Abstract

The use of carbon fibre reinforced polymers (CFRP) is growing significantly in all areas of lightweight construction. Nevertheless, the bonding performance for this material is well reduced because of the contamination with release agents or the relatively thick resin film occurring during the manufacturing process. To achieve full bond-strength, adhesion of the adhesive to the components is essential; this can only be accomplished by adequate surface pre-treatment. One innovative method of surface pre-treatment is the application of laser radiation to achieve a selective removal of resin without impairing the fibres. Therefore a UV-laser with the wavelength of $\lambda=308\text{nm}$ and a NIR (near infrared) laser with a wavelength of $\lambda=1064\text{nm}$ were used to pre-treat specimens manufactured from 120°C curing epoxy prepreg systems. To evaluate the influence of the laser parameters on the surface topography optical and SEM analyses of the surfaces have been performed. Lap-shear specimens have been pre-treated bonded with an one-component epoxy film adhesive and tested. The laser pre-treated specimens achieve the same bond strength as references prepared by manual abrading. Furthermore the mechanisms of interaction between laser radiation and matrix material as well as fibres are discussed considering the different heat deposit and absorption behaviour of the emitted radiations.

1 Introduction

The present high demands for lightweight vehicles and eco-friendly transportation can be complied with by the use of CFRP. However, the advanced properties of these materials can only be utilized if they are not used like “black metal sheets” and if design and especially joining technology are adapted. 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 fibres leading to decreased strength. Additionally, the holes result in local stress step-ups that make oversizing necessary. Therefore a joining technology that enables the designing engineer to fully capitalise the advantage of light weight construction is required. However, the bonding performance for this material is well reduced because of the contamination with release agents or the relatively thick resin film occurring during the manufacturing process that inhibits a direct application of force into the reinforcements. 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, manual abrading or grit blasting. These methods have several disadvantages that necessitate the use of an alternative method. One innovative method for the pre-treatment of CFRP is the application of laser radiation to achieve a selective removal of resin without impairing the fibres. With this selective removal it is possible to achieve a direct application of force into the reinforcements and in the same time to remove the contaminations like a release agent. Former investigations show that one of the most important parameters is the absorption of the radiation, which defines the portion of energy deposit within the material and the penetration depth. As a result of that an excimer laser with a wavelength of $\lambda=308\text{nm}$ was used to pre-treat specifications manufactured from curing epoxy prepreg systems which are currently applied in aviation industry.
On the other hand a solid state laser with laser radiation in the near infrared range with an absorption behavior not near as good as a UV laser was used because of the robustness and the versatility of these types of laser sources. This paper describes the application of laser radiation for the removal of surface contaminations and discusses potential deterioration caused by the pre-treatment process. The aim is to achieve a reliable process of surface pre-treatment of CFRP laminates.

2 Pre-treatment of CFRP

State-of-the-art for pre-treating CFRP parts before adhesive bonding are abrading, different blasting processes or the use of peel-plies. The disadvantages of e.g. manual abrading are mainly the low process speed and the fact that the process is mostly performed wet, which means that subsequent rinsing and drying is necessary. Furthermore, grit-blasted surfaces are often contaminated with residues and dust which in turn makes further cleaning necessary. For aerospace parts manufactured today, peel-plies is often used for surface pre-treatment. Peel-plies ensures a reproducible roughness and a more or less clean surface. However, because peel-plies have to be laminated into the parts this method increases manufacturing efforts and is also not applicable for repair bonds. Furthermore, peel-plies surfaces show varying thicknesses of the resin layer. In Figure 1, the resulting surface conditions referring to a contaminated surface with e.g. a release agent are displayed.

Especially since the late 80s of the 20th century, various works have been performed in the area of laser pre-treatment of bulk and reinforced polymers. Different wavelengths from the UV [1,2], visible green [3] near IR [4,5] to the far IR [6] have been tested and the effects on bond strength described. Since there is a wide range of laser sources as well as of different composite materials (matrix, reinforcing fibre material and length) and also a rapid development in both sectors, further research in this sector is still required.

3 Laser CFRP interactions

The difficulties in machining with conventional tools inspire the use of alternative machining technologies with the twofold objectives of achieving high machining speed and product reliability and at the same time preventing the damage of the material. 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 leads to extended thermal damages. These aspects are clearly evidenced in Table 1 which lists the thermal properties of three common polymer matrixes with respect to the ones of carbon fibres.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity [W/mK]</th>
<th>Density [g/cm³]</th>
<th>Specific heat [cm²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin</td>
<td>0.1</td>
<td>1.21</td>
<td>1884</td>
</tr>
<tr>
<td>PPS</td>
<td>0.29</td>
<td>1.66</td>
<td>795</td>
</tr>
<tr>
<td>PEEK</td>
<td>0.25</td>
<td>1.32</td>
<td>320</td>
</tr>
<tr>
<td>Carbon fibre</td>
<td>50*</td>
<td>1.85</td>
<td>710</td>
</tr>
</tbody>
</table>

The result of the interaction between laser radiation and material depends on various parameters, like wavelength, intensity, time of interaction, absorption, beam profile, topography of treated surface, etc. and is quite complex. Therefore, a detailed estimation of the surface activation has to be evaluated for each considered application. One of the most important parameters is the absorption resp. transmission of the laser radiation, which defines the portion of energy deposited within the material and which defines the penetration depth.

Figure 2 displays the transmission rate for various matrix materials in dependence of the incident laser radiation. The absorption can be described by the Lambert-Beer law (1)

\[ I(z) = I_0 e^{-\alpha z} \]  

with \( I = \) Intensity, \( \alpha = \) absorption coefficient and the depth of the laser radiation \( z \), thus the intensity of the laser radiation decreased in correlation with the penetration depth. The reciprocal of the
absorption coefficient is so called the light penetration depth. The values for the coefficient and this penetration depth are listed in Table 2.

Table 2: Absorption coefficient and the penetration depth of different laser radiations

<table>
<thead>
<tr>
<th>λ [nm]</th>
<th>α [1/m]</th>
<th>1/α [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>308</td>
<td>~46000</td>
<td>22</td>
</tr>
<tr>
<td>355</td>
<td>~46000</td>
<td>22</td>
</tr>
<tr>
<td>1064</td>
<td>931.6</td>
<td>1073</td>
</tr>
<tr>
<td>10600</td>
<td>26491.6</td>
<td>37</td>
</tr>
</tbody>
</table>

A second important parameter for the surface activation is the photon energy of the radiation, which continuously rises with shorter wavelength. For a chemical activation of the surface, the photon energy has to be larger than the inter-molecular forces of the material (1-photon-absorption). This means that this type of surface activation is favoured by a short wavelength in the UV range. In addition the absorption behaviour can be considered as a surface absorption. The above mentioned chemical surface activation or rather a bond breaking of the molecules of both, fibres and matrix, can be realized by the large photon energy of the UV radiation (3.49eV), 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 [8]. The authors suggested that both photochemical and thermal mechanisms, the last due to energy release by excited molecules, contribute to the ablation process. The ablation depth per pulse \(D_{\text{total}}\) is then given by the sum of two terms \(D_{\text{photochemical}}\) and \(D_{\text{thermal}}\):

\[
D_{\text{total}} = 1/\alpha \ln \left( \frac{E_{\text{Dth}}}{E_{\text{D}}/T} \right) + A \cdot \exp \left( \frac{E_{\text{Dth}}}{RT} \right)
\]

where \(E_{\text{D}}\) is the energy density [J/mm²], \(\alpha\) the absorption coefficient and \(E_{\text{Dth}}\) the threshold energy density. At low \(E_{\text{D}}\), thermal effects are negligible. At higher \(E_{\text{D}}\) these effects become significant and derive from the Arrhenius law, being \(A\) a constant depending on the process boundary conditions, \(T\) the temperature, and \(R\) the gas constant. Starting from this theoretical consideration the \(E_{\text{D}}\) threshold values of both matrix and carbon fibres were determined experimentally for a PEEK/carbon fibre material. Experiments have been carried out ablating grooves on a thin PEEK film as a common polymer and on a pure fibre lamina, perpendicularly to their orientation. A threshold value of about 5mJ/mm² can be experimentally derived for PEEK which is two orders of magnitude lower respect to the one estimated for the carbon fibres [2]. This phenomenon explains the complexity of the ablation process which must ensure enough energy to remove the fibres and prevent heat damage of the matrix as well. In addition the two different ablation thresholds allow a selective excavation of the fibres from the adherent matrix material by means of a precise control of the process parameters. The selective removal of the matrix material provides an adhesive strength improvement because of the direct application of force into the reinforcements.

A detailed consideration of laser radiation in the NIR range shows that the photon energy is too low for a chemical activation and the absorption is very low. The results with the N-IR laser system show that parameters could be chosen to ensure complete removal of the resin layer although the bad absorption behavior of NIR laser radiation in the resin. But the risk of fibre damaging and delamination in the material by driving too much thermal energy into the material is shown in Figure 3.

In contrast, the UV laser radiation is absorbed by the resin layer and the ablation occurs from the surface so there is no delamination in the material. Nonetheless the application of a higher amount of laser pulses leads to adhesion failure which might be caused by damaging the seizing.

### 4 Experimental and Materials

This paper describes results gathered with the application of UV laser (\(\lambda=308\)nm) and NIR laser (\(\lambda=1064\)nm) radiation. In case of the NIR laser radiation a typical laser machining set up with galvometer driven scanner as shown in Figure 4 is used.

The laser machining set-up for the NIR laser consists of the laser source (a), beam shaping device (b), galvometer scanner (c), f-theta lens (d) and xyz-axis system (e). The two galvometer driven mirrors in scanning head allows the high beam deflection up to 5,0m/s and the f-theta lens enables the laser material ablation in a planar work field. In the case of the laser machining of CFRP or rather the selective ablation of a matrix, the process is realized by hatching the area with parallel laser lines with a meander shape. If necessary the hatching direction...
was alternated 0°-90° for every couple of layers in order to flatten the ablated surface, thus neglecting the influence of the fibre orientation on the depth of the cavity.

In case of the UV laser the specimens were irradiated with a Coherent excimer laser LPXpro 305 at a wavelength of 308 nm and a 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. Employing a dual-axis beam homogenizer, a 1 % rms overall line field fluence homogeneity was preserved during processing.

A 120 °C curing aerospace composite material (prepreg – based, unidirectional (UD) HTS carbon fiber reinforced) was selected. The specimens were used as UD laminates with a thickness of 2 mm. They were manufactured in a closed mould inside a press according to the materials technical data sheets. The lower surface was covered with release film to prevent adhesion to the mould. A release agent (Marbocote TRE, solvent-based, containing polysiloxane) was applied to the top half of the mould to create surfaces with a selected level of release agent residues. The adhesive bonds were manufactured using a one-component epoxy-based film adhesive with a curing temperature of 120 °C and a nominal thickness of 241 µm. The lap shear specimens were cured in a jig that ensures constant overlap and avoids tilt of the adherends. Testing of the lap shear specimens was performed according to DIN EN 1465 with a testing speed of 5 mm/min.

5 Results

The effect of the surface pre-treatment methods on the bonding strength of CFRP-CFRP bonding was investigated by using the abovementioned lap shear strength test (DIN1465). The single lap shear tests show first of all complete adhesion failure (AF) at a low bond strength for the untreated specimen which vividly demonstrates the necessity of surface pre-treatment (Figure 5).

The abraded references show complete cohesive failure (CF) inside the adhesive at bond strengths in the magnitude of the achievable values, which are given by the strength of the adhesive itself. The specimens treated by the N-IR laser with a wavelength of 1064 nm show nearly complete cohesive failure inside the adherends (CSF).

Nevertheless, the specimens achieve bond strengths nearly in the magnitude of the references. The specimens treated with the UV laser show complete cohesive failure (CF) inside the adhesive at bond strengths in the magnitude of the achievable values like the reference.

6 Conclusion

The presented investigations on the surface pre-treatment of CFRP for adhesive bonding by using UV and NIR laser radiation show that, with both wavelengths, the strength of the abraded references can be achieved and thus the full potential of the bonds can be utilized. Furthermore, the demand for pre-treatment has been shown by the complete adhesion failure and the low bond strength of the untreated specimen. But with the NIR laser the process window is very small and the risk of damaging the material and of delamination is far too high.

Anyway, both laser sources, the solid-state laser as well as the excimer laser show a high potential for industrial applications for the bonding pre-treatment of CFRP. The area rate for the excimer laser is in the magnitude of up to 10 m²/h, the one for the 20 W solid-state laser about 1 m²/h. Both processes are scalable with the power of the laser source.

References

Meet the Author

Dr. rer. nat. Fabian Fischer is the head of the Departments Adhesive Bonding and Composite Technologies at the Institute of Joining and Welding at the Technical University of Braunschweig, Germany. Mr. Fischer is a Chemist and has a PhD in Technical Chemistry with the main focus in the development of semiconductors used as photocatalysts. For the last years Mr. Fischer has delved deeply the field of the laser treatment of reinforced and unreinforced polymers.
Figure 1: A contaminated Surface (a) and the resulting surface of three surface treatment methods (b-d)
Figure 2: The transmission rate for various matrix materials in dependence of the incident laser radiation.
Figure 3: Delamination in the material of N-IR laser treated specimen
Figure 4: A galvometer driven scanner controlled laser set-up with a) laser source, b) beam shaping device, c) galvometer scanner, d) f-theta lens and e) xyz-axis system
Figure 5: The maximum shear strength of an untreated and different surface pre-treated specimens.