Laser Surface Treatment of CFRP Composites for a Better Adhesive Bonding Owing to the Mechanical Interlocking Mechanism

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Adhesion can be greatly improved by the correct surface preparation techniques. One of the most common and useful technique is specific surface structuring which leads to mechanical interlocking and greater adhesion. This work describes the effect of laser-induced line pattern surface structuring on the mechanical interlocking mechanism and so on the adhesive bonding of carbon fiber reinforced polymer (CFRP) composites. Surface patterns with different laser scribes were obtained by CO2 laser treatment. The effect of the number of a laser shot, the scribe depth, the number of the scribe and the angle between the direction of the laser scribes and mechanical test direction on the adhesive bonding strength of CFRP/CFRP joints was investigated by performing the single lap shear tests according to the ASTM D5868-01. After destructive tests, damaged surfaces were analyzed for determining the failure mechanisms. Mechanical tests showed that laser scribe characteristics especially the number of laser shot and the number of scribes have significant effects on the mechanical interlocking mechanism and so on the adhesion bonding strength. It is suggested that in order to improve the adhesion strength of CFRP/CFRP joints, mechanical interlocking mechanism shall be obtained by optimized laser scribe patterns. POLYM. COMPOS., 2019. © 2019 Society of Plastics Engineers

INTRODUCTION

Composite materials are increasingly used in aircraft components due to their superior weight to strength ratio. This tendency becomes evident with the composite usage for commercial aircraft exceeding 50 wt% and so it is important to develop bonding techniques for composite structures [1–3]. There is an increasing interest in developing alternative methods for joining carbon fiber reinforced polymer (CFRP) composites. For instance, traditional mechanical joints such as bolted or riveted are being replaced by adhesively bonded joints partially for the advantages of corrosion resistance, lower weight increment, damping, good insulation performance, good smooth aerodynamic shape and more uniform load stress distribution [1–5]. The term adhesion in the adhesive bonding defined as “the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking action, or both” in ASTM D907 [6]. In adhesive bonding, there are two prominent adhesion mechanisms: chemical bonding and mechanical interlocking. Chemical bonding is a specific adhesion between the adhesive chemical group and one of the adherents which are held together with covalent bonds, hydrogen bonds, Lifshitz-van der Waals forces and acid-based interactions [7]. Mechanical adhesion consists of between the adhesive and a rough adherend surface that holds the parts together by mechanical interlocking that creating anchorage spots [8, 9]. While specific adhesion is described in terms of the adsorption theory, mechanical adhesion is only considered possible with porous materials [10]. So, if adherends have a surface with pores and/or cavities, then the applied adhesive may enter the irregularities [11]. Following then when the adhesive hardens the adherends are then held together by mechanical interlocking mechanism obtained between adhesive and adherends [12]. For this reason, as with the case of specific adhesion, the use of suitable surface preparation is equally important when considering mechanical adhesion [9]. In order to obtain a proper surface before adhesive bonding, surface treatments are usually applied to the substrates with the aim of increasing the roughness or surface free energy [13].
Several researchers studied the modification of fiber reinforced polymer (FRP) composite surfaces for adhesive bonding by means of abrasion, peel-ply [14–16], grit blasting [17–19], plasma treatments [20–24] and acid chemical etching [25, 26]. Most commonly employed mechanical methods such as abrading and blasting processes have major disadvantages such as fiber fracture, fiber matrix delamination and requirement of a secondary cleaning operation. Additionally, the use of peel-ply for the preparation of CFRP surfaces is a popular technique in the aerospace industry; however, it has disadvantages of increasing manufacturing complexity and cost [27]. Laser processing has the potential to overcome virtually all of these drawbacks and also offers advantages for the surface preparation of CFRP surfaces. As being non-contact techniques, laser processing minimizes the mechanical damage and avoids tool wear and surface contamination [28]. In order to improve the efficiency of the surface preparation process for adhesive bonding of CFRP composites, laser ablation method has been evaluated with these advantages [29]. Many researchers have studied laser ablation of CFRP composites [30–33]. Kreling et al. [30] studied the analytical characterization of CFRPs that was laser treated by excimer laser radiation with SEM and XPS. Authors performed the excimer laser treatments by scanning the laser spot all over the sample surface for cleaning the CFRP surfaces in order to prepare for adhesive bonding. In a similar paper, CFRP surfaces were prepared by laser treatment to achieve two challenges such as an efficient removal of release agent and/or surface contaminations and an exposure of the surface fibers [31]. Yokozeki et al. [32] have also studied the surface cleaning of CFRP with laser treatment to remove the contaminated release agent on the CFRP surface. Laser surface modification of CFRP composite was also studied by Nattapat et al. [33]. They investigated the technical feasibility of using a low power continuous wave carbon dioxide laser for removing the top resin layer of CFRP without damaging the underlying fibers. Tao et al. investigated the effects of carbon dioxide laser irradiation surface pretreatments on the mode I fracture toughness of adhesively bonded CFRP composite joints [34]. In that report, a light surface cleaning with minor changes of surface roughness was performed by low pulse fluence, and also higher pulse fluence was deployed to fully expose carbon fibers. In another study, Hernandez et al. analyzed the effect of laser micro-machined planar patterns with different shape and area fractions on the bond toughness of CuZn 40/epoxy joints [35].

However; there is not any effort identified for preparing regularly oriented surface roughness to gain mechanical interlocking in adhesive bonding of CFRP composites. Therefore, in this study laser-induced line patterns (laser scribes) were regularly oriented on the CFRP composites to possess mechanical interlocking in adhesive bonding. The laser processing and structure pattern parameters such as the number of a laser shot, the scribe depth, the number of the scribes and the angle between the direction of the laser scribes and mechanical test direction were investigated according to their effect on the adhesive bonding strength of CFRP/CFRP joints.

**MATERIALS AND METHODS**

Composite adherends were prepared from unidirectional carbon fiber/epoxy composite [0]₃ laminates with the dimensions of 1.6 × 25.4 × 101.6 mm³ (Fig. 1). CFRP laminates supplied from Kompozitsan Co. from Izmir/Turkey were manufactured by using resin transfer molding (RTM). Surface treatment of CFRP composite adherends was performed using a pulsed CO₂ laser (200 W) which allows selective removal of the adherend matrix material from the fibers due to different absorption characteristic. This laser operates 10.6 μm wavelength with a pulse duration in the range of 5–400 μs and repetition rate range between 5 kHz and 100 kHz. To deflect the laser beam, a galvanometric system was used together with a 160 mm focal length F-Theta lens to focus the laser beam. During surface treatment, plates were fixed at the focal point of the F-Theta lens. The position of the samples at the z-axis was aligned using a manual stage. On the samples, an area of 25.4 mm × 25.4 mm was irradiated in the air by scanning the surface as line by line with parallel laser beam traces. Scanning electron microscopy (SEM) was used for measuring the dimensions of laser-induced scribes. In addition, surface roughness topography of laser treated CFRP samples was obtained by Nanovea PS50 non-contact 3D laser profilometer. Laser surface treatment setup, performed laser parameters and three-axis linear translation stages to provide a precision control of the bondline thickness are illustrated in Fig. 2. Bondline thickness was selected as 50 μm.

The two-component structural liquid adhesive “Hysoi® EA 9396TM” was chosen to bond the CFRP adherends together. This adhesive is a low viscosity adhesive and its mixed density is 1.14 g/mL. At least five coupons were prepared at the same time by a manually stage micrometer controlled apparatus as shown in Fig. 2b. All adhesive bonded coupons were cured at 66°C for 1 h in an electrical furnace.

**FIG. 1.** CFRP sample and standard single lap joint of CFRP/CFRP adhesive joint. [Color figure can be viewed at wileyonlinelibrary.com]
The effect of laser-induced scribe depth, the number of laser scribe and the angle between the scribe direction and mechanical test direction on the mechanical interlocking adhesion mechanism of CFRP/CFRP bonding was investigated by using single lap shear tests. Tests were performed according to ASTM D5868-01 with the crosshead speed of 13 mm/min by a Dartec® universal test machine equipped with a 60,000 N load cell. The modification to ASTM D5868-01 regarded how the bonded test samples were gripped (Fig. 1). By adding to the grips on both sides of the test sample, applied load was transferred along the bondline region. After mechanical tests, a digital camera was used to observe the damage mechanisms which were occurred on the CFRP composite surfaces.

RESULTS AND DISCUSSION

To obtain a mechanical interlocking mechanism with a controlled roughness on the CFRP surfaces, line type scribes were created with a parameter controlled laser machine. Not to break fibers fully in one plane line length was determined as 4 mm (Fig. 3). First of all, the number of laser shot and also the obtained line scribe depth effect on the lap shear strength of adhesive bonded CFRPs were investigated.

For this purpose, various scribe depths were obtained by selected laser parameters as given in Table 1. Three types of samples were prepared with 340, 850 and 1,360 J/cm² laser accumulated fluences. Laser accumulated fluence effect with increasing the number of laser shots on the CFRP surfaces was observed with SEM and was illustrated in Fig. 4. From the SEM investigations, widths of laser affected regions for a varied number of laser shots are given in Table 2. It was clearly determined from Fig. 4 and Table 2, that the width of the laser affected total region was continuously increased from 614 μm to 746 μm with the increment of the number of laser shot. On the other hand, the width of the laser affected the main region was increased up to five laser shots, but the further increment of laser shot to eight did not significantly change the width.

SEM images in Fig. 4 let one know only the two-dimensional changes on the surface, however, scribe depth

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Power (W)</th>
<th>Velocity (mm/s)</th>
<th>Laser accumulated fluence (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (33 scribes with 2 shot laser)</td>
<td>38</td>
<td>200</td>
<td>2 × 170 = 340</td>
</tr>
<tr>
<td>2 (33 scribes with 5 shots laser)</td>
<td>38</td>
<td>200</td>
<td>5 × 170 = 850</td>
</tr>
<tr>
<td>3 (33 scribes with 8 shots laser)</td>
<td>38</td>
<td>200</td>
<td>8 × 170 = 1,360</td>
</tr>
</tbody>
</table>
that could be changed with the increased number of laser shot should be investigated in detail. For this purpose, scribe roughness topography of each sample was determined by profilometer and the results were given in Fig. 5. It was seen in topography images and the roughness curves that the scribe depth was increased from 5.1 μm to 20.1 μm with the increment of the number laser shot from 2 to 8. Additionally, shoulders on both side of the laser scribe were observed along the scribe line. These shoulders occurrence is attributed to the cut and delaminated upward fibers. It was clear that laser accumulated fluence increment caused an increment of scribe depth. So, the first section of this study was performed for the investigation of the scribe depth effect on the mechanical interlocking and so on the shear strength of adhesive bonded CFRPs.

Single lap shear test results as shear strength of adhesively bonded CFRP samples with and without laser treatment are shown in Fig. 6. Minimum and maximum levels

<table>
<thead>
<tr>
<th>Number of laser shot</th>
<th>Width of laser affected total region (μm)</th>
<th>Width of laser affected main region (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>614</td>
<td>200</td>
</tr>
<tr>
<td>5</td>
<td>694</td>
<td>227</td>
</tr>
<tr>
<td>8</td>
<td>746</td>
<td>232</td>
</tr>
</tbody>
</table>

FIG. 4. SEM images of laser affected regions on the CFRP surfaces for varied number of laser shot (a, 250x, b, 500x). [Color figure can be viewed at wileyonlinelibrary.com]
from the averaged shear strength values were illustrated with error ranges on the bars. The average shear strength of the untreated adhesive bonding samples was obtained as 22.5 MPa and it was decided as a reference sample. Compared to untreated CFRPs, it was clear that the number of laser shot and so the accumulated laser fluence had a significant effect on shear strength. Due to the increment of the laser shot from 2 to 5; the shear strength was increased from approximately 21 MPa to 24 MPa. However, this shear strength increment was then decreased again to 21.5 MPa levels with a further increment of the number of laser shot from 5 to 8.

This phenomenon can be attributed to the larger scale roughness that causes air trapping and surface contaminations to remain especially at the bottoms of the narrow and deep scribes [36, 37]. In addition to this, the adhesive could not get into deeper of the scribes and so these adhesive-free unbonded regions limit adhesion strength by reducing both

FIG. 5. Laser scribe topography and roughness measurements: (a) 2 shot, (b) 5 shot and (c) 8 shot. [Color figure can be viewed at wileyonlinelibrary.com]

FIG. 6. Effect of the number of laser shot on the shear strength of adhesive bonded CFRPs.
chemical and physical bonds [38]. In order to support the results of shear strength, images were taken from the surfaces of the fractured parts after mechanical tests given in Fig. 7 for determination of failure modes. A strong dependence of the number of laser shot can also be seen in the failure modes of the single lap-shear tested samples (Fig. 7).

Untreated samples showed three different failure mechanisms such as: adhesive failure (AF-blue arrows), cohesive failure (CF-yellow arrows) and light fiber tear failure (LFT-red arrows) which had established unsatisfying...
bonding between adhesive and CFRP adherends. So in order to increase the shear strength of CFRP adhesive bonding by mechanical interlocking mechanism, 33 scribes were treated by two laser shots but shear strength could not be improved or even decreased. This result can be supported by the LFT failure that was observed dominantly in Fig. 7b. This failure mode was occurred within the FRP substrate near the surface, characterized by a thin layer of the FRP resin matrix visible on the adhesive, with few carbon fibers transferred from the substrate to the adhesive. Interestingly with the 33 scribes obtained by two laser shots on the CFRP surfaces, it was expected that a mechanical interlocking mechanism would increase the shear strength but these scribes decreased the potential of chemical bonding by decreasing the surface area of epoxy–epoxy (matrix-adhesive) bonding. It was thought that this phenomenon is a matter of balance between mechanical interlocking gain and chemical bonding loss. Thirty-three scribes obtained by two laser shots showed dominantly chemical bonding loss according to mechanical interlocking gain. Furthermore, the increment of the number of laser shots from 2 to 5 changed the failure mode from light fiber tear failure to fiber tear failure (red arrows in Fig. 7c). This kind of failure mode can be clearly seen in an adhesively bonded joint exclusively within the FRP matrix, characterized by the appearance of reinforcing fibers on both ruptured surfaces. Optimally treated surfaces with five laser shots showed dominant fiber tear failure in the adhesive so that the performance of the adhesive bonding could be fully utilized by obtaining the highest shear strength. In this sample expected mechanical interlocking gain is more dominant than chemical bonding loss. However, with the eight laser shots laser accumulated fluence gets too high and the samples failed by large excessive fiber tear failure that inhibits lower shear strength (red arrows in Fig. 7d). This phenomenon was attributed to the degraded top fiber layers which were torn during the lap shear test. So, it should be noted that laser-induced line scribe depth should be optimized with the number of laser shot for the best mechanical interlocking and shear strength of adhesive bonded CFRPs. As a result, the number of laser shot was determined as five for the next evaluation about the effect of the number of scribe on the adhesion strength of CFRPs. After optimizing the number of laser shot and so the laser accumulated fluence in the first section of this study, the second investigation was performed for the effect of the number of scribes on the mechanical interlocking and on the shear strength of adhesive bonded CFRPs. The number of laser-induced scribes was varied such as 13, 23, 33 and 45. Laser parameters were same as with the five shots laser treated sample type as given in Table 1. Patterns with a different number of laser scribes are illustrated in Fig. 8.

Single lap shear test results as shear strength values of adhesively bonded CFRP samples with a different number of laser scribes are shown in Fig. 9. The number of laser-induced line scribe has also a significant effect on the shear strength of adhesive bonded CFRPs. It was clear that higher shear strength values were achieved for the samples containing fewer laser scribes. Shear strength value of the samples with 13 laser scribes was obtained approximately

![Diagram showing failure modes with different laser shots](Color figure can be viewed at wileyonlinelibrary.com)
as 26.5 MPa and with the increment of the number of laser scribe from 13 to 45 this value was decreased to approximately 17.5 MPa progressively. For estimating the adhesive bonding strength, the effects of both mechanical interlocking and thermodynamic interfacial interactions could be taken into account. In most cases, the improvement of adhesion strength by mechanical interlocking mechanism can be attributed simply to the increase in interfacial area due to the surface roughness of adherends [38, 39].

In this investigation, it was estimated that the increment of the number of laser scribes would provide an increment in the interfacial area and adhesion strength. Contrary to this, when the laser treated the scribes on CFRP, the epoxy matrix was removed and carbon fibers came in view. In this situation, the adhesion between the epoxy resin and the epoxy-based adhesive was turned into the adhesion between the carbon fibers that come in view and epoxy-based adhesive. Therefore, this obtained physicochemical adherend/adhesive mismatch regressed the estimated adhesion increment which could be gained by the mechanical interlocking. In this case, it is important to note that the adhesive and the adherend must be chemically compatible in terms of diffusion and miscibility [12].

![FIG. 11. Microscopic images of different type of laser treatments with varying angles to test direction. [Color figure can be viewed at wileyonlinelibrary.com] ](image-url)
between the mechanical interlocking gain and chemical bonding loss was lost due to the dominant mechanical interlocking levels for the fewer laser scribes such as 13 so that the shear strength was increased to 26.5 MPa levels.

Fig. 10 presents the fractured surfaces of the CFRP adherends with a different number of laser scribes. It can be seen that for the fewer laser scribes as 13, large CF regions were observed which could be the possible reason for the higher shear strength. With the increment of the number of the laser scribes, CF regions were decreased and large light fiber tearing (LFT) regions (yellow arrows) occurred which caused lower shear strengths. Therefore, it could be concluded that to achieve a good mechanical interlocking mechanism it should be noted that fewer laser scribes would be effective. For this, optimal treatment parameters of 13 laser treated scribes with five shots were chosen to investigate the effect of the angle between the directions of laser scribes and the test on the shear strength of the CFRPs adhesive bonding.

According to the aforementioned two important discussions; a new scribe pattern with five shots laser treated 13 scribes was treated with different angles on the CFRP samples as can be seen with the microscopic images illustrated in Fig. 11. After laser treatment in one scribe, test direction and laser scribes direction can be clearly seen. Additionally, the scribe widths according to the different laser treatment angles were measured and given in Table 3. These measurements indicated that the width difference due to the laser interaction was increased with the increment of the angle from 0° to 90°. This phenomenon can be attributed to the laser-induced heat dissipation which was occurred easily through the fiber direction at 0° compared to 90°. So, the largest width of the laser affected main region was obtained as 435 μm for 0°. Especially for the largest widths of laser affected total region obtained at the angles of 60° and 75°, shear strengths were obtained at minimum levels with an interesting opposite correlation as can be seen in Fig. 12. The effect of the angle between the test direction and the direction of the laser scribes on the shear strength of adhesive bonded CFRPs is also presented in Fig. 12. One-way univariate analysis of variance (ANOVA) was undertaken to test for significant differences in shear strength between the groups with \( \alpha = 0.05 \) established as the level of statistical significance, there is no statistically significant difference in shear strengths between the groups \( (p = 0.3533) \) as shown in Table 4. However, large standard deviations of shear strengths were obtained at all angles except the angle of 45°. This kind of result such as less standard deviation without any gain on the shear strength was also reported on a monolithic AA6082-T6 aluminum material by Ferreira [40]. Therefore, in order to obtain both high and repeatable adhesion shear strength which has a low standard deviation; it is

<table>
<thead>
<tr>
<th>Angle</th>
<th>Width of laser affected main region (μm)</th>
<th>Width of laser affected total region (μm)</th>
<th>Width difference due to the laser interaction (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>435</td>
<td>612</td>
<td>177</td>
</tr>
<tr>
<td>15</td>
<td>242</td>
<td>584</td>
<td>342</td>
</tr>
<tr>
<td>30</td>
<td>257</td>
<td>615</td>
<td>358</td>
</tr>
<tr>
<td>45</td>
<td>171</td>
<td>623</td>
<td>452</td>
</tr>
<tr>
<td>60</td>
<td>280</td>
<td>742</td>
<td>462</td>
</tr>
<tr>
<td>75</td>
<td>268</td>
<td>828</td>
<td>568</td>
</tr>
<tr>
<td>90</td>
<td>176</td>
<td>630</td>
<td>454</td>
</tr>
</tbody>
</table>

FIG. 12. Effect of the angle between the laser scribes and the lap shear test direction on the adhesion strength. [Color figure can be viewed at wileyonlinelibrary.com]
recommended that the scribes should be treated with the angle of 45°.

Failure modes according to the angle between the direction of the laser scribes and the test direction were investigated with the images which are shown in Fig. 13. It was clear that the higher shear strengths obtained at the angles of 0°, 15°, 45° and 90° could be attributed to the dominant LFT failures [41]. LFT failure regions showed good mechanical bonding which was obtained at the scribe regions. However, besides LFT failure mode there are large AF regions obtained at the angles of 30°, 60° and 75° which caused lower shear strength values.

**TABLE 4. Analysis of variance (one-way ANOVA) comparing shear strength of different groups.**

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares (SS)</th>
<th>Degree of freedom (df)</th>
<th>Mean square (MS)</th>
<th>F-ratio</th>
<th>p-value</th>
<th>F-table</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between group (BG)</td>
<td>29.55922439</td>
<td>6</td>
<td>4.9265374</td>
<td>1.194219</td>
<td>0.353356</td>
<td>2.661305</td>
</tr>
<tr>
<td>Within group (WG)</td>
<td>74.25580048</td>
<td>18</td>
<td>4.12532225</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>103.8150249</td>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**FIG. 13.** Demonstration of the failure modes according to the angle between the laser scribes and the lap shear test direction. [Color figure can be viewed at wileyonlinelibrary.com]
CONCLUSIONS

An experimental investigation was carried out on the adhesion performance of CFRP/CFRP composite joints with the laser-induced line pattern surface structuring. Adhesion strength of CFRP/CFRP composite joints tried to be enhanced by the mechanical interlocking mechanism which may be obtained between the laser surface structured adherends. The following conclusions can be summarized:

1. The effect of the number of laser shot and so the obtained scribe depth on the adhesion strength was investigated and it was concluded that for better adhesion strength CFRP surfaces should be structured for optimized depth with an optimized number of laser shot.
2. The effect of the number of laser-induced line scribe with the optimized depth on the adhesion strength was investigated and it was concluded that it has significant because higher shear strength values were achieved for the joint adherends containing fewer laser scribes.
3. Lastly, the effect of the angle between the test direction and the direction of the laser scribes on the adhesion strength was investigated and it was concluded that large standard deviations were obtained at all angles except the angle of 45°. However, there is no significant gain on the shear strength compared to the standard angle of 90°.

As a summary, it can be concluded that the laser-induced surface structuring is a suitable method to obtain a mechanical interlocking mechanism and to enhance the adhesion strength of CFRP adhesive joints. In order to fully benefit from laser-induced surface structuring, optimum laser and scribe pattern parameters should be used.

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