PRE-TREATMENT OF CFRP FOR ADHESIVE BONDING USING LASER RADIATION

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Abstract : High demands for light weight construction and eco-friendly transportation can be attained by the use of carbon fibre reinforced plastics (CFRP). One major challenge is the joining technologies. For these reasons adhesive bonding may allow an increased utilization of the light weight potential of CFRP. A major challenge when adhesively bonding plastics is the surface treatment. This is necessary because besides different contaminations like grease or dust there are often residues of release agents on the. This paper describes mechanical tests that have been performed with laser pre-treated CFRP parts. The laser pre-treated specimens are compared to manual abraded ones. The results show good bond-strength if decent laser parameters are applicated. The laser process is suitable to achieve cohesive failure within the adhesive and bond strengths in the magnitude of the abraded specimen.

1. Introduction

As well the automotive as the aviation industry shows growing interest in light weight structures manufactured from carbon fibre reinforced plastics (CFRP). However the advanced properties and high weight safing potential 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 leightweight potential 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 agent and other surface contaminations without damaging the load carrying fibers and the exposition of the fibers to allow direct load introduction into the fibers. The latter is required because in adhesive bonds the load is not introduced nearly uniform among the thickness as it is with mechanical fasteners, but through the surface, which makes weak surface layers critical to the achieveable bond strength.
This paper describes the application of laser radiation for the removal of surface contaminations and discusses potential deterioration caused by the pre-treatment process.

2. Pre-treatment of CFRP for adhesive bonding

Processes that are currently used for pre-treating CFRP parts before adhesive bonding are abrading, different blasting processes or the removal of peel-plies. The disadvantages of the most often used manual abrading process are mainly the low process speed and the fact that the process is mostly performed wet, which means that adjacent rinsing and drying is necessary. Furthermore the automatization of grinding is quite complex and the process most often needs prior and subsequent cleaning. Additionally the grinding is mostly performed manually which firstly renders the process unsuitable for larger production lots and/or areas and secondly limits the reproducability and involves the risk of fibers being damaged, due to too intense treatment or that surface contaminations are not removed completely. The latter risk also prevails for all other mechanical surface pre-treatments, such as blasting processes. Furthermore, grit-blasted surfaces are also often contaminated with residues and dust which in turn makes further cleaning necessary.

In the aerospace industry for most parts that are manufactured peel-ply is used for surface pre-treatment. The main reason for this is that it ensures a reproducible roughness and clean surface and thus guarantees consistent bonding results. However because peel-plies have to be laminated into the parts this method increases manufacturing efforts and is also not applicable for repair bonds, and it is inevitable to do the bonding immediately after the removal of peel-ply becauce the activation process cannot be repeated. Furthermore peel-ply surfaces show varying thickness of the resin layer. Also several research projects report that residues of release agents can transfer from the peel-ply onto the part surfaces [1], that for some peel-plies the achieved surface roughness may become harmful to the bond [2] and that, depending on the type of peel-ply fabric, and the toughness and ability of the resin to impregnate the fabric the achievable G_{IC}-values and lap shear strengths are strongly influenced [3].

3. Application of laser radiation for adhesive bonding pre-treatment of CFRP

Especially since the increasing application of CFRP in aircrafts has started in the late 80s of the 20th century various work has been performed in the area of laser pre-treatment of bulk and reinforced polymers. Different wavelengths from the ultra violette range (UV) (248 nm or 355nm)[4, 5, 6], the visible green range (532 nm) [7], the near infra red (NIR) (1064 nm)[8,9] to the middle infra red (MIR) (10600 nm)[10] have been tested and the effects on bond strength described. The first experiments on laser machining of CFRP laminates have been conducted in the 1980s with common continious wave IR sources [11]. Herzog et al. [12] recently demonstrated that these IR lasers could represent an alternative for cutting but, as thermally acting tools, are not suitable for texturing purposes. First approaches to laser surface texturing of CFRP were then undertaken in the 1990s [13] using Excimer lasers with a wavelength in the UV range which are absorbed well not only by the fibers but also by the polymer matrix. Even though these results were very promising, the very low process speed, due to the reduced pulse repetition rate (200–500 Hz), hindered the industrial use. Such drawbacks are then overcome by the new generation of diode pumped solid state (DPSS) lasers in which an efficient frequency tripling, generates UV radiation of 355 nm. Short and ultrashort pulses can be produced at repetition rates of several 100 kHz keeping a Gaussian beam profile with a very high beam quality. Fischer et al. [14] proved that with short pulsed lasers that it is possible to obtain a very detailed ablation mechanism based on the direct sublimation of the irradiated material along with a negligible heat affected zone (HAZ). A bond breaking of the molecules of both, fibers and matrix, can be realized by the large photon energy of the UV radiation (3.49 eV), which is often described as “cold” ablation. Actually the photochemical–thermal nature of this bond scission is frequently argued as reported by Sato and Nishio [15]. The authors suggested that both photochemical and thermal mechanisms contribute to the etching process. At low energy density (ED) in [J/mm2], thermal effects are negligible for the UV-shortpulse ablation. At higher energy density these effects become significant.

In the case of the IR laser sources Cenna et al. [16] presenting an overview of the development in laser treatment of fibre-reinforced plastics by laser radiation with a wavelength of 1064 nm. Concluding their review the authors pointed out that despite of the experimental models till then developed, the lack of knowledge about the material removal mechanism and the unavoidable presence of HAZ hindered the industrial use of IR lasers for CFRP processing. As a matter of fact photons emitted in the infrared 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. Consequently, CFRPs processing with IR lasers has generally a thermal nature which induces a large HAZ due to the fast conduction along the fibers. This phenomenon could result in a degradation of the matrix and in a reduction of the internal integrity of the laminate and is closely linked to the absorption behaviour of the matrix material.
Since there is a large bandwith of laser sources as well as of different composite materials (matrix, reinforcing fiber material and length) and also a rapid development in both sectors, further research in this sector is still required. Especially the ablation mechanisms and the interaction between fiber, matrix resin and laser radiation are highly dependent on individual parameters and still not completely researched.

4. Materials and testing methods

Focus of the work described in this paper is the treatment of epoxy based CFRP materials which are commonly used in the aircraft industry. To achieve as low as possible influence of the manufacturing process on the results of the laser treatment two standard and certified prepreg materials (see **Table 1**) have been chosen, which allow the manufacturing of specimen with a low variance in the top resin layer.

Material	**Curing temperature**	**Ply-thickness**
Hexply 913 UD	120 °C (250 F)	~ 0,125 mm
Hexply 913 Weave	120 °C (250 F)	~ 0,5 mm
Cycom 977-2	180 °C (350 F)	~ 0,125 mm

Table 1: Prepreg-Materials

The 120 °C curing materials are commonly used for repair purposes whilst the 180 °C curing system is used for primary body parts. From these materials sheets with a size of 300 x 300 mm have been manufactured by press processing in a closed mould. The lower surface was covered with release film to prevent adhesion to the mould. To the top half of the mould release agent (Marbocote TRE, solvent-based, containing polysiloxane) was applied to create surfaces with a selected level of release agent residues.
The lay-up of the sheets for the different test-types is shown in **Table 2**.

Application	**Lay-up**	**No. of plies**	**Cured thickness**
Surface characterization	$(0/90/90/0)_{sym}$	8	1 mm
Lap-shear testing	0°	16	2 mm

Table 2: Lay-up of the test-sheets

This paper describes results gathered with the application for one thing of a pulsed solid-state laser source with a wavelength of 1064 nm, a pulse duration in the nano second range and an average output power of 100W. And for another thing a continious wave gas laser (CO_2)

emitting laser radiation at 10600 nm and an output power of 200W. The main advantage of solid state laser systems is the fact that they are quite portable and sturdy and are therefore suitable for mobile repair and surface pre-treatment applications. Furthermore laser-light with a wavelength of 1064 nm can be led through an optical fiber which further increases the versatility of the system. The advantage of the CO_2 laser source which is not as portable and easy to handle is that the emitted wavelength is nearly completeley absorbed by the resin matrix which changes the interaction behaviour between laser radiation and composite materials. **Table 3** shows the absorption coefficient **α** and the penetration depth (the reciprocal value of **α**) for the polymer materials PEEK and Epoxy by different wavelengths.

	PEEK		**Epoxy**	
λ [nm]	**α [1/m]**	**1/ α [m]**	**α [1/m]**	**1/ α [m]**
355	29826,6	3,4 10-5	2231,4	4,5 10-4
1064	3809,8	2,6 10-4	526,8	1,9 10-3
10600	11982,9	8,3 10-5	7570,6	1,3 10-4

Table 3: Penetration depth and absorption coefficient of UV-, NIR- and MIR-laser radiation for two exemplarily polymers (thermoplastic: PEEK and thermoset: Epoxy)

The calculated penetration depths shown in **Table 3** with differences in the range of one to two orders of magnitude between the different wavelengths emphasize that a defined surface pre-treatment of polymer materials with NIR radiation is usually not possible. The laser ablation mechanism for the laser treatment of CFRP with NIR laser radiation is not a typical laser material ablation. With the weak absorption of the polymer, on the one hand, and the carbon fibre, which can be regarded as a 100% absorber, on the other hand, the laser ablation mechanism of CFRP bulk material by using NIR laser radiation is rather a blast away of the matrix material which is above the ignited plasma on the carbon fibre. Thus, the laser ablation of matrix material with a NIR laser involves a heating of the fibres and a blasting of the top matrix layer because of thermal stress and, as a consequence of this, the risk of thermal degradation of the fibre exists. The absorption behaviour of the polymer by using MIR laser radiation – with the absorption coefficient displayed in **Table 3** – it is so called surface absorption. As a result the risk of thermal damaging of the laminae is greatly reduced and the ablation process is a defined laser polymer ablation. Furthermore a selective removal of the matrix without damaging the fibres is possible. Anyway it cannot be guided through fibre-optic cables which decreases the flexibility of application. For these reasons the focus of the investigations described here lies on the application of the solid-state laser, the results gathered with the MIR source are shown to compare the interaction mechanisms and the wave-length dependency of the ablation process.

The adhesive bonds were manufactured using a one-component epoxy based film adhesive with a curing temperature of 120 °C (250 F) and a nominal thickness of 241 µm (9.5 mils). The lap shear specimens were cured in a jig that ensures constant overlap and avoids tilt of the adherends. Testing of the single lap shear specimens was performed according to DIN EN 1465 with a testing speed of 5 mm/min.

5. Results

The aim of the experiments described here is to achieve complete removal of the top resin layer of the fiber-reinforced polymer material to enable direct bonding to the exposed fibers. Thus the first step was 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 a parameter screening was performed and the surfaces were visually observed after treatment.

Figure 1 shows examples of surfaces which have been treated by a solid state IR laser with a wavelength of 1064 nm.

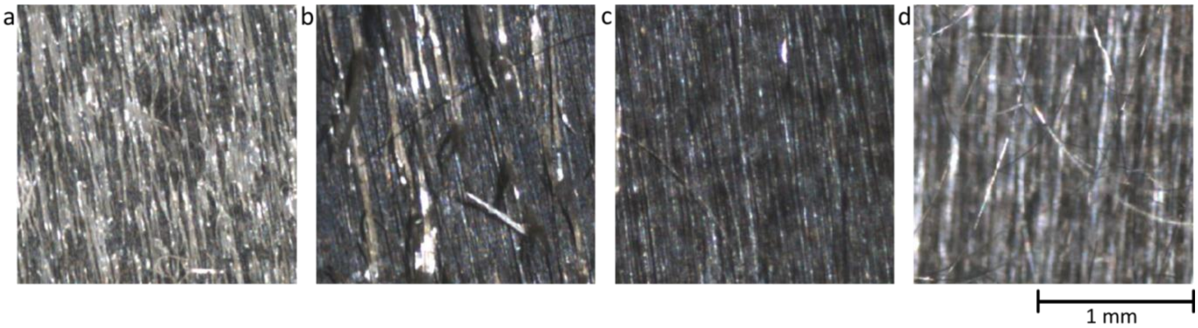

Figure 1: Surface appearances after laser treatment by a solid state laser. a: nearly closed resin layer. b: detached matrix resin is left on the surface after pre-treatment. c: fibers are exposed, neither resin nor visible damage on the surface. d: fibers visibly damaged

The results displayed in **Figure 1** contain the assumption that a thermal damaging can be prevent by using laser parameter that avoids the damaging of the fibres because of the abovementioned absorption behaviour and ablation mechansim.

The effects shown in the microscope pictures in **Figure 1** can be shown in the scanning electron microscope pictures (SEM), as well. In **Figure 2** are shown laser treated specimen exemplaryily with the caption according to figure 1a and 1d.

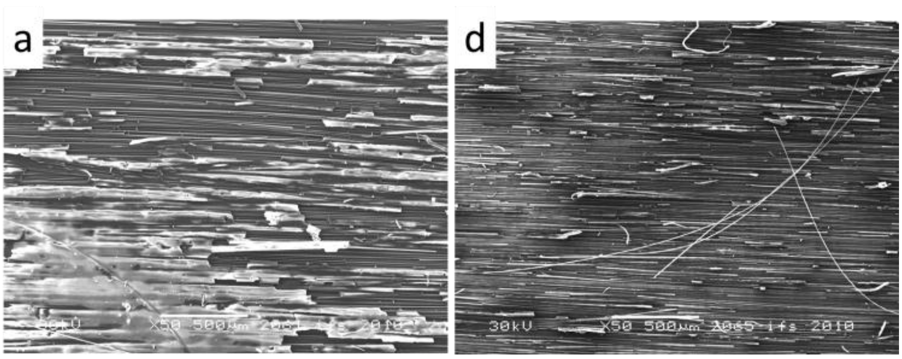

Figure 2: SEM pictures of solid-state laser treated surfaces resin left on the surface (left) and some damaged fibers (right)

The surface pictures already hint in the direction that when chosing the laser-parameters it is important to control the energy that is put into the base material very closely to prevent damaging fibers on the one hand but to achieve complete removal of the resin.

The surface appearance after CO_2 laser treatment is shown in **Figure 3**. With this treatment complete removal of the resin is achieved and no fibers are visibly damaged.

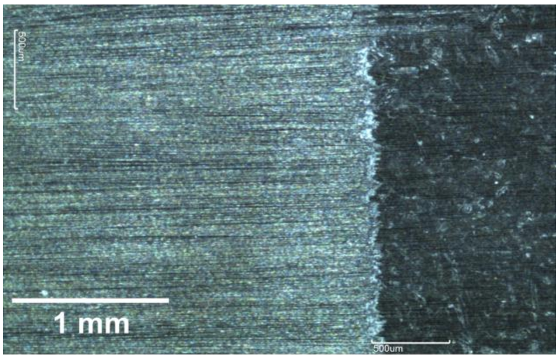

Figure 3: Surface appearance after CO_2 laser treatment (left side). Resin is thoroughly removed and fibers are exposed. No fiber damage visible.

With both laser sources complete removal of the surface resin layer is possible, nevertheless some of the surfaces treated with the solid state laser with higher intensities also show raised fibers. This effect only occurs at very high intensities when the CO_2-laser source is used.

After the visual inspection of the surfaces, parameters for both laser sources were chosen and single lap shear tests were performed. **Figure 4** shows the different fracture surfaces that occurred after laser pre-treatment. Compared to conventional adhesive bonds were mostly either adhesion failure or cohesive failure occurs, depending if the surface pre-treatment is adequate, on the laser pre-treated CFRP also two different kinds of delaminations occurred. On specimens treated with the SSL where the resin layer was not thouroughly removed the top resin layer is ripped off. The samples treated with higher intensities tend to show delamination beneath the uppermost ply.

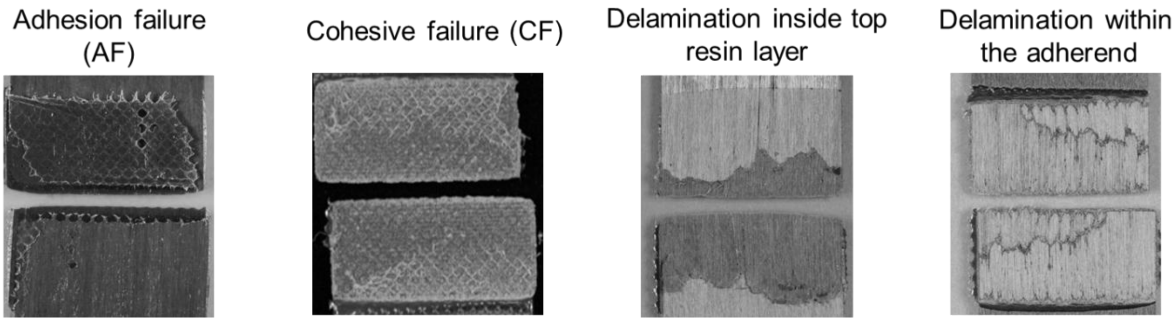

Figure 4: Fracture mechanisms occuring after SSL laser pre-treatment

The results of lap shear tests on UD laminae with the 120 °C curing matrix resin are shown in **Figure 5**. It is displayed, that with both employed laser sources joint strength in the magnitude of the manually abraded references can be achieved.

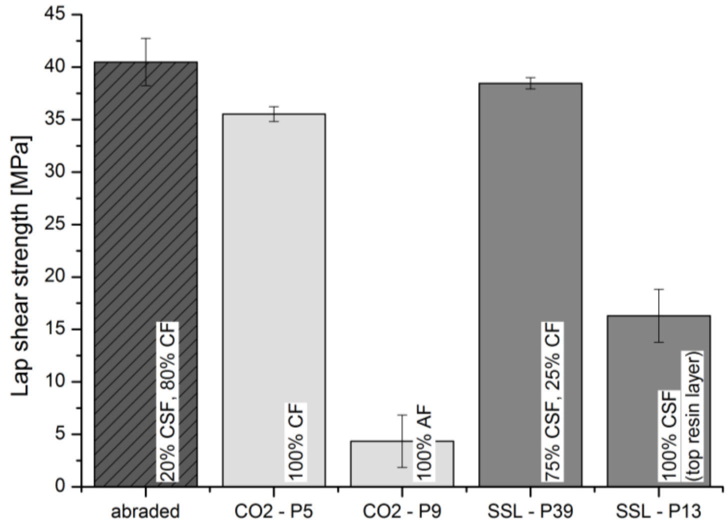

Figure 5: Lap shear results of UD reinforce 120°C curing matrix resin, pre-treated by solid state and CO_2 laser

Anyway if not the right parameters are chosen (CO2-P9 and SSL-P13) either adhesion failure or complete delamination in the top resin layer occurs achieving very low bond strength. The reason for the CO_2 laser treated samples is that the release agent has not been removed from the surfaces completely and thus no adhesion occurs between the CFRP and the adhesive. The samples treated with the SSL fail inside the top resin layer, that is an interesting observation that has been made is, that as well in the references that were pre-treated by manual abrading as in the SSL-P39 treated specimen local delamination beneath the top fiber layer occurs at bond strength higher than at the CO2-P5 treated specimen which fail completely cohesively inside the adhesive layer. A possible explanation might be compensation of stress peaks by local deformation. Nevertheless this thesis could not be verified yet and is part of current research.
The comparison of the results of lap shear tests on UD laminae with the 120 °C and 180°C curing matrix resin are shown in **Figure 6**.

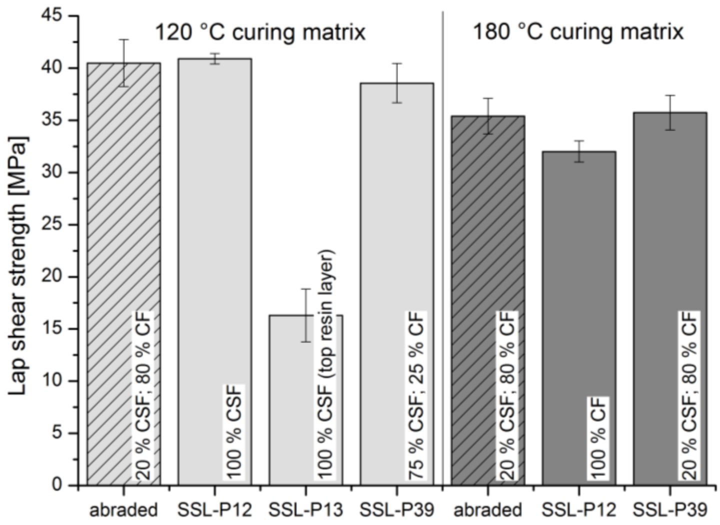

Figure 6: Comparison of lap shear results of 120°C and 180°C material pre-treated by solid-state laser

Lap shear tests with the same parameters have been performed with the120°C and the 180 °C curing matrix resin. The results of these tests (**Figure 6**) show, that the joint strength of the abraded references are achieved by laser-treatment for both curing matrices systems. In contrast to the 120 °C material the fracture appears mostly cohesively inside the adhesive, this shows, that delaminations are caused by the laser process. This results indicate that the CFRP with the 180 °C curing matrix is not as sensitive to delaminations caused by the laser process.

6. Conclusion

The presented investigations on surface pretreatment of CFRP by using laser radiation for adhesive bonding show that the full potential of the joint can be utilized by the application of both laser sources with the wavelength of 1064 nm and 10600 nm. Nevertheless by using unsuitable laser parameters the risk of an adhesion failure or complete delamination in the top resin layer exists. Especially the lower temperature curing matrix resin tends to show delamination fracture inside the laminae.

By comparing the two used laser sources it appears that two objectives have to be discussed. On the one hand, the laser-material interaction of MIR laser radiation and the CFRP bulk material enables a non-damaging laser material ablation without a delamination or damaging of the fibres. On the other hand, the NIR laser source deposits more heat inside the material because of the bad absorption respectively the high transmission behaviour. The resin is nearly completely transparent to the wavelength of 1064 nm and the energy is coupled into the fibres. Consequently causes thermal degradation underneath the topmost fiber-ply. Nevertheless the investigations show the high potential of laser-pretreatment for CFRP parts which can be utilized if adequate parameters are applied.

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