = 14 \text{ MPa above the level of the low ED_{Area} values. The scatter range drops stepwise from 5.8 MPa to 3.8 MPa at 48.1 or 71.2 J/cm², respectively.}

Additionally, the shear strengths, standardized strength in percent to the TDF of the adhesive manufacturer and the fracture behavior of the hybrid joints are given in Table 5 and Table 6.

3.3 Fracture patterns

The fracture patterns are evaluated visually (considering DIN EN 10365:2020 [46]). We observed adhesion failure on both adherents (AF), cohesion failure in the adhesives (CF), substrate near cohesion failure (SCF) and failures inside the CFRP (CSF). Different combination and percentage with the mentioned pattern occurred, see also Table 5 and Table 6. Overall, the fracture pattern within one pretreatment method varies with
the applied adhesive. In Figure 7 a), the breakage pattern with different sections is given with a NIR02.3 pretreatment. Thereby, sections with areas of black vertical structures are visible. The uprooted carbon fibers are visible in the breakage pattern in Figure 7 b) and c) due to the black horizontal lines inside the green UK 2015 and red HP-60k adhesive on aluminum side.

The EP 5065 joints with a NIR-density of 2.3 and 16.8 J/cm² have mostly CF failure inside the adhesive with teared out matrix and carbon fibers (CSF). With NIR02.3, small section of the breakage had a CSF between the CFRP matrix and the carbon fibers. Higher laser densities of 28.6 – 71.2 J/cm² lead to CF inside the adhesive (CF) and mostly a CSF breakage pattern on CFRP side. Thereby, teared out carbon fibers are visible. With the higher density, the CSF pattern is becoming dominant with the applied EP5065. The reference pretreatments AC, P and SB have mostly a CF breakage pattern inside the adhesive, however some sections in the boarder of the overlap area have an AF failure on aluminum side. The UV treatments led to CF breakage in the adhesive and small areas with CSF on CFRP side, in comparison to the NIR treatment, the amount is less than with NIR radiation. The breakage path leads with NIR16.8 – 71.2 from a CF pattern inside the adhesive into a CSF pattern on CFRP side. With UV radiation, CSF begins at the border of the overlap on CFRP side. With AC, P and SB treatment, AF pattern begins at the end of the overlap on aluminum side.

In contrast to this, the breakage behavior of UK 2015 is different. With NIR02.3 and NIR16.8, an AF + CSF takes place on CFRP side. Higher NIR treatments (NIR28.6 - NIR71.2) had mostly a CSF pattern on CFRP side with a reduced amount of CF pattern inside the adhesive. The reference methods acetone, sand blasting, plasma and UV-treatments exhibit a different pattern. With plasmatic and acetone treated surfaces, an AF breakage pattern on the CFRP side occur. Sand blasted and UV-treated specimens exhibit an AF pattern on the CFRP side and CF inside the adhesive. With all NIR and UV laser treatments, a clear fracture path is not discernible. With AC, P and SB treatment, the CF pattern begins on the border of the overlap on CFRP side.

With the HP-E60K, the breakage occurs on the CFRP side (CSF) and inside the adhesive (CF) with all NIR-energy densities. NIR-densities NIR37.3 and 48.6 lead to a pattern with a higher percentage inside the adhesive and less with SCF on CFRP side. Both mentioned NIR-densities have a higher shear strength. NIR71.2 also have a high shear strength, however the breakage pattern is mostly CSF on CFRP side and a few areas with CF inside the adhesive. The breakage pattern on the reference treatments acetone
and plasma is fully/nearly fully AF on the aluminum side. With sand blasting, the breakage takes place inside the adhesive and in a few areas as AF on aluminum side. With the UV-pretreatment, a mixed pattern of CF inside the adhesive and CSF inside the CFRP takes place. The breakage path with SB begins on aluminum side at the border of the overlap and goes into a CF pattern inside the adhesive. With NIR02.3 and NIR16.8, the CF pattern starts on the edge of the overlap on the CFRP side within den adhesive.

4. Discussion

4.1 Surface pretreatment and microstructural characterization

The investigations revealed that the ablation behavior of NIR-pretreatment can be classified in three grades: i) for NIR < 16.8 J/cm²: irregular matrix ablation with only limited fiber damage, ii) for NIR 16.8 - 28.6 J/cm² extensive ablation of matrix with line-like residual matrix and visible carbon fiber damage, respectively ablation and iii) for NIR ≥ 37.3 J/cm²: complete removal of matrix with significant carbon fiber ablation. Depending on the energy absorbed by the carbon fiber, de-polymerization of the matrix and associated volume expansion causes the matrix to be repelled by the recoil pressure [6,8]. At the same time fiber damage takes place, even for very low energy input (NIR16.8).

There are two effects. First, the absorption of the NIR-laser energy takes place almost completely through the carbon fibers [50]. Above a critical temperature of approx. 400°C [51], the carbon fibers are burned off under the atmosphere, narrowing the carbon or rounding off the ends. Second, some fibers have straight fracture surfaces. The reason for this is the anisotropic thermal expansion of the graphitic fibers, which become thicker and shorter with increasing temperature [52]. The matrix stretches in all directions due to the thermal expansion when heated. This leads to thermally induced tensions in the carbon fiber-matrix interface, which results in breaks in the carbon fiber [7]. If the CFRP is exposed with NIR radiation <16.8 J/cm² the surface appear white which indicate a damage of the fiber-matrix-adhesion [9], Figure 3 b), NIR02.3. UV-pretreated surfaces exhibit a change of the surface structure, the more the higher the energy input. With a higher energy input, the stresses in the carbon fibers are also rising due to the heat which causes more breakage and fiber damage. The investigation with different NIR-laser parameters also revealed that the laser energy density has a significant influence on the fiber damage. Comparable findings were done by Leone et al. [15], Sun et al. [16] and Genna et al. [17]. A damage free full ablation of the matrix is not possible with NIR-radiation.
Within cross section depth measurements, the visible fiber damage in the SEM images (Figure 3) are quantitatively shown (Figure 5, b)) where higher NIR energy densities led to a higher average exposed carbon fiber depth. With the focus of a full matrix ablation (NIR≥28.6), the average exposed carbon fiber depth is already higher than the average carbon fiber depth of the untreated CFRP. In case of the UV radiation, UV80.0 led to a fully exposure of the carbon fibers with a comparable average depth as the initial carbon fiber depth.

The measured surface roughness is rising with the exposed carbon fibers from initial $S_a = 3.16 \mu m$ to $5.77-6.97 \mu m$ (NIR28.6-71.2) mean arithmetic roughness. The roughness is thereby dominated by the exposed carbon fibers and not by the applied laser parameters. However, residue matrix particles on the surface radiated CFRP surface strongly increase the roughness at NIR16.8. As it is not possible to check the extent to which the matrix is still firmly bonded to the carbon fibers with this type of measurement, the roughness values obtained should be viewed with caution. On the other side, sandblasting enables a higher roughness as the NIR parameters with exposed fibers, Figure 5 b). This is not expected because the surfaces do not appear to be especially roughened on the macroscopic images, while the SEM images reveal surficial microscopic grooves and cracks with chipped matrix particles without exposed fibers. These grooves and cracks in the matrix may strongly increase the roughness. The explained coherences above lead to the conclusion that a surface parameter does not directly allow a statement about the achievable roughness.

The observed deepenings after UV-pretreatment with 40 J/cm² (Figure 3 a)) are most likely caused by thermoplastic particles which are embedded in the epoxy matrix and melt before the thermoset matrix is vaporized [53]. Due to the insufficient energy, the average removal of the matrix with UV40.0 is less than the doubled energy to UV80.0, where an almost complete fiber exposure can be achieved. In Reitz et al., UV80.0 already damaged the fiber-matrix adhesion in deeper sections of the CFRP [7]. The determination of free surface energy were only successful at low energy densities without matrix ablation due to critical changes in the surface state after structuring. At an energy density of NIR16.8 respectively UV40.0 and higher, the fibers are exposed over a large area which leads to high roughness (Figure 5 a)), open porosity and increased polarity, and consequently exerts a high spreading pressure on the test liquids. The deposited droplet spreads spontaneously on contact with the surface, regardless of its chemical composition, and thus contact angle measurement is no longer successful.
4.2 Shear strengths and fracture behaviour of hybrid joints

The different surface pretreatments allow for different mechanical lap shear strengths for all three adhesives. For each adhesive, one or more pretreatment methods/parameters can contribute to a tensile shear strength of the adhesive bond in the range of the expected tensile shear strength according the technical data sheets. However, the trends shown vary depending on the adhesive in combination with the pretreatment method. All three adhesives are discussed in more detail below.

Through the use of EP5065 all pretreatment methods show a high mech. tensile shear strength in the range of $\tau_{\text{EP5065}} = 19.2 - 26.1$ MPa ($\tau_{\text{EP5065,rel.}} = 77-105\%$). Either a sufficiently good wetting at AC/P or an increase in surface roughness lead to a tensile shear strength of 25 MPa. The trend of decreasing tensile shear strength with increasing laser energy density seen in Figure 6 can be justified as follows. With partial exposure of the carbon fibers (NIR02.3 and 16.8), the adhesive binds to the surface. However, it can be seen that already damaged fiber-matrix bonds cause the matrix to detach from the carbon fibers, Figure 9 a) & b). Thereby, most of the surface exhibit a cohesive failure inside the adhesive, see framed area in Figure 9 a). In some sections, areas with adhesion failure between matrix and carbon fibers are present, dashed section of Figure 9 a). A detailed view is given in Figure 9 b). Vertically running structures and isolated carbon fibers indicate that the fracture occurred between the matrix and the carbon fibers. However, this circumstance cannot be proven to lead to a measurable deterioration of the tensile shear strength. The matrix residues in NIR16.8, some of which lie over a large area, are also not sufficient to have a negative effect on the bonded joint. The reason for this may be that the low viscosity of the adhesive allows the detached matrix residues to flow around and fill the gaps between these residues and the carbon fibers. Comparable evidence was found in the work of Harder et al. [9] as well as Liu et al. [11]. If the laser processing is carried out with $\geq$NIR48.6, the tensile shear strength decreases noticeably. Reasons for this behavior may be the removed matrix and carbon fibers (Figure 5 b)), which increases the resulting adhesive gap from approx. 200 $\mu$m to up to 250 $\mu$m. A comparable result with decreasing strength was demonstrated by Sun et al. [16]. Another reason may be deep damage in the fiber composite due to a heat-affected zone. In the work of Harder et al. [9] and Reitz et al. [7], damage could be found in deeper areas of the fiber composite, an application of adhesive could not infiltrate and heal these areas. In exemplary selected SEM images Figure 8 a) & higher magnification at b) it can be shown that the breakage pattern on the aluminum side contains carbon fibers which do not show
any typical processing marks through the NIR laser pretreatment such as tapers (Figure 3, b)) or oxidations. This is an indication that the fracture plane went close to the surface in the CFRP through a damaged matrix-fiber-bond. Comparable fracture patterns also occurred at lower energy densities, see Table 5. Regarding the results with UV laser radiation, the reduction of the tensile shear strength with UV80.0 can also be explained by the slightly higher adhesive layer thickness as well as the also existing deep damage [7]. Another reason may be the lack of surface roughness. The white light interferometer measurements showed a significant higher roughness with UV40.0, compared to UV80.0. Sorrentino et al. showed that a structuring/topography of the matrix gives a very high tensile shear strength compared to full surface exposure of the matrix [27].

With the UK2015 adhesive, a different behavior can be explained with regard to the tensile shear strength depending on the pretreatment. With the pretreatment methods AC/P/SB, a strength close to the target tensile shear strength can be achieved. The reason for the lower strength with the pretreatments NIR02.3 and NIR16.8 can be explained by the higher viscosity of the UK2015, Table 2. This means that the matrix residues that have already been detached but are still on the surface cannot be infiltrated. A comparable finding was made by Liu et al. [11] with four different adhesives. Similar to the EP5065 adhesive, the shear strength curve of UK2015 is explained by increasing NIR laser energy densities. A maximum at NIR28.6-37.3 is indicated, with further increasing NIR laser energy density the tensile shear strength decreases due to a larger heat-affected zone and thus depth damage (fiber-matrix bond) in the CFRP. Torn fibers were found in the fracture pattern on the aluminum side. Also, a comparable situation is given with the UV laser pretreatment. The partial matrix ablation with UV40.0 performs better than the full ablation UV80.0. This coincides with the results of Goa et al. in which surfaces with partial ablation also achieved higher shear strengths than with complete ablation [29]. Furthermore, the assumption is that the UK2015 on carbon fibers, both NIR and UV pretreated, does not form the bond. Figure 10 a) & b) shows both a NIR37.3 and UV80.0 fracture surface on the aluminum side. Negative imprints of the carbon fibers can be seen, indicating that fracture has occurred there without carbon fibers being torn out. This suggests that oxidation and associated increase in roughness of the carbon fibers does not increase adhesion in combination with this adhesive and an AF breakage pattern takes place.

The mechanical shear strength of the HP-E60K varies more than the other two adhesives. The reference pretreatment sand blasting achieves the highest mechanical
strength of $\tau_{\text{HP-E60K}}$ 17.4 MPa ($\tau_{\text{HP-E60K,rel}}$ 124 %). The pretreatment by reference methods AC/P/SB and UV shows that the adhesive benefits from increased surface roughness, see Figure 5 a). The pretreatments SB, UV.40 allow a high tensile shear strength which exceeds the expected strength. The processes with no or little surface enlargement such as AC/P and NIR02.3 or NIR16.8 achieve lower strengths. With the NIR pretreatments, the reasons for this can be depth damage and insufficient wetting of carbon fibers, which are hidden by detached matrix residues. With the NIR pretreatment of $\geq$NIR28.6, the tensile shear strength runs along the expected tensile shear strength. However, the relative low amount of CSF breakage pattern of CFRP side with NIR laser treatment (Table 5 and Table 6) compared to the other adhesives can be explained due to the lower expected shear strength of the adhesive.

Relating to the constant high shear strengths of all adhesives with sand blasted surfaces, the results confirm the resistance of modern adhesives to surface contaminations by Wit et al. [2]. Also, correlation between the surface roughness in macro- or microscale have a positive effect on the shear strength. It can be also concluded, that the fiber damage and ablation, generated by NIR radiation, does not lead to a significant reduction in the strength and all three adhesives can achieved their expected shear strength on exposed carbon fibers. However, if the applied energy is to strong, the fiber-matrix adhesion in the sub-surface of the CFRP is damaged. In combination with high strength adhesives such as UK2015 and EP5065, the shear strength will be reduced. The NIR laser pretreatment also ablate with rising laser energy density more carbon fibers. This lead to a thicker adhesive layer of up to 250 µm at NIR71.2. With the adhesives UK2015 and EP5065, the achieved shear strengths reduces with rising laser energy density, which can be, beside if the rising sub-surface damages, a result of the thicker adhesive thickness.

5. Conclusion

In this work, two laser systems with different wavelengths were applied to pretreat the CFRP surface before bonding to aluminum. The aluminum substrate was laser structured with one parameter. In addition, acetone, plasma and sand blasting were used as reference treatment methods. The following conclusions can be drawn:

1. The variation of laser process parameters shows that the laser energy density can be a parameter to grade the machining intensity of the CFRP with laser radiation. The qualitative images (microscope, SEM) and quantitative depth measurements show that with increasing energy density, more matrix and subsequently carbon fibers are
removed. Therefore, it enables a direct comparison of different laser pretreatment parameters and allows the determination of the required energy input to depolymerize the matrix in the transition zone between carbon fibers and the thermoset matrix. However, the effects of similar ED\(_{\text{Area}}\) for different wavelengths are not comparable due to the wavelength-dependent absorption coefficient.

2. Depending on the applied adhesive and pretreatment method, the achievable mechanical strength varies. By applying the surface pretreatments sandblasting, NIR radiation with moderate laser energy density (NIR28.6-37.3) with full exposure of the carbon fibers as well as UV40.0 radiation to produce a matrix surface with high roughness, all three adhesives form an adhesion to the surface that is in the range of the expected cohesive strength.

3. The differences between the adhesives are particularly evident in the reference processes, a laser pretreatment with partial fiber exposure and a laser pretreatment with very high energy density. For example, the HP-60K adhesive shows that an increase in surface roughness (e.g. sandblasting, NIR parameters with fiber exposure and UV40.0 pretreatment with partial matrix removal) leads to higher tensile shear strengths.

The UK2015 forms a high tensile shear strength on smooth surfaces as well as on surfaces of higher roughness. However, the high viscosity of the adhesive means that matrix residues that have already been detached but remained on the fibers cannot be infiltrated, which reduces the tensile shear strength.

Pretreatment with high energy density (NIR>48.6 or UV80.0) results in a reduction of the achievable tensile shear strength to varying degrees. Two effects are at work here. On the one hand, the tensile shear strength decreases with increasing adhesive layer thickness due to the removal of matrix and carbon fibers. Secondly, increased heat input causes damage between the carbon fibers and the matrix near the surface of the CFRP. With higher expected tensile shear strength according the technical data sheets of the adhesive, the depth damage has a negative effect on the tensile shear strength if the weakened matrix-fiber bond near the surface in the CFRP can absorb lower stresses than the bond between the exposed carbon fibers and the adhesive. This leads to an altered fracture pattern inside the CFRP which torn-out carbon fibers are visible without typical processing traces i.e. tapered or oxidations due to the laser radiation.
4. With an NIR-laser source, a complete ablation of matrix without fiber ablation is not possible. In this publication, the ablation can be classified in three grades: a) for NIR $< 16.8 \text{ J/cm}^2$: irregular matrix ablation with limited fiber damage, b) for NIR $16.8 - 28.6 \text{ J/cm}^2$: extensive ablation of matrix with line-like residual matrix and visible carbon fiber damage, respectively ablation and c) for NIR $\geq 37.3 \text{ J/cm}^2$: complete removal of matrix with significant carbon fiber ablation. However, the superficial removal of the carbon fibers has no discernible negative influence on the tensile shear strength, provided that the machining is not stronger than NIR37.3.

Declaration of interest statement
No potential competing interest was reported by the authors.

Acknowledgements
This research was supported by Dr. R. Kohlstrung from Henkel AG & Co. KGaA and Dr. B. Faißt from TRUMPF Laser- und Systemtechnik GmbH.

Funding
This work was supported by the German Federal Ministry of Education and Research within the program “FH-Impuls” (Project SmartPro, Subproject InDiMat) under Grant 13FH4I03IA.
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[34] Alfano, M.; Lubineau, G.; Furgiuele, F.; Paulino, G. H. Study on the role of laser surface irradiation on damage and decohesion of Al/epoxy joints. *International


[54] Material Data Sheet - Hexcel HexPly UD M21 35% 286 T800S.


### Table 1: Mechanical characteristics of the CFRP and aluminum substrates

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unit</th>
<th>CFRP M21/T800s unidirectional</th>
<th>EN AW 5754, H22</th>
<th>EN AW 6082, T6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear strength</td>
<td>MPa</td>
<td>2700 [54]</td>
<td>220-270 [55]</td>
<td>≥310 [56]</td>
</tr>
<tr>
<td>Elastic moduli</td>
<td>MPa</td>
<td>170.000 [54]</td>
<td>70.500 [55]</td>
<td>70.000 [56]</td>
</tr>
<tr>
<td>Poisson coefficient</td>
<td>-</td>
<td>0.35 [57]</td>
<td>0.33 [58]</td>
<td>0.33 [58]</td>
</tr>
<tr>
<td>In-plane strengths</td>
<td>MPa</td>
<td>165 [57]</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

### Table 2: Technical specifications of the used adhesives HP-E60K, TEROSON® EP 5065 and LOCTITE® UK 2015 [59–61] for adhesive bonding of CFRP/AlMg3 joints

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Name</th>
<th>Chemical base</th>
<th>Color of the mixture</th>
<th>Viscosity in Pa s</th>
<th>Pot life</th>
<th>Curing time in min</th>
<th>Curing temperature T in °C</th>
<th>Shear strength τ in MPa</th>
<th>Adhesive film thickness t in mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HP-E60K</td>
<td>2-C epoxides</td>
<td>transparent/ red&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7 - 9.5 (at 23 °C)</td>
<td>1h</td>
<td>80</td>
<td>80</td>
<td>≥14</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>EP 5065</td>
<td>2-C polyurethane</td>
<td>black</td>
<td>23 (at 23 °C)</td>
<td>1h</td>
<td>30</td>
<td>75</td>
<td>≥25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UK 2015</td>
<td></td>
<td>green</td>
<td>350 - 700 (at 20 °C)</td>
<td>6 - 10 min</td>
<td>75</td>
<td>75</td>
<td>≥20</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<sup>a</sup>Colored with mineral pigment

### Table 3: Technical specifications of NIR- and UV-laser sources

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unit</th>
<th>TRUMPF TruMark 5020</th>
<th>TRUMPF TruMark 6350</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>λ in nm</td>
<td>1062</td>
<td>355</td>
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<tr>
<td>Average power</td>
<td>P&lt;sub&gt;avg&lt;/sub&gt; in W</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Beam quality</td>
<td>M&lt;sup&gt;2&lt;/sup&gt;</td>
<td>&lt; 2</td>
<td>&lt; 1.5</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>t&lt;sub&gt;i&lt;/sub&gt; in ns</td>
<td>t&lt;sub&gt;i&lt;/sub&gt; = 9 – 200</td>
<td>-</td>
</tr>
<tr>
<td>Pulse width</td>
<td>t&lt;sub&gt;w&lt;/sub&gt; in µs</td>
<td>-</td>
<td>t&lt;sub&gt;w&lt;/sub&gt; = 1 – 50 at 20 kHz</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>f&lt;sub&gt;p&lt;/sub&gt; in kHz</td>
<td>1 – 1000</td>
<td>1 – 120</td>
</tr>
<tr>
<td>Scanner head</td>
<td>-</td>
<td>Scanlab ScanCube 10</td>
<td>Scanlab intelliSCAN 10</td>
</tr>
<tr>
<td>Focal length</td>
<td>f in mm</td>
<td>160 / 254</td>
<td>160</td>
</tr>
<tr>
<td>Focal diameter</td>
<td>d&lt;sub&gt;f&lt;/sub&gt; in µm</td>
<td>72 / 114</td>
<td>36</td>
</tr>
</tbody>
</table>
Table 4: UV- and NIR-laser parameters for surface preparation of CFRP and aluminum AlMg3

<table>
<thead>
<tr>
<th>Laser source</th>
<th>Material</th>
<th>NIR</th>
<th>UV</th>
<th>NIR</th>
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<tr>
<td>Characteristics</td>
<td>Unit</td>
<td>2.3</td>
<td>16.8</td>
<td>28.6</td>
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<tr>
<td>Average laser power</td>
<td>$P_{\text{avg}}$ in W</td>
<td>12.0</td>
<td>20.5</td>
<td>20.5</td>
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<td>Pulse repetition rate</td>
<td>$f_{\text{rep}}$ in kHz</td>
<td>100.0</td>
<td>103.0</td>
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<tr>
<td>Pulse power</td>
<td>$P_{p,\text{max}}$ in kW</td>
<td>1.48</td>
<td>4.10</td>
<td>7.72</td>
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<tr>
<td>Pulse duration</td>
<td>$t_L$ in ns</td>
<td>30</td>
<td>100</td>
<td>70</td>
</tr>
<tr>
<td>Pulse width</td>
<td>$t_w$ in µs</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Spot diameter</td>
<td>$d_o$ in µm</td>
<td>114</td>
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<td>-</td>
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<tr>
<td>Hatch distance</td>
<td>$d_{\text{hatch}}$ in µm</td>
<td>104</td>
<td>25</td>
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<td>Scanner velocity</td>
<td>$v_{\text{scan}}$ in mm/s</td>
<td>5000</td>
<td>1175</td>
<td>690</td>
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<tr>
<td>Energy density</td>
<td>$ED_{\text{Area}}$ in J/cm²</td>
<td>2.31</td>
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<tr>
<td>Pulse overlap</td>
<td>PO in %</td>
<td>56.3</td>
<td>90.0</td>
<td>90.0</td>
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<tr>
<td>Track overlap</td>
<td>TO in %</td>
<td>9.2</td>
<td>-</td>
<td>-</td>
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Table 5: Results of shear strength in MPa and normalized in percent to TDS plus fracture pattern of CFRP/Al single-lap joint specimens bonded with HP-E60K, EP 5065 and UK 2015 after NIR-surface pretreatments on CFRP with different energy densities in ascending order. Estimated percentage of the fracture pattern amount of each sample batch

<table>
<thead>
<tr>
<th>Name</th>
<th>Unit</th>
<th>NIR02.3</th>
<th>NIR16.8</th>
<th>NIR28.6</th>
<th>NIR37.3</th>
<th>NIR48.1</th>
<th>NIR71.2</th>
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</thead>
<tbody>
<tr>
<td>EP 5065</td>
<td>MPa</td>
<td>25.5±2</td>
<td>25.0+1.0</td>
<td>23.6+1.8</td>
<td>24.9+1.6</td>
<td>23.3+1.0</td>
<td>19.2+2.0</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>102</td>
<td>100</td>
<td>94</td>
<td>100</td>
<td>93</td>
<td>77</td>
</tr>
<tr>
<td>Fracture pattern</td>
<td>40% CSF CFRP</td>
<td>80% CSF CFRP</td>
<td>80% CSF CFRP</td>
<td>80% CSF CFRP</td>
<td>90% CSF CFRP</td>
<td>90% CSF CFRP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>60% CF Adhes.</td>
<td>20% CF Adhes.</td>
<td>20% CF Adhes.</td>
<td>20% CF Adhes.</td>
<td>10% CF Adhes.</td>
<td>10% CF Adhes.</td>
</tr>
<tr>
<td>UK 2015</td>
<td>MPa</td>
<td>15.1±0.8</td>
<td>12.9±0.6</td>
<td>18.7±1.5</td>
<td>18.3±2.5</td>
<td>16.7±1.2</td>
<td>16.8±1.4</td>
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<td></td>
<td>%</td>
<td>75</td>
<td>65</td>
<td>93</td>
<td>91</td>
<td>84</td>
<td>84</td>
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<tr>
<td>Fracture pattern</td>
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<td>30% AF CFRP</td>
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<td>NA</td>
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<tr>
<td></td>
<td>%</td>
<td>30% CF Adhes.</td>
<td>50% CF Adhes.</td>
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</tr>
<tr>
<td></td>
<td>%</td>
<td>40% CF Adhes.</td>
<td>20% CF Adhes.</td>
<td>30% CF Adhes.</td>
<td>20% CF Adhes.</td>
<td>20% CF Adhes.</td>
<td>20% CF Adhes.</td>
</tr>
<tr>
<td>HP-E60K</td>
<td>MPa</td>
<td>11.7±1.5</td>
<td>11.6±2.7</td>
<td>12.0±2.8</td>
<td>16.2±5.1</td>
<td>14.2±4.4</td>
<td>14.0±1.3</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>84</td>
<td>83</td>
<td>86</td>
<td>116</td>
<td>101</td>
<td>100</td>
</tr>
<tr>
<td>Fracture pattern</td>
<td>30% CSF CFRP</td>
<td>80% CSF CFRP</td>
<td>80% CSF CFRP</td>
<td>20% CSF CFRP</td>
<td>40% CSF CFRP</td>
<td>90% CSF CFRP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>70% CF Adhes.</td>
<td>20% CF Adhes.</td>
<td>20% CF Adhes.</td>
<td>80% CF Adhes.</td>
<td>60% CF Adhes.</td>
<td>10% CF Adhes.</td>
</tr>
</tbody>
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Table 6: Results of shear strength in MPa and standardized in percent to TDS and fracture modes of CFRP/Al single-lap joint specimens with bonded with HP-E60K, EP 5065 and UK 2015 after reference surface pretreatments on CFRP with reference processes. An estimated percentage of the fracture pattern amount of each sample batch is given

<table>
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<tr>
<th>Name</th>
<th>Unit</th>
<th>AC</th>
<th>P</th>
<th>SB</th>
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<th>UV80.0</th>
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<tr>
<td>EP 5065</td>
<td>MPa</td>
<td>26.1±1.2</td>
<td>24.2±1.1</td>
<td>26.1±1.5</td>
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<td>%</td>
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<td>97</td>
<td>105</td>
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<td>20%</td>
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<td>AF Al</td>
<td>CSF CFRP</td>
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<td>80%</td>
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<td>UK 2015</td>
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<td>74</td>
<td>91</td>
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<td>AF CFRP</td>
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<td>CF Adhes.</td>
<td>70%</td>
<td>CF Adhes.</td>
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<tr>
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<td>CF Adhes.</td>
<td>70%</td>
<td>CF Adhes.</td>
<td>70%</td>
<td>CF Adhes.</td>
</tr>
<tr>
<td>HP-E60K</td>
<td>MPa</td>
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<td>17.4±5.1</td>
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<td>%</td>
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<td>124</td>
<td>107</td>
<td>90</td>
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<td>10%</td>
<td>10%</td>
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<tr>
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<td>AF Al</td>
<td>AF Al</td>
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<tr>
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<td>CF Adhes.</td>
<td>90%</td>
<td>CF Adhes.</td>
<td>90%</td>
<td>CF Adhes.</td>
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</tbody>
</table>
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Figure 2: a) Shear strength test according to DIN EN 1465:2009 \cite{47} with mounted frame b) Sketch of range of interest (ROI) after shear test c) Representative fracture pattern of laser pretreated CFRP-surfaces (upper image: CFRP substrate, lower image: aluminum substrate).
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Figure 5: a) Arithmetic roughness $S_a$ in µm of the initial and pretreated surfaces of CFRP and Aluminum. b) Average exposed carbon fiber depth in µm of the initial CFRP and of NIR/UV parameter with carbon fiber exposure
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