Atmospheric-Pressure Plasma and UV-Laser radiation – A Comparison for surface pre-treatment of CFRP

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Abstract

In this paper analytical and mechanical tests are described that have been performed with laser pre-treated and atmospheric-pressure plasma treated carbon fiber reinforced plastics (CFRP) parts. The work describes the different mechanisms of interaction between laser radiation resp. plasma technique and matrix resin. Furthermore effects of different parameters for both methods and thus fluence are discussed and the mechanism of the risk of damaging the laminate is investigated. The laser and the plasma pre-treated specimens are compared to manual abraded and untreated ones. The results show good bond-strength if decent parameters are applicated but also damaging within the material can be caused if both methods are used with too high intensities. The results show the totally different interaction mechanisms depending on the method – laser or plasma - as well as that both methods can achieve cohesive failure within the adhesive and bond strengths in the magnitude of the abraded specimen.

1. Introduction

Fiber reinforced plastics are widely used as a modern construction material especially in aviation industry, but due to increasing energy costs their potential for light weight construction increases their attractiveness for automotive industry, too. Thermosets like epoxy still build a major part of deployed matrix material. Typical methods for structural joining of CFRP parts are bolting and riveting, which require bores that locally cut the fibers leading to decreased strength. Additionally the holes result in local stress step-ups that make oversizing necessary. Adhesive bonding may allow an increased utilization of the light weight potential of fiber reinforced plastics, but a major challenge when adhesively bonding plastics is the surface pre-treatment. This is necessary because besides different contaminations like grease (e.g. fingerprints) or dust which can occur due to handling or storage there are often residues of release agents on the surface those are caused by the manufacturing process. The contaminations have a negative impact on adhesion and must therefore be removed before adhesive bonding. To achieve full bond-strength, adhesion of the adhesive to the components is essential; this can only be accomplished by adequate pre-treatment of the surfaces. Common methods for pre-treatment are the using of peel-plies and manual abrading or grit blasting. These methods have several disadvantages that necessitate the use of an alternative method. During this work the application of UV-laser radiation and atmospheric-pressure plasma are used for the pre-treatment of CFRP specimens.

2. Pre-Treatment of CFRP

Different methods (e.g. by grinding, etching, sand blasting) and resulting surface conditions have been reported in literature for a number of materials [1, 2, 3]. These methods for surface pre-treatment have several disadvantages. After the peel-ply removal the surface is covered with a relatively thick resin film, thus the adhesive binds to this layer and not directly to the fibers which result in a potential weak layer and hinders direct transmission of force into the fibers. The disadvantages of manual abrading and grit blasting are among others the danger of damaging the fibers and the necessity for a secondary cleaning step because of contaminations occurring during the process.

Lasers, as non-contact and wear-less machining tools, exhibit unique advantages in processing anisotropic and inhomogeneous materials like CFRP. Nevertheless the fact that polymers used as matrixes are characterized by vaporisation temperature and thermal conductivity of one or two orders of magnitude lower than carbon fibres, which typically leads to extended thermal damages [4]. The influence of the surface pre-treatment with CO_2 laser radiation (λ = 10.6 µm) on epoxy resins was investigated in [5]. For this, specimens made of CFRP were pre-treated and bonded with a resin matrix curing at 120 °C. The results of this investigation show that when using a bonding system curing at room temperature, no improvement in the lap shear strength can be achieved by the pre-treatment. According to the authors due to the treatment by means of CO_2laser, a reduction in the quantity of hydroxy groups occurs at the surface and which leads to a deterioration of the joint strength. The authors attribute this to the insufficient temperature stability of the matrix resin.

By means of XPS (X-ray Photoelectron Spectroscopy) it could be shown that with less temperature-resistant matrix resins (120 °C curing system), water molecules are dissociates and a double bond is formed in the resin chain; this leads to reduction of the polarity and thus to deterioration of adhesion. The effect could not be observed with a resin system resistant to higher temperatures (180 °C curing resin system). With this matrix system, the adhesive joints strengths are in the same range then the manually abraded specimen. In [6] investigation in terms of the efficiency of removing release agents from the surface by excimer laser systems were performed. The results of this investigations show that the release agent could be removed by laser treatment. Furthermore the XPS analysis indicates a direct correlation between the quality of adhesive bonding and the removal of the release agent.

In [5], the results concerning the investigation of the pre-treatment of epoxy resin and Polyether ether ketone (PEEK) fiber-reinforced plastics by means of CO2 laser are described. These show that the ablation by means of CO2 laser is nearly exclusively thermal. Investigations as regards the bonding pre-treatment of carbon fiber rein-forced PEEK by means of excimer laser radiation with a wavelength of 193 nm show a clear improvement in the bonding strength, compared to SiC-treated specimens [7]. According to the authors, this is due to the modification of the surface topography as well as to the formation of carbonyl groups on the surfaces and the removal of contaminations verified by means of XPS. The authors further differentiate between effects of photo-chemical interaction at low pulse energies (0.18 J/P) and nearly exclusively photo-thermal effects at pulse energies of 1J/P.

The investigations as regards the pre-treatment by means of Nd-YAG laser of three different epoxy resin matrix carbon-fiber reinforced materials are described in [3]. The results of the lap shear tests show that the strengths obtained by the grit blasted specimens can be achieved.

In one of the three tested fiber-reinforced systems, a significant drop in substrate strength occurs with laser treatment at a higher intensity. The cause for this effect was not investigated in detail in this project and/or is not described in the publication. In [8], too, glass- and carbon-fiber reinforced epoxy resin specimens produced by vacuum fusion procedure were pre-treated with Nd-YAG laser and then bonded with a cold-curing 1K-epoxy adhesive (Scotch Weld® AF163, 3M). This resulted in high bonding strengths on the pre-treated CFRP adherends, but the fracture patterns showed partial delaminations. The investigations on glass-fiber reinforced materials show strong damage to the material, due to optical effects of the glass fibers (low absorption of the laser radiation), and as a result, delaminations of complete rovings, occur.

Besides the laser treatment the modification of the polymer surface by using a plasma treatment is one of most frequently applied pre-treatment method [9]. During this process the polymer/composite surface is exposed to atmospheric or low pressure plasma. While the process setup is different in the mentioned applications the basic principles are the same. The specimen surface interacts with high energetic gas particles which are ionized using e.g. a high frequency alternating electric field as energy source. The interaction leads to a modified surface morphology and chemistry in respect to the specific gas and treatment parameters [10]. After the plasma treatment inside a vacuum chamber (low pressure plasma) or at ambient conditions (atmospheric pressure) the surface shows a higher surface energy and improved wettability, which leads to improved adhesive conditions [11]. The main effects are the removal of very low amounts of contamination and the creation of functional compounds by breaking chemical bonds of the substrate polymer [12].

One of the major challenges in adhesive bonding of CFRP is the residual release agent and other contaminations which remain on the surface after the manufacturing process. The effect of cleaning a surface with plasma is widely investigated on polymer substrates. Due to the fact that the contaminations on polymer or composite surfaces are often the same (mostly organic substances like oils, additives or the mentioned release agents) it is possible to extend the results from the plasma cleaning of polymer surfaces to fiber reinforced polymers. It could be shown that with the use of low-pressure O_2 plasma all organic contaminations on a polypropylene foil can be removed [13]. The challenge while using plasma for surface cleaning is to find the right treatment duration. If the duration is too short the cleaning effect cannot be reached, but if the treatment time is too long the cleaning leads in an etching process and thermal damage of the polymer might occur [14]. The question in terms of bonding preparation of FRP is, if the contaminations can be completely removed. While the low pressure plasma seems to be effective in removing contaminations on polymers [13] or on CFRP [15,16], the removal with an atmospheric plasma seems to be difficult. Holtmannspötter et al. published that the atmospheric plasma treatment for adhesive bonding of CFRP was only effective for specimens with a small amount of contaminations [17]. Even after plasma treatment the bonding failure was adhesively dominated for specimens with a high amount of contaminations. Here it has to be mentioned, that during the etching process oxidation products can occur, which lower the adhesion properties of the polymer [18]. The most important application of the plasma technology for adhesive bonding is the deposition of functional groups on the polymer or composite surface. The type of functional group is mainly depending on the process gases. For example Zaldivar et al. used helium as a carrier and oxygen as the active gas for plasma treatment of CFR epoxy. It could be proven that with this process the functional groups (i.e. C-O, C=O, O-C=O) could be formed at the surface [19]. In this specific case it was shown, that the increased lap shear strength correlated well with content of carboxyl groups on the surface. Due to the fact that these good adhesion properties are based on the functional groups the space of time between plasma treatment and the bonding process is especially critical [20]. However this disadvantage can be technically reduced by an adjusted joining process.

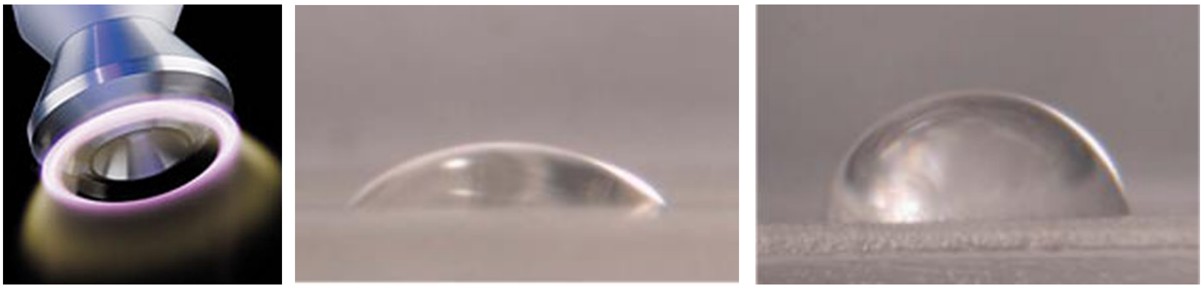

Figure 1: Rotary nozzle from the used Openair® Plasma System – left;

In the presented investigations an Openair® Plasma System from Plasmatreat GmbH, Germany with a rotary nozzle (see Figure 1, left) was used to achieve an equal activated surface. This Technology is characterized by three features: activates the surface, discharge the surface and as a result decreases the surface tension. Determination of surface tension with a contact angle messurement (see Figure 1, right) shows that, with low surface tension, wetting is impossible. After activation with Openair® plasma, the surface is fully wettable.

For the laser pre-treatment the specimens were irradiated with two different UV-laser sources from Coherent (Deutschland) GmbH. An excimer laser model LPXpro 305 at a wavelength of 308 nm and pulse duration of 28 ns. Both axes of the excimer laser beam were independently shaped to achieve a large per-shot processing footprint of 30 mm x 1.8 mm. By varying the excimer laser pulse energy it was easily possible to achieve fluences up to 1,000/cm^2. In the experiments, fluences between 400 and 800 mJ/cm^2 were applied, and the number of pulses per area was varied between 1 and 48 pulses.

And a frequency tripled diode pumped solid state laser (DPSS laser) with 355nm wavelength with a pulse duration of 15 to 30ns and a repetition rate of 90 to 300kHz was used. In this way it was possible to determine the range of variation of process parameters with the twofold objective of quick fiber machining and reduced heat affected zones (HAZ).

3. Results

3.1. Mechanical Tests

The effect of the abovementioned surface pre-treatment methods (atmospheric-pressure plasma and UV-Laser on the bonding strength of CFRP-CFRP bonding was investigated by using a lap shear strength test (DIN1465). The test method is a single lap shear test with 2.0 mm thick UD laminate specimens (Hexply 913 epoxy matrix, HTS fibres, cured ply thickness 0.125 mm, all plies orientated 0°, 100 mm by 25 mm), a testing speed of 5 mm/min and a 120°C curing epoxy film adhesive (Scotch-Weld AF163, thickness 0.14 mm). The laminae were manufactured in a heated press at 125°C for 60 min using a metal mould coated with a silica based release agent (Marbocote TRE). The results of the lap shear strength tests are displayed in Figure 2.

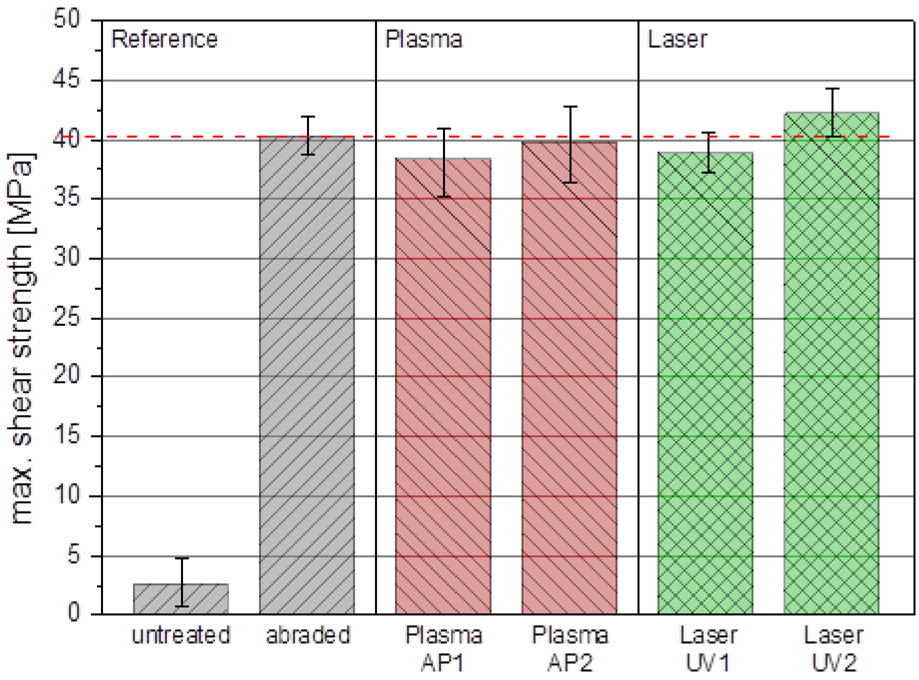

Figure 2: Maximum shear strength of different surface pre-treated specimens

The UV-laser treated specimens as well as the atmospheric-pressure plasma treated specimens have a max. shear strength – shown in Figure 2 - with the same level then the abraded reference specimen. Both UV-laser treated sets of specimen (UV1: excimer laser with 2 pulses of 600mJ/cm²; UV2: DPSS with 90kHz, average power of p_{Av}=23W, deflection speed v_F=400mm/s) laser fail mostly cohesively inside the adhesive. Both atmospheric-pressure plasma treated specimens (AP1: power p=300W, deflection speed v_F=500mm/min; AP2: power p=300W, deflection speed v_F=5000mm/min) show good bond strength. The AP1 specimens show a complete cohesive failure in the adhesive. The AP2 specimens show a bond strength in the same range then the reference but a 10% adhesion failure thus with the higher deflection speed of 5000mm/min the treatment is not sufficient.

3.2. X-Ray photoelectron spectroscopy

With the quantitative spectroscopic technique XPS (X-Ray photoelectron spectroscopy) the measuring of elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material is possible. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed.

Figure 3 shows the XPS spectra of an untreated specimen and specimens treated by excimer laser with different parameters. The focus of the XPS measuring is on the elements oxygen, nitrogen and silicon. Oxygen is in the focus to determine the degree of oxidation. The element nitrogen is a part of the functional amino group of the hardener of the epoxy resin. And silicon is the main component of the polysiloxane-based release agent.

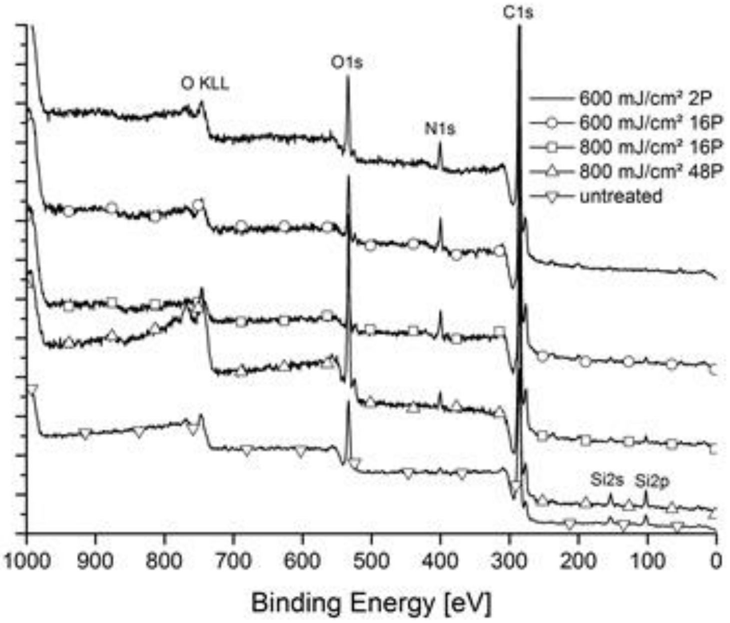

Figure 3: XPS spectra: untreated and excimer laser treated specimen

The XPS spectrum of the untreated specimen in Figure 3 shows the typical peak of Si2p with a binding energy of around 103 eV because of the abovementioned used release agent on the surface. Furthermore the spectrum does not show the nitrogen peak which is probably covered by the release agent. In opposition to this the XPS analyses of the excimer laser treated specimens detect the nitrogen peak but there is no signal of the element silicon. These data suggest that the release agent is completely removed by the laser treatment. These results correspond to the prior assumption for the untreated specimen of the surface covering by the release agent.

In Figure 4 a XPS spectra of an untreated and a plasma treated specimen are displayed.

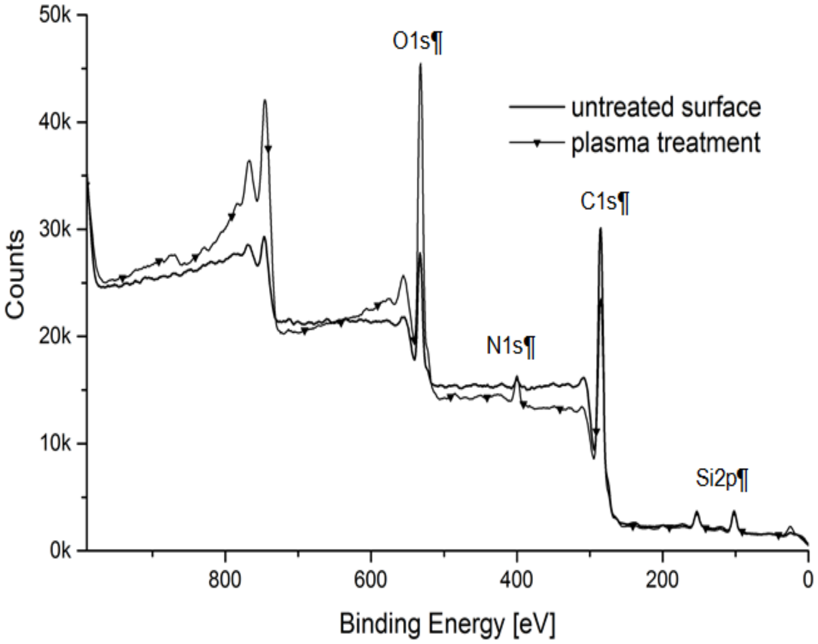

Figure 4: XPS spectra: untreated and atmospheric-pressure plasma treated specimen

The XPS spectra of the plasma treated specimen in Figure 4 show massive increase of the O1s peak and formation of N1s peak after plasma treatment. The increased O1s peak could be seen as an indicator for the surface activation. The Si peak is an indicator for the release agent and is not removed by the plasma process. This demonstrates the above mentioned results of Holtmannspötter et al. [17] that a removing of a release agent is just possible with small amount of this on the surface.

4. Conclusion

The investigations presented in this paper illustrate that the laser based pre-treatment as well as the atmospheric-pressure plasma pre-treatment of the epoxy matrix material of CFRP laminates is a suitable method to improve the adhesive bonding. The results of the shear strength tests show that with both laser sources a thermal damaging can be avoid. This is illustrated by the mostly cohesive failure behaviour for both laser sources thus there is no cohesive failure in the substrate. The specimens treated by atmospheric-pressure plasma show good bond strength and a thermal damaging can be avoid as well. Nevertheless with atmospheric-pressure plasma it is not ensured that the contaminations like a release agent can be removed.

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