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CFRP bonding pre-treatment with laser radiation of 3 µm wavelength: influence of different treatment parameters

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Abstract

Due to the mold-based production of composite parts, the surfaces are contaminated with mold-release agent residues. Those contaminations hinder the adhesion of the surface and therefore prevent the structural adhesive bonding of the untreated parts. To achieve and guarantee a durable bond, a surface pre-treatment prior to the bonding process is inevitable. Laser radiation is promising, but unfortunately common laser sources have a high risk to cause material damage. The bad absorption (IR-laser) or the high amount of thermal interaction (CO_2-laser) hinder the establishment of this treatment method in industrial applications. To solve this problem laser radiation of 3 µm wavelength (which has a high absorption inside the resin and less thermal interaction) was generated by frequency conversion of an industrial IR laser and applied to the composite. The results show a good and sensitive treatment of the surface, resulting in high bonding strengths.

Keywords: Surface treatment; ablation, composite frequency conversionyour

1. Introduction

A reduced product weight can increase its specific performance significantly. For example, the CO_2 emissions of cars with conventional drive systems can be decreased by reducing the weight of the car and therefore its eco efficiency resp. performance is increased. The reduction of structural weight also increases

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the performance of cars with an electrical engine or airplanes by enlarging their range. One approach to reduce the structural weight is the application of components, which are manufactured out of carbon fiber reinforced plastics (CFRP). While the application of this material is favored by the specific properties (e.g. stiffness), its processing and out of the process resulting facts are relevant challenges to establish this material class. Besides high material costs, the cycle times in which the CFRP-parts can be produced are relatively high and therefore the acceptance in the automotive industry is relatively low. In addition, one of the most relevant reasons hindering the application of CFRP-parts, is the joining technology. For thermoset CFRP traditional joining technologies (especially welding) are not usable and mechanical joining technologies (for example riveting) weaken the structure by destroying the load-bearing fibers. However, an efficient joining of those parts is theoretically possible by adhesive bonding due to the favorable load distribution in the joint. To achieve a durable bond, a sufficient adhesion between the adhesive and the CFRP has to be guaranteed. Unfortunately, the adhesion is reduced by the presence of mold-release agent residues and other contaminations and therefore the bonding performance is limited [Parker and Waghorne, 1982].

Due to that fact, a bonding pre-treatment of the CFRP surface prior to the application of the adhesive is necessary to achieve the goal of a high performing joint, which allows an embedding of the CFRP-part in the entire structure to increase the product performance.

2. State of the art

Mold release agents (for example silicones) are necessary to guarantee the demolding of the cured CFRP-parts. Unfortunately, during the curing of the thermoset resin, parts of the mold release agent diffuse into the resin of the future part and remain on the surface. The presence resp. absence of these surface contaminations is the relevant question for the bonding performance. Therefore, the task for a good surface pre-treatment is to provide a reproducibly clean surface without any contaminations.

2.1. CFRP bonding pre-treatment

The first applications of CFRP-parts were products, which did not have a high production volume (sports cars or airplanes). Based on this fact, classical pre-treatment methods are also limited in terms of process speed. Those methods are namely the application of so-called peel-plies or manual grinding processes [Holtmannspötter et al., 2013]. Peel-plies are fabrics, which are laminated on top of the structural fibers of the CFRP part prior to curing and torn out after the curing process. This process prevent the presence of mold release agents but it is relatively time-consuming and some residues of the peel-ply can remain on the surface. The other conventional approach (and still in application in the aviation industry) is the manual grinding of the surface. In addition to high process times, this method has the disadvantage that there is a high risk of destroying the fibers and reduce the structural performance of the part.

Besides those methods, which have a bad automatization potential, there are methods, which allow an automated bonding pre-treatment. The most relevant method is the pre-treatment with an atmospheric plasma [Kusano et al., 2007]. Due to the treatment with a plasma jet, the surface of the CFRP is on the one hand slightly cleaned (dust or fingerprints can be removed) but on the other hand the good bonding performance after a plasma pre-treatment can be justified by the activation of the surface due to the deposition of functional groups on the polymer surface. Unfortunately, the cleaning effect of this method is relatively low and therefore the highly relevant contaminations, which are caused by the mold release agent, cannot be reliably removed without damaging (etching) the polymer matrix. A method, which allows the removal of those contaminations, is the pre-treatment of the surface within a blasting process. However, the process has disadvantages in terms of the environmental contamination (classical grit blasting) or part geometry (low pressure blasting) [Kreling et al., 2014].

2.2. Application of laser radiation

An alternative approach for the bonding pre-treatment is the application of laser radiation. Based on its contactless interaction, the application has a good automatization potential considering the geometry freedom and the almost wearless application. Nevertheless, the interaction between the laser radiation and the material is highly depending on the applied wavelength and the correlating absorption of the radiation inside the resin and the photon energy.

The application of laser radiation for the treatment of un- and reinforced plastics has been widely investigated. The first investigations were made in the 1980's when UV-lasers were used for the pre-treatment of unreinforced plastics. Due to the relatively good absorption and the potential for a photochemical ablation, a smooth and controllable ablation could be stated for unreinforced [Kawamura et al., 1982; Andrew et al., 1983] and carbon fiber reinforced plastics [Galantucci et al., 1996]. Although, a sufficient ablation process and therefore a good bonding pre-treatment is possible with UV-laser sources [Kreling et al., 2013], the industrial application for a bonding pre-treatment is hindered by the high investment costs and the fact, that the beam cannot be guided within a fiber.

The surface treatment with laser radiation with wavelengths in the range of 1 µm has on the one hand the advantage, that the investment costs are relatively low and those lasers have a high potential to be implemented in a production environment due to their fiber guidance possibility. On the other hand, the absorption of this radiation inside the top resin layer is bad and therefore the laser energy is nearly completely absorbed inside the carbon fibers. Due to this fact, there is a high risk to cause delaminations between the top resin and the first fiber layer and between the first and the second fiber layer [Fischer et al., 2012]. Nevertheless, also these laser sources can be used for a sufficient bonding pre-treatment by a complete removal of the top resin layer and a subsequent bonding on the exposed fibers [Kreling, 2015; Reitz et al., 2017] but the process window is relatively small, which almost exclude their industrial application.

Concerning the absorption inside the resin, the radiation emitted from CO_2 laser (> 9000 nm) sources is favorable due to its high absorption. However, the pre-treatment efficiency is limited by the low photon energy of the emitted radiation [Garrison and Srinivasan, 1985]. Based on this fact, the ablation of chemically bonded contaminations is only possible by breaking up the chemical bonds. Therefore several photons have to interact with the chemical bond and the related vibration of this bond lead to a failure of this bond. This interaction finally leads to the ablation process, but is correlated with a relatively strong heat development. This temperature is one major disadvantage of a pre- with these radiations, because it increases the risk of a thermal degradation of the matrix, which lowers the substrate performance [Kreling, 2015]. However, a sufficient pre-treatment with a removal of the contaminations is possible with those laser sources [Kreling, 2015; Hartwig et al., 1997] but the experimental set-up (including beam guidance by mirrors) and the thermal degradation of the pre-treated CFRP limit the application for an industrial bonding pre-treatment.

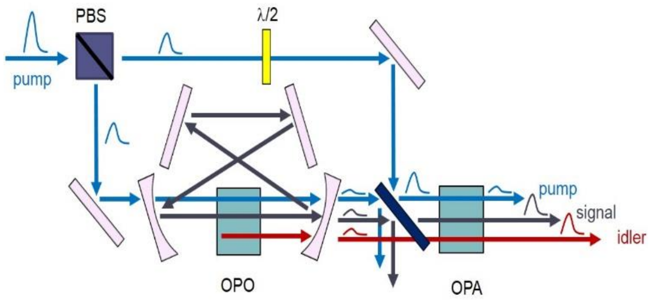
Besides the application of these conventional wavelengths, the application of wavelength in the range of 3 µm shows several advantages. The absorption inside the epoxy resin is high and the photon energy is higher compared to CO_2 lasers, which lowers the risk of a thermal damage. While this radiation is if at all used for medical applications [Walsh et al., 1989; Stern et al., 1988], there are already investigations shown by the authors about its interaction with un- and reinforced plastics [Blass et al., 2016]. In the presented investigations it could be shown, that the ablation based on a treatment with 3 microns wavelength is a top-down process, which allows the removal of surface contaminations.

3. Experimental set-up

Within the presented examinations, representative CFRP-specimens were treated with laser radiation, subsequently bonded and afterwards tested to quantify the bonding performance and therefore the pre-treatment efficiency.

3.1. Laser system

The output of an industrial solid state IR laser (CleanLASER CL 150, Clean-Lasersysteme GmbH, Herzogenrath, Germany) was frequency converted from 1 µm to 3 µm. The laser provides up to 105 W of average power at a pulse duration of 120 ns and a pulse frequency of 11 to 15 kHz. The randomly polarized output and limited beam quality ($M^2 = 18$) of the laser represent a challenge, however, for efficient conversion. The conversion setup is implemented as a two-stage scheme comprising an optical parametric oscillator (OPO) as to generate the target wavelength and an optical parametric amplifier (OPA) as to amplify the OPO output and to utilize the full power of the randomly polarized fundamental laser source, (see fig. 1). The conversion setup and first results of the OPO performance have already been presented in [Blass et al., 2016]. An optimized setup using high quality periodically poled lithium niobate (PPLN) crystals allowed for the generation of 8 W at 3 µm wavelength and 12 kHz pulse frequency out of the OPO and a subsequent amplification to 16 W in the OPA. This corresponds to a pulse energy of 1.33 mJ. The output is led into a process chamber comprising a galvanometer scanner and an F-Theta optics allowing for a machining area of 20x20mm² in the processing experiments.



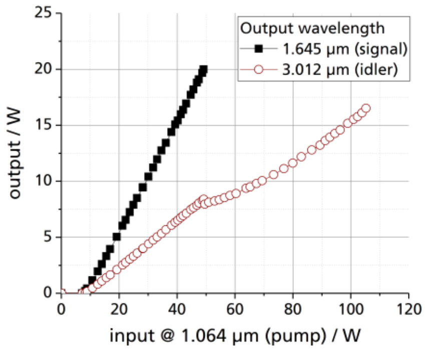


Fig. 1. Scheme of the frequency conversion setup (left) and characteristic curve of the two-stage frequency converter (right): The first portion up to 50 W of input belongs to the OPO, the part above 50 W represents the amplification by the OPA.

3.2. Materials and measurements

The CFRP-specimens were manufactured out of a typical aerospace prepreg system (HexPly® 913, HTS fiber from Hexcel Composites GmbH Stade, Germany) which has a curing temperature of 125 °C. The lay-up was chosen to be $[0°/90°/0°/90°/0°]_s$ which results in a post-cure thickness of roughly 2.5 mm. The CFRP plates were manufactured in an autoclave with an applied pressure of 7 bar, while the vacuum was approx. -0.8 bar compared to the atmosphere. To achieve typical surface contaminations the mold was coated with a polysiloxane-based release agent (Chemlease® R&B EZ from Chem-Trend L.P. Howell, Michigan, United States) and no additional release film was applied.

The demolded CFRP plates were cut with a water-cooled circular saw. After the laser pre-treatment with a single scanning process, the specimens were bonded with a typical one component epoxy based adhesive (3M^{TM} Scotch-Weld^{TM} Structural Adhesive Film AF 163-2K from 3M corp. St. Paul, Minnesota, United States) with a curing temperature of 125°C and a post-cure thickness of around 0.1 mm was used.

The bonding performance and the correlating efficiency of the bonding pre-treatment was mechanically tested within the single lap shear test (following to DIN EN 1465). Due to the size of the machining area, the width of the specimens was reduced to 20 mm and the testing rate was set to 10.0 mm/min. The mechanical tests were performed using a universal testing machine Instron 5584 (Instron Deutschland GmbH, Darmstadt, Germany).

To compare the different pre-treatment parameters, the applied aerial energy was calculated by multiplying the average amount of laser pulse hits per surface increment with the laser pulse fluence (following Kreling, 2015).

4. Results and discussion

The aim of the experiments presented in this paper was to prove the effectiveness of a laser based bonding pre-treatment with a radiation wavelength of 3012 nm. Furthermore, the influence of different pre-treatment parameters resp. treatment strategies should be investigated.

As mentioned before, due to the mold-based fabrication of CFRP, the initial bondability of untreated CFRP specimens is bad which results in low bonding strength based on an adhesion failure between the CFRP specimen and the adhesive (see fig. 2 a). To achieve higher bond strengths the failure should occur inside the adhesive (cohesion failure see fig. 2 b) which represents the maximum performance of the adhesive.

Fig. 2. Representative fracture patterns: (a) adhesion failure (AF); (b) cohesion failure (CF); (c) substrate close cohesion failure (SCF)

This fact is also visible within this investigation. Focusing the lap shear strengths of the untreated specimens in figure 3, there is a clear difference between the untreated specimens and mechanically abraded specimens, which represents the reference specimens.

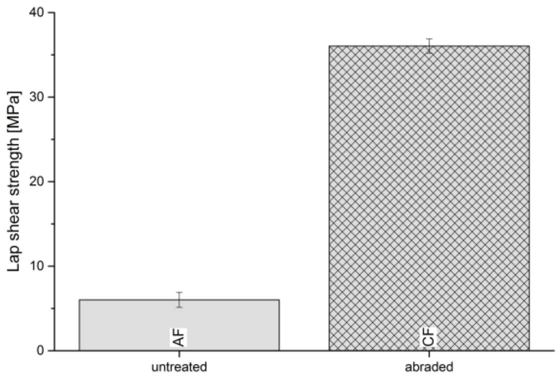


Fig. 3. Lap shear strengths of untreated and mechanically abraded specimens (reference)

The untreated specimens show a clear adhesion failure which results in a lap shear strength of 6.03 ± 0.89 MPa. In contrast, the lap shear strength of the reference specimens is 36.04 ± 0.83 MPa and also the failure mode changes to an cohesion failure.

Due to the fact, that the pre-treatment should as intense as needed and as sensitive as possible [Chin and Wightman, 1996], the initial pre-treatment strategy was to identify the effective aerial energy (by adapting the scan speed and therefore the pulse overlap), which results in a sufficient cleaning of the surface and therefore good bonding strength. The results of this approach are shown on the left side of figure 4. Besides, the variation of the average output power resp. the pulse fluence is shown in this diagram. Focusing the results, it can be seen that a treatment with an aerial energy of 20 mJ/mm² do not lead to a sufficient cleaning and results in a lap shear strength around 10 MPa with an adhesion failure. The increase of the treatment intensity to an aerial energy of 45 mJ/mm² significantly improve the lap shear strength. Both parameter sets show a mixed failure consisting out of parts with an adhesion failure and parts with a substrate close cohesion failure (cf. fig. 2. c) which already indicates a fairly good cleaning process. The specimens treated with average output power of 7.5 W achieve a lap shear strength of 24.50 ± 3.39 MPa and those treated with 5 W average output power show a lap shear strength of 20.36 ± 4.27 MPa. This difference can be justified by the mode of action of the contamination removal. The contaminated layer is removed by removing small parts of this layer with a single laser pulse. If the fluence is higher, the amount resp. the volume of removed contamination layer is increased. Therefore, the cleaning effect is better, for treatments with higher pulse fluences. For smaller fluences the ablation is more depending on the spot overlap and a superimposed effect of several laser pulses, which all remove only a small volume of the contamination layer. This effect becomes visible for the highest applied treatment intensities. By increasing the treatment intensity to 90 mJ/mm², the bondability is comparable with the reference specimens and is in the range of 32 MPa. In contrast to the strength of the reference specimens, the scatter band is increased, which indicates, that the cleaning effect is on the border to be fully sufficient. This is underlined by the fracture patterns, which are dominated by a cohesion resp. a substrate close cohesion failure. In this case the difference in terms of the pulse fluence is neglected by the relatively high spot overlap of around 90 % and the accumulated ablation, which is finally higher than or in the range of the thickness of the contamination layer.

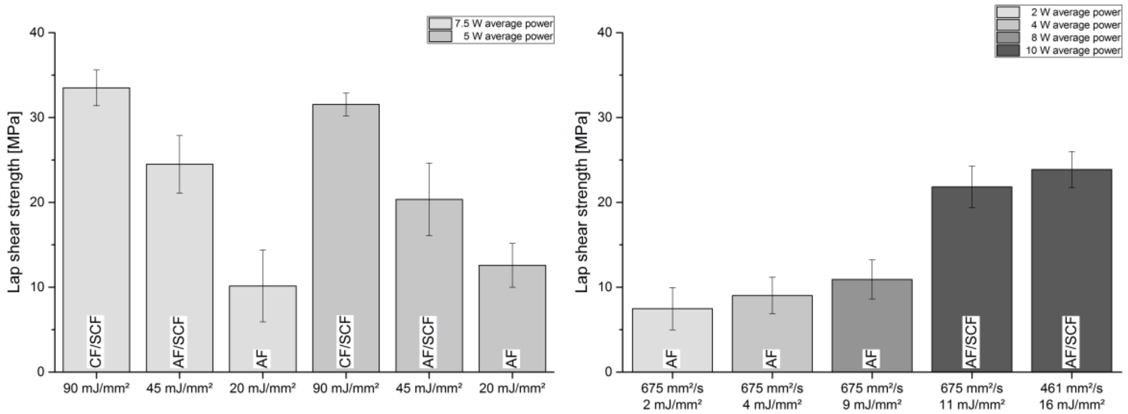


Fig. 4. Lap shear strengths for the variation of aerial energy (left) and clad rate (right)

The diagram on the right side of figure 4 shows the variations in terms of the clad rate and the aerial energy. Due to aim to establish the presented pre-treatment method in industrial processes, the clad rate should be as high as possible. Therefore, the clad rate was set relatively high to 675 mm²/s or 461 mm²/s and the aerial energy (also named in the diagram) was varied by changing the average output power. As seen before, a treatment with aerial energy under 20 mJ/mm² and average output power of below 10 W do not result in a sufficient cleaning and therefore the bonds fail with adhesion failures and low lap shear strengths. In contrast to the previously mentioned results, the treatment with aerial energy of 11 resp. 16 mJ/mm² and a relatively high pulse fluence (based on the average output power of 10 W) already show a cleaning effect. Even if the cleaning effect is still limited and the fracture pattern always show parts of adhesion failure, there is a significant increase in terms of the lap shear strength of roughly 350 % or almost 400 % compared to untreated specimens. Here, the mentioned effect of the impact of the pulse fluence becomes more obvious. Although the trend is already visible comparing the treatment with 2, 4 and 9 mJ/mm², the effect is especially visible comparing the treatment with 9 and 11 mJ/mm². Between these parameters, the spot and line overlap remained constant and only the pulse fluence was increased by roughly 27 % from 7.55 to 9.61 mJ/mm². This leads to a significant increase of the lap shear strength due to the more intense removal of the contamination layer, resulting in a less contaminated surface.

The mentioned effect of the pulse fluence impact is independent from the creation mode. As well the above presented investigations in which the pulse fluence was varied by changing the average power as investigations in which the pulse repetition rate underline the positive effect of an enlarged pulse fluence.

5. Conclusions

The shown examinations prove the effectiveness of a CFRP bonding pre-treatment with laser radiation of 3012 nm wavelength. By increasing the treatment intensity, the bonding performance (measured within the single lap shear test) could be constantly increased which indicates a sensitive and effective cleaning of the surface.

Furthermore, the pulse fluence respectively the pulse energy could be identified as the main influence parameter, while the other parameters (e.g. scan speed) can be equalized by others. With increased pulse energy a significant cleaning effect was already visible for small aerial energies, resulting in major increases of the bonding performance.

Further investigations have to be done once in terms of the influence of additional laser parameters (especially the pulse duration) and second the bonding performance after the laser treatment has to be quantified in additional load cases (above all under peeling loads) and after aging.

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