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Surface Structuring of CFRP by Using Modern Excimer Laser Sources

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Abstract

High demands for lightweight construction can be attained by the use of carbon fiber-reinforced plastics (CFRP) including one major challenge: the joining technology. Adhesive bonding may allow an increased utilization of the lightweight potential of CFRP. But this technology requires a surface pre-treatment because of residues of release agents. This paper describes surface pre-treatment of CFRP specimens by using modern excimer laser and the mechanical tests that compare the achieved strength to manually abraded ones. The laser process is suitable for achieving cohesive failure within the adhesive and bond strengths in the magnitude of the abraded specimen.

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1. Motivation /State of the Art

Both, the automotive and the aviation industries show growing interest in lightweight structures which can be manufactured from carbon fiber-reinforced plastics (CFRP). However, the advanced properties of these materials can only be utilized if they are not used like “black metal sheets”, but if design and especially joining technology are adapted.

Punctiform joining methods like rivets, bolts or flow drill screws do not allow the utilization of the complete lightweight potential of fiber-reinforced plastics (FRP) because they cause damage in the load-carrying fibers and also lead to stress peaks in the areas of the inevitable holes. Structural adhesive bonding might be a way to take full advantage of the potential of FRP for lightweight construction. However, there are still some major challenges that have to be met to allow structural adhesive bonding, especially in industrialized processes. Two of these challenges are the efficient removal of release agents and other surface contaminations without damaging the load-carrying fibers and the exposure of the fibers

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to allow direct load introduction into the fibers. The latter is required because, in adhesive bonds, the load is not introduced into the bulk material as it is with mechanical fasteners, but through the surface, which makes weak surface layers critical to the achievable bond strength.

Lasers have been proposed as an alternative technique for machining of CFRP over the past 30 years. First experiments on laser machining of CFRP laminates have been conducted by Caprino and Tagliaferri [1] in the 1980s, with common IR sources. Cenna and Mathew [2] presented an overview of the development in IR laser cutting of fiber-reinforced plastics. As a matter of fact, photons emitted in the infrared range induce molecular and lattice vibrations (due to the so-called “Inverse Bremsstrahlung” phenomenon) which can be detected by an increase in temperature of the workpiece. As a direct consequence, a chemical degradation of the reinforcements increased delaminative effects. The use of ultrashort IR laser pulses for micromachining CFRPs also shows some limitations as demonstrated by Moreno et al. in [3]. In order to overcome the above-mentioned negative aspects, mainly due to thermal damaging, a first approach to laser engraving of CFRP was undertaken in the early 1990s by Tönshoff et al. [4]. Excimer lasers (wavelengths of 248 nm and 193 nm) were used to minimize the thermal effect and for a precise energy deposition. Authors found that HAZ of only 5–30 μm could be obtained for several material types, including unidirectional laminates. Also a new generation of diode-pumped solid-state (DPSS) lasers can be used to texture CFRP materials [5]; in these lasers, the beam quality allows an efficient frequency doubling or tripling using non-linear crystals to generate laser radiation in the UV-range (355 nm) with short pulses (typically between 15 and 50 ns), combined with high repetition rates of 200-300 kHz and a Gaussian beam profile of very high quality factor (M2 < 1.2). With both UV-laser sources this is due to the fact that photons emitted at these short wavelengths are characterized by high photon energies (see Table 1).

Table 1. Wavelengths and their corresponding photon energies

| Wavelength | λ [nm] | 1064 | 355 | 308 | 248 |
|------------|-------|------|-----|-----|-----|
| Photon Energy | E_ph [eV] | 1.17 | 3.48 | 4.02 | 5.00 |

The photon energy of laser radiation in the UV-wavelengths of 3.49eV to 5.00 eV enables the cracking of the molecular structure of the bulk material, carrying out smooth surfaces and clean edges. The polymer matrix material consists for the most part of covalent bonds, which have a binding energy of more or less 5.78 10−19 J or 3.61 eV. Actually, whether it is the photochemical or the photothermal nature of this bond scission is frequently argued, as reported by Sato and Nishio [6]. The authors suggested that both, photochemical and -thermal mechanisms, the latter due to energy release by excited molecules, contribute to the etching process.

Even if results obtained both with the excimer laser and the frequency tripled DPSS laser were very promising in the field of micro-machining, the laser system properties allow only a very low process speed (5-10 mm²/s with the excimer laser and up to 100 mm²/s with the DPSS laser), thus hindering the industrial use. Furthermore, the use of a small section of the large raw beam of an excimer laser with fixed masks limited the flexibility of the process and the availability of the total output power. Such drawbacks are now overcome by modern excimer laser sources which allow higher process speeds up to a few 1000 mm²/s, because of the efficient beam shaping. This beam shaping enables a laser spot with a rectangular geometry and the dimensions of 30.0 mm by 1.8 mm.

2. Experimental

This paper describes a modern excimer laser as a surface treatment system for CFRP bulk material.
The engaged laser system is the excimer laser LPX Pro™ 305 (Coherent (Deutschland) GmbH) with an average power of 30 W, a repetition rate of 50 Hz and pulse duration in a nanosecond range. The important system specifications are displayed in Table 2.

### Table 2. System specifications the two considered excimer lasers from the Coherent (Deutschland) GmbH

|                     | LPXpro™ Series | LAMDA SX™ C-Series |
|---------------------|----------------|-------------------|
| Wavelength [nm]     | $\lambda=308$ | $\lambda=308$     |
| Pulse Duration [ns] | $\tau=25$     | $\tau=29$         |
| Max. Pulse Energy [mJ] | $E_p=800$ | $E_p=900$         |
| Max. Repetition Rate [Hz] | $\nu_f=50$ | $\nu_f=600$     |
| Max. Average Power [W] | $P_{AV}=30$ | $P_{AV}=540$ |

The parameters for the repetition rate of $\nu_f=50$Hz, the pulse duration of $\tau=25$ns and the max. pulse energy of $E_p=800$mJ/cm² in combination with the abovementioned rectangular beam shape with the dimensions of 30.0 mm by 1.8 mm and a pulse overlap of 50 %, the LPX Pro™ 305 allow surface treatment rates of up to 1377 mm²/s. The influence of different pulse overlaps and different pulse energies on the ablation behaviour and on the bonding strength of CFRP-CFRP adhesive bonds are in the focus of this investigation. The second excimer laser (LAMBA SX™ C-Series) listed in Table 2 is a high-power excimer laser with the same wavelength and a pulse duration in the same range but a max. average power of 540 W and a repetition rate of up to 600 Hz. The results of up-scaling the achievable process rate with the LAMBA SX™ C-Series are noted in Chapter 3.

The experimental set-up used for the surface texturing of CFRP specimens with excimer laser radiation is displayed in Fig. 1, left.

![Fig. 1.](image1)  
(a) the experimental laser set-up with the laser source, beam shaping device, beam guiding with mirrors and x,y positioning system; (b) the universal tension/compression machine – Instron 5567 used for the lap shear tests

The beam shaping device (see Fig. 1) converts the raw beam with the dimensions 10,0mm by 24,0mm to a rectangular shape with the dimensions 1,8mm by 30,0mm. The converted beam is guided by mirrors to CFRP specimen which is laying on the x,y positioning system. The speed of the positioning system in combination with the repetition rate result in the pulse overlap, thus there is a direct influence of these parameters on the surface condition.
The effect of the surface treatment with the excimer laser on the bonding strength of CFRP-CFRP adhesive bonding was tested by performing single lap shear tests with a testing speed of 5.0mm/min according to DIN 1465 with the universal tension/compression testing machine Instron 5567, Instron Deutschland GmbH (see Fig. 1, right). For the manufacturing process to have as little influence as possible on the results of the laser treatment, two standard and certified prepreg materials have been chosen, which allow the manufacturing of specimens with a low variance in the top resin layer. The materials are the 2.0mm thick unidirectional laminate specimens (Hexply® 913 epoxy matrix, HTS fibers, cured ply thickness 0.125mm, all plies orientated 0°, dimensions 100mm x 25mm) and a 120°C curing epoxy film adhesive (Scotch Weld® AF163, thickness 0.14 mm). The laminates were machined for 60min in a heated press at 125°C using a metal mold coated with a silicone-based release agent (Marbocote® TRE Marcote, Ltd., Middlewich, UK).

3. Results and Discussion

The aim of the experiments described in this paper is to achieve two challenges of preparing surface conditions. On one hand is the efficient removal of release agents and/or other surface contaminations and on the other hand the exposure of the fibers to allow direct application of force into the fibers. SEM pictures of the untreated surface and the mentioned two surface conditions are shown in Fig. 2.

![SEM pictures of the untreated surface and two surface conditions](image)

Fig. 2. SEM pictures of: (a) the untreated surface; two surface conditions: (b) the removal of release agent or other contaminations; (c) the exposure of the fibers

In both results of the abovementioned surface conditions (see Fig. 2 b) and c)) is the aim to perform a process without damaging the load-carrying fibers next to a accurate treatment of the surface. Thus the first step is to find laser parameters that on the one hand remove most of the resin but on the other hand do not cause any visible damage. For this reason the parameters pulse energy and the pulse repetition respectively the pulse overlap are varied. In Fig. 3 the resulting ablation depths for two different pulse energies and different pulse repetitions are displayed.
The ablation depths for different pulse energies and different pulse repetitions (Fig. 3) show that the specimens have top resin layer with a reproducible thickness of 7.5μm ± 1.5μm. And in addition to this the ablation threshold of the matrix is exceeded with both pulse energies contrary to the ablation threshold of the fiber. The ablation threshold of the fiber is up to two orders of a magnitude higher than the ablation threshold of the matrix [7], thus the lower pulse energy with 400mJ/cm² is not sufficient and the obtainable ablation depth stops after removing the top resin layer. With the higher pulse energy of 800mJ/cm² the ablation threshold of the fiber is exceeded and the achievable depth increases beyond the thickness of the top resin layer.

After the visual inspection of the surfaces, parameters for the laser source were chosen to achieve a non-destructive and a surface treatment with a high process reliability. Afterwards the treated specimens were bonded and tested by a single lap shear test. Fig. 4 shows the different resulting fracture surfaces that occurred after the excimer laser treatment.
A strong dependence on the laser parameters used cannot only be seen in the surfaces, but also in the failure patterns of the lap-shear specimens (Fig. 4). Untreated surfaces show adhesive failure (AF), as no bonding can be established between adhesive and fiber-reinforced material. With optimally treated surfaces cohesive failure (CF) occurs in the adhesive so that the potential of the joint can be fully utilized and the requirements on the laser treatment are completely complied with. If the laser energy is too high, degradation occurs below the top fiber layer and a cohesive substrate failure (CSF) can be observed.

The effect of the surface pre-treatment with the excimer laser on the bonding strength of CFRP-CFRP adhesive bonding was tested by the abovementioned single lap shear test according to DIN 1465. The achieved strengths are shown in Fig. 5.

Fig. 5. The achieved shear strength of excimer laser treated adhesive bonded CFRP specimens with different pulse energies and different pulse overlaps

The max. shear strength shown in Fig. 5 illustrate the potential of the excimer laser treatment of CFRP material. The strength of the abraded references are achieved or even exceeded by the different excimer laser parameters. Conspicuous are on one hand that the treatment with a pulse overlap of 16 pulses tends to show adhesion failure independent on the pulse energy. On the other hand that the max. shear strength of the specimens treated with a pulse overlap of two pulses is in the same range as the references or even higher and independent on the pulse energy, as well.

Remarkable is that the specimens treated with a pulse energy of 600mJ/cm², a pulse overlap of two pulses and a repetition rate of 50Hz have the highest shear strength and in addition a complete cohesive failure occurs in the adhesive. The achievable area rate of excimer laser treatment using a LPX Pro™ 305 with this parameters is 0.16m²/min or resp. 9.6m²/h. Furthermore the area rate by using a LAMBA SX™ C-Series with the same pulse energy and overlap but a repetition rate of 600Hz (system specifications see Table 2) of 0.97m²/min or resp. 58.3m²/h would be achievable. Thus with the LAMBA SX™ C-Series is a notable area rate possible and therefore the system would be suitable for industrial applications.
4. Conclusion

The presented investigations on surface pretreatment of CFRP for adhesive bonding by using excimer laser radiation show that the full potential of the joint can be utilized by the application of laser radiation with a wavelength in the UV range. The obtained strength of the abraded references are achieved or even exceeded. Nevertheless, by using unsuitable laser parameters the risk of an adhesion failure of the specimens or delamination in the substrate exists. But in contrast to a surface treatment by a laser source with a wavelength in the IR range no significant damage inside the material can be observed.

The high potential of this surface treatment method for industrial application is constituted by the area rate of up to 9.6m²/h with an average output power of 30W and a repetition rate of 50Hz. In addition to it the laser process is scalable with laser sources like the excimer laser LAMBA SX™ C-Series with an average output power of 540W and a repetition rate of 600Hz so that an area rate of more than 50m²/h seem to be achievable. But in same time the investment costs are appreciable improving.

Nevertheless further investigation of the removal of release agent via XPS, the adhesion failure at specimen treated with 16 pulses, Peel-tests and ageing behaviour of excimer laser treated CFRP material is necessary.

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