Enhancing structural integrity of adhesive bonds through pulsed laser surface micro-machining

Thesis by

Edwin Hernandez Diaz

In Partial Fulfillment of the Requirements

For the Degree of

Masters of Science

King Abdullah University of Science and Technology, Thuwal,
Kingdom of Saudi Arabia

June, 2015
The thesis of Edwin Hernandez Diaz is approved by the examination committee

Committee Chairperson: Gilles Henn Fernard Lubineau
Committee Member: Marco Alfano
Committee Member: Ravi Samtaney
ABSTRACT

Enhancing the effective peel resistance of plastically deforming adhesive joints through laser-based surface micro-machining

Edwin Hernandez Diaz

Inspired by adhesion examples commonly found in nature, we reached out to examine the effect of different kinds of heterogeneous surface properties that may replicate this behavior and the mechanisms at work. In order to do this, we used pulsed laser ablation on copper substrates (CuZn40) aiming to increase adhesion for bonding. A Yb-fiber laser was used for surface preparation of the substrates, which were probed with a Scanning Electron Microscope (SEM) and X-ray Photoelectron Spectroscopy (XPS). Heterogeneous surface properties were devised through the use of simplified laser micromachined patterns which may induce sequential events of crack arrest propagation, thereby having a leveraging effect on dissipation. The mechanical performance of copper/epoxy joints with homogeneous and heterogeneous laser micromachined interfaces was then analyzed using the T-peel test. Fractured surfaces were analyzed using SEM to resolve the mechanism of failure and adhesive penetration within induced surface asperities from the treatment. Results confirm positive modifications of the surface morphology and chemistry from laser ablation that enable mechanical interlocking and cohesive failure within the adhesive layer. Remarkable improvements of apparent peel energy, bond toughness, and effective peel force were appreciated with respect to sanded substrates as control samples.
ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my advisor Gilles Lubineau, who throughout my pursuit towards a masters degree, always inspired me to find true meaning by looking at things from a fundamental point of view, and for his incisive criticism that helped made this project possible.

Furthermore, I would also like to heartily thank Marco Alfano, whom I collaborated with closely, for his invaluable suggestions, for his patience, and for his guidance in every stage of this project.

My sincere appreciation also goes to Ravi Samtaney, for his time and effort in checking this manuscript.

Gratitude is also due to the King Abdullah University of Science and Technology, for their generous grant which enabled me to carry out this research project.

My appreciation also goes to the composite and heterogeneous materials analysis and simulation laboratory, and my fellow classmates, who provided their assistance unconditionally.

Most importantly, I would like to thank my loved ones, who have supported me throughout the entire process, and encouraged me to always do my best. I will be forever grateful for your love and dedication.
# TABLE OF CONTENTS

Examination Committee Approval ......................................................... 2

Copyright ........................................................................... 3

Abstract ........................................................................... 4

Acknowledgements ................................................................ 5

List of Abbreviations ................................................................. 9

List of Symbols ..................................................................... 10

List of Figures ....................................................................... 12

List of Tables ........................................................................ 17

1 Introduction ........................................................................ 18

1.1 Overview of the field of interest ........................................... 18

1.2 Adhesive bonding mechanisms ............................................. 19

1.3 Surface treatments ............................................................ 21

1.3.1 Adhesive bonding failure ............................................... 24

1.4 Pulsed laser ablation as a reliable means for surface preparation 26

1.5 Interfaces with heterogeneous surface properties ............... 27

1.6 Thesis outline ................................................................. 30

2 Laser based surface modification of CuZn40 ............................ 32

2.1 Materials ......................................................................... 32

2.1.1 Tensile tests and characterization .................................... 33

2.2 Basic concepts of pulsed laser ablation (PLA) ...................... 35

2.3 Description of the laser system available at KAUST ............ 36

2.3.1 Estimating laser scanning speed ..................................... 39

2.4 Laser irradiation of copper substrates .................................. 40
3 Improving the adhesion of CuZn40/epoxy joints through laser surface irradiation 48
3.1 Sample fabrication and testing 48
   3.1.1 Mechanical testing of the samples 49
   3.1.2 Fracture mechanics interpretation of the T-peel test 50
3.2 Mechanical response of homogeneous interfaces 53
3.3 Analysis of failed surfaces 56
   3.3.1 Segregation of the bond toughness from the apparent peel energy 58

4 Effective peel resistance of adhesive bonded substrates with heterogeneous surface properties 62
4.1 Design of heterogeneous interfaces 62
4.2 Surface patterning 63
4.3 Load extension response of T-peel joints with heterogeneous interface 66
   4.3.1 Circular patterns: analysis of interfacial splitting for constant area fraction 66
   4.3.2 Complementary patterns with 50% area fraction 68
   4.3.3 Effect of area fraction 70
4.4 Results analysis 71
   4.4.1 Distance between peak loads 71
   4.4.2 Effective peel force analysis 72
4.5 Issues and limitations 76

5 Concluding Remarks 79
5.1 Summary 79
5.2 Future Research Work 81

References 87

Appendices 90
A.1 Protocols and tools 91
   A.1.1 Control panel settings 91
   A.1.2 Sample preparation 93
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BSI</td>
<td>British Standards Institution</td>
</tr>
<tr>
<td>CFRP</td>
<td>Carbon Fiber Reinforced Polymer</td>
</tr>
<tr>
<td>COHMAS</td>
<td>Composite and Heterogeneous Materials Analysis and Simulation</td>
</tr>
<tr>
<td>CZM</td>
<td>Cohesive Zone Model</td>
</tr>
<tr>
<td>DCB</td>
<td>Double Cantilever Beam</td>
</tr>
<tr>
<td>FE</td>
<td>Finite Element</td>
</tr>
<tr>
<td>HAZ</td>
<td>Heat Affected Zone</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>KAUST</td>
<td>King Abdullah University of Science and Technology</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PLA</td>
<td>Pulsed Laser Ablation</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>YAG</td>
<td>Neodymium doped yttrium aluminium garnet</td>
</tr>
</tbody>
</table>
LIST OF SYMBOLS

\( a \)  Length variable for shape geometry construction
\( A_s \)  Laser spot size

\( B \)  Width of T-peel samples, represents the bonded width

\( d \)  Distance from the line of the applied load to the crack tip
\( \delta_f \)  Final opening for the trilinear cohesive zone model
\( d_s \)  Diameter of the laser beam spot

\( \epsilon_f \)  Elongation at break
\( E \)  Young’s modulus

\( f \)  Laser pulse frequency
\( F_p \)  Laser pulse fluence

\( H \)  Height of T-peel samples
\( I_p \)  Laser irradiance

\( L \)  Length of T-peel samples, represents the bonded length
\( \lambda \)  Distance between centers of patterned shapes
\( \lambda_1 \)  Shape parameter for the trilinear cohesive zone model
\[ \lambda_2 \] Shape parameter for the trilinear cohesive zone model

\[ n \] Number of features, or circles, per side

\[ P_{ave} \] Average force after the peak, or the plateau load that is reached, in a self-similar T-peel test

\[ P_{peak} \] Peak load achieved during a T-peel test

\[ \Phi \] Area under the traction-separation relation for the trilinear cohesive zone model

\[ r \] Radius of a circle

\[ \sigma_f \] Tensile strength

\[ \sigma_{max} \] Cohesive strength for the trilinear cohesive zone model

\[ t \] Thickness

\[ T_g \] Glass-liquid transition temperature

\[ t_p \] Laser pulse duration

\[ v \] Speed of the laser beam relative to the substrate

\[ W \] Laser average output power
LIST OF FIGURES

1.1 Summary of the different adhesion mechanisms. Where (a) represents the chemical and adsorption theories of bonding, (b) describes the electrostatic theory, (c) displays the basis behind mechanical interlocking, and (d) shows the diffusion theory........................................... 20
1.2 High resolution SEM images of surfaces treated under different processes........................................... 22
1.3 Different kinds of bond failure mechanisms........................................... 25
1.4 Example of laser ablation being carried on a Carbon Fiber Reinforced Polymer (Carbon Fiber Reinforced Polymer (CFRP)) sample using the facilities available at KAUST........................................... 26

2.1 Dimensions in millimeters for tensile test samples........................................... 34
2.2 Tensile test results for the tested copper samples: engineering stress-strain curves........................................... 34
2.3 Calculated true stress vs. true strain for the copper samples tested........................................... 35
2.4 Schematic of a laser pulse........................................... 36
2.5 Laser configuration displaying the z-axis displacement and beam focus. Where $d_s$ corresponds to the diameter of the laser beam spot........................................... 37
2.6 Layout of laser system where (a) is the exhaust fan, (b) is the working surface of the laser machine, (c) is the computer that functions as a control unit, and (d) is the service inlet gas........................................... 38
2.7 Relation of the laser machine speeds (in %), and the measured laser speeds........................................... 39
2.8 High resolution SEM images of (a) as received and (b to d) sanded CuZn40 substrates at different magnification levels........................................... 42
2.9 High resolution SEM images of laser treated CuZn40 substrates at power $W=30$ W and speed $v=50$ mm/s (a to c), 250 mm/s (d to f), and 500 mm/s (g to i). ...................................................... 43
2.10 Laser ablated copper substrate with laser test parameters........................................... 44
2.11 Cu2p XPS survey spectra of laser treated CuZn40 for various set of processing parameters. ........................................ 45
2.12 Expanded view of the O1s region pertaining to laser treated CuZn40 for a various set of processing parameters. .................. 46
2.13 Atomic percent abundance of copper, oxygen, nitrogen and carbon as determined through the analysis of XPS scan survey spectra. .... 47

3.1 T-peel test configuration and characteristic geometrical dimensions (H=80 mm; L=60 mm; B=15 mm). ............................. 49
3.2 (a) deformed shape and schematic of typical load-extension response for a T-peel sample which achieves self-similar debonding during crack growth (i.e. d=const.); (b) schematic of typical T-peel sample failing without achieving self-similar (steady state) debonding. Note: $P_{\text{peak}}$: peak load; $P_{\text{ave}}$: average load after the peak. .......................... 52
3.3 Comparison among the load-extension responses of sanded and laser treated T-peel joints. Self similar debonding was achieved in both cases. 53
3.4 T-peel tests results summary. All quantities are normalized with respect to samples treated in air at 250 mm/s speed. (a) Peak force ($P_{\text{peak}}$) recorded during the tests; (b) Average force after the peak ($P_{\text{ave}}$) achieved in the plateau region; (c) T-peel strength as defined in the ASTM D1876-08; (d) Total energy absorbed (per unit bonded area) during the tests. Notice that the quoted numbers represent averaged data over a minimum of five tests. The error bar represent the corresponding standard deviation. ......................... 55
3.5 Fractured surfaces of the sample treated at $W=30 \text{ W}$ and $v=250 \text{ mm/s}$. (a),(b): Typical appearance of adhesive interlocked within the cavity created by the ablation process. (c): Back scattered version of (b). (d),(e): Fracture surfaces of the mating substrates. (f): Back scattered version of (e). (g) and (h): high resolution imaging of typical island of surface oxide decohered from the substrate during sample debonding. (i): back scattered version of (h). For all figures: crack propagation was from left to right. ..................................................... 57
3.6 Comparison among experiments and simulations in the plateau region of the global response pertaining to laser treated samples. The insert shows the traction separation relation employed in the simulations along the main input parameters. ................................. 60
4.1 Circular pattern design, where (a) is the representative square area, C1 is the single feature pattern, C2 is the double feature pattern, C5 is the triple feature pattern, and C5 is the area with five features.

4.2 Substrate treated with both kinds of circular patterns: supplementary, and complementary.

4.3 Optical microscopy image of patterns treated with a geometry offset: concentric circles and offset rhombi.

4.4 Load-extension response curves for different patterns with a treated area fraction of 50%, the yellow band between dashed lines indicates the response range of homogeneously treated samples.

4.5 Total energy absorbed (per unit bonding area) obtained during the tests of supplementary, and complementary treated patterns. All quantities are normalized with respect to homogeneously treated samples.

4.6 Total energy absorbed per unit bonding area obtained from samples tested with a variation in the area fraction. All quantities are normalized with respect to homogeneously treated samples.

4.7 $2\lambda_{\text{nominal}}$ against $2\lambda_{\text{measured}}$ for samples with different treatment conditions.

4.8 From left to right: representative load-extension curves from patterned samples, where the detailed view details the effective peel force, and the dip, or valley that arises from the heterogeneous interface. The next figures (C1, C2, and C3) detail the average effective peel force, and the average minimum force, with respect to the area fraction. The yellow bands represent the range of average loads for homogeneously treated samples.

4.9 Optical microscope images showing the crack front evolution for two different samples with three area splittings, and two area fractions: 50%, and 75%.

4.10 Proposed crack evolution diagram for three different area fractions.

4.11 Different laser processing times for different patterns.

4.12 Samples where substrate failure was present, either partially, or completely.

5.1 Plot of the area fraction as a function of a circle’s radius.

5.2 Proposed geometries for pattern analysis.
5.3 Plot of the area fraction as a function of the variable geometry length normalized with respect to the representative square area. .... 83
5.4 Complete plot of the area fraction as a function of the variable geometry length normalized with respect to the representative square area. 84
5.5 Evolving features as the variable length increases. (a) represents the shapes for \( a < b/2 \), (b) represents the shapes when they reach the critical area fraction \( a = b/2 \), and (c) represents the shapes for \( a > b/2 \). 85
A.1 Laser settings control panel screen for the PLS6MW. ............... 92
A.2 New document screen in CorelDraw X7. Where (a) is the size of the sheet which should match the laser working surface, (b) are the Horizontal and Vertical offset boxes on the Property bar, (c) is the Uniform area fill settings, and (d) is the line color settings. ............... 95
A.3 Print dialog box. Where (a) designates the laser system as the print destination, (b) leads to the laser settings control panel, (c) displays the print range, and (d) shows the number of copies, or repetitions. .... 97
A.4 CorelDraw X7 Welcome screen. .................................. 99
A.5 CorelDraw X7 Import settings. ................................. 100
A.6 Alignment of the laser head with the protective plate. ............ 102
A.7 Access to laser control screen via task-bar icon. .................. 103
A.8 Laser control screen with “Focus View” tool selected for positioning and alignment of the sample. ............................... 103
A.9 Protective plate for laser ablation with specimen positioning guide markings. ......................................................... 105
B.1 Thermal distortion on a copper substrate induced by high laser irradiation intensity; it can be seen that the warping was severe in the lower portion, which caused the surface to be out of the laser’s focus. .... 107
B.2 Typical tools that are required for laser processing. ............... 108
B.3 Preliminary procedure for adhesive bonding of copper substrates, where (1) shows the mixing of the adhesive, (2a) shows the adhesive being spread over the substrate surface, (2b) shows the substrate with the release film before adhesive layer application, (3) shows the adhesive impregnated copper substrates being placed in contact with each other, (4) shows the clamping method during curing, and (5) shows the bending method. ......................................................... 110
B.4 Improved sample fabrication procedure for bonding. ................ 111
B.5 Improved fabrication procedure for bending the samples to 90 degrees. 111
B.6 Typically encountered fabrication defects, where (a) shows the twisting of the bent portions, and (b) shows the 90 degree deviation.

C.1 Load-displacement responses for the homogeneously treated samples under different processing conditions. (a): Samples processed at 250 mm/s in air, (b): samples processed at 500 mm/s in air, (c): samples processed at 250 mm/s in nitrogen, (d): samples processed at 500 mm/s in nitrogen, and (e) samples with no laser treatment, and a sanded surface.

C.2 Load-displacement responses for heterogeneously treated samples with a circular pattern and constant area fraction of 50%. (a),(c),(e),(g): correspond to 1, 4, 9, and 25 area splittings with a supplementary treated area. (b),(d),(f),(g): correspond to 1, 4, 9, and 25 areas splittings with a complementary treated area.

C.3 Results for patterned circles with area fraction of 25%. (a),(b),(c),(d): correspond to 1, 4, 9, and 25 area splittings respectively.

C.4 Results for patterned circles with area fraction of 75%. (a),(b),(c),(d): correspond to 1, 4, 9, and 25 area splittings respectively.

C.5 Results for patterned rhombus shape with area fraction of 50%. (a),(b),(c): correspond to 1, 4, and 9 area splittings respectively.

C.6 Results for patterned hexagon shape with area fraction of 50%. (a): corresponds to the single hexagon, while (b): corresponds to a rotated single hexagon. Note there is no significant difference between either. (c),(d): correspond to 4, and 9 area splittings respectively, of the rotated hexagon shape.

C.7 Results for patterned ellipse shape. (a),(c): correspond to 1, and 9 area splittings of the ellipse, while (b),(d): correspond to 1, and 9 area splittings of a rotated ellipse.
LIST OF TABLES

2.1 Laser processing parameters. ..................................... 40

4.1 Circular feature size for 50% area fraction, and spacing ($\lambda$) .......... 72
Chapter 1

Introduction

1.1 Overview of the field of interest

Adhesive bonding is a suitable joining technique for a wide range of structures in aerospace, solar, rail and construction industries. However, bonded structures show a rich array of failure mechanisms, which hinders their use in primary structural applications.

For instance, interfacial fracture between adjacent layers, which is usually the result of improper surface preparation, is a very widespread mechanism of failure of built-up structures.

Indeed, fabrication of reliable adhesive bonds depends not only on joint design as well as the type of adhesive employed, but it strongly relies on the preparation of the mating surfaces [1, 2].

It follows then, that the performance of adhesive joints heavily relies on the choice of an appropriate surface treatment prior to bonding [1, 2, 3].

Adhesion theories, such as the weak boundary layer, propose that a clean surface can promote a strong bond to adhesives. Conversely, contaminants such as rust, oils, and greases, will form a layer that is cohesively weak.

Surface treatments can act by removing potential weak boundary layers, by altering surface topography, or by modifying surface chemistry of the substrate surface,
or by a combination of these mechanisms. By ensuring intimate molecular contact between the substrate and the adhesive, the adhesive will flow and fill microscopic asperities, enabling mechanical interlocking. Some of the surface treatments that can be performed include:

- Solvent wiping
- Mechanical grinding/sanding
- Chemical etching
- Plasma
- Laser irradiation (i.e. cleaning, texturing, patterning)

Typically laser ablation refers to material removal through heating, melting, and vaporization with the use of a pulsed laser, although it is also possible to ablate material by using a continuous wave laser beam if the laser intensity is high enough.

Pulsed Laser Ablation (PLA) is an alternative surface preparation technique that assists in the development of significant modifications of surface morphology [4, 5], and surface chemistry as well [6, 7]. This is expected to result in a higher bond toughness [8, 9], and long term joint stability [10], which are necessary to guarantee the reliability of adhesive bonds.

### 1.2 Adhesive bonding mechanisms

Adhesive bonding consists of joining materials by surface attraction forces, arising mainly from chemical origins (interatomic or intermolecular bonds) between substrate and the adhesive. The forces enabling adhesive bonding give rise to what is known as adhesion.
Five mechanisms underlying the phenomena leading to adhesion will be discussed. Afterwards, different surface treatments and their classification will be covered; an additional section will explain the failure mechanisms. A last section will introduce an alternative method called pulsed laser ablation.

Figure 1.1: Summary of the different adhesion mechanisms. Where (a) represents the chemical and adsorption theories of bonding, (b) describes the electrostatic theory, (c) displays the basis behind mechanical interlocking, and (d) shows the diffusion theory.

Chemical bonding

The formation of covalent, ionic, or hydrogen bonds across the interface are invoked in the theory of adhesion known as chemical bonding.

Adsorption theory

Adsorption theory contributes to all adhesive bonds, and it is the most acceptable theory of adhesion, given that the basis is that van der Waals forces occurring between
all atoms and molecules close together, exist across the interface.

**Electrostatic bonding**

This theory originated from the proposal that if two materials are placed in contact, electrons will be transferred between them, forming an electrical double layer which contributes with forces of attraction.

**Mechanical interlocking**

The mechanical theory of adhesion originated from the proposition that if the substrate has an irregular surface, then the adhesive may enter, and fill the cavities prior to hardening.

**Diffusion theory**

Finally, diffusion theory takes into consideration polymers, where interdiffusion will occur if the polymer chains are mobile (above $T_g$), and compatible, so that the initial boundary is eventually removed.

### 1.3 Surface treatments

It is important to consider that the performance of the joint is directly related to the successful implementation of surface pre-treatment. Additionally, if a cohesively weak boundary layer (e.g. lubricant, polymer additives, weak metal oxides) is present in an adhesive joint, then failure will occur at a low applied load.

Not all contaminants will form a weak layer, considering that in some cases, such as Acrylic structural adhesives, they are dissolved by the adhesive.

Topography affects adhesive-substrate contact, and in turn, surface wetting. In combination with adhesive rheology, it may result in mechanical interlocking. Surface
chemistry is important because it affects the wetting of a surface and the degree of interaction across the adhesive-substrate interface.

Surface preparation, unlike surface treatments, includes the removal of dust, oxides and coatings with poor adhesion, as well as the degreasing with organic solvents.

Primers, usually in the form of organic coatings, are often used as an alternative to surface treatments. Since they have lower viscosities, they can achieve better contact with the substrate. They also contain corrosion inhibitors, and can protect a surface until the bonding process is carried out [11].

Surface treatments can be classified into these different categories:

- Mechanical: includes abrasion by grit-blasting, and grinding.
- Chemical: includes surface removal using non-oxidizing acids, and surface creation using oxidizing acids.
- Physical: includes the use of a flame, plasma or laser.
- Electrical: includes the use of low pressure plasma, and an electrical discharge (e.g. corona).

![as-produced, grit-blasted, laser irradiation, chemical etching](image)

Figure 1.2: High resolution SEM images of surfaces treated under different processes.

In Figure 1.2, it can be seen from the SEM analyses, the surface topography of the same material that was prepared under different surface treatment methods. The different processing types will be detailed next.
Mechanical

Mechanical treatments consist of mechanical abrasion by means of sanding or grit-blasting; however, limited repeatability and potential surface contamination from the debris formed during the processing actually reduce the overall bond performance.

Chemical

Chemical treatments can be classified into the use of:

- Non-oxidizing acids (e.g. hydrochloric acid, diluted sulfuric acid), which cause an electrochemical oxide, or acid reaction which results in the removal of the naturally forming oxide layer, this is also called acid degreasing.

  The surface becomes not only chemically clean, but also rough in its submicroscopic structure. Chemically active sites are created on the surface, which are a prerequisite for the formation of adhesive bonds.

- Oxidizing acids (e.g. nitric acid, phosphoric acid, chromic acid) with or without the addition of oxidizing salts such as sodium or potassium dichromate, induce the formation of an additional firmly adhering conversion coating (e.g. phosphate or chromate oxide layer), this method is known as “phosphatizing”.

  The application of an electric current to the adherent can enhance the chemical reaction. Since the parts to be treated are generally used as the anode, this process is called anodizing.

The use of acids as chemical treatments play a major role in aerospace engineering [12], however, these treatments create a large volume of hazardous wastes which pose a great risk to the environment and human health. Proper disposal of this waste also makes the process more expensive, and they have been progressively subjected to stricter control regimes by governmental organizations [13].
Physical

Physical treatments include flame treatments, in which polymer materials are gently touched by an open flame with a surplus of oxygen, this induces an oxidative effect that improves adhesion properties, especially in the case of non-polar plastics. Flame treatment is an environmentally safe, continuous method with short treatment periods.

Another kind of physical treatment is Plasma treatments, where a plasma arc is initiated by means of a pilot arc. The process gas between the electrode and the work piece becomes ionized and the flow of gas directs the plasma to the surface to be treated.

Electrical

An electrical surface treatment is the coronal discharge, where a high frequency voltage is applied between two electrodes, or between an electrode and the substrate material. This causes the atmosphere between the electrodes to become ionized, and a corona discharge is ignited. When an insulator is introduced between the electrodes, its surface is targeted with ions and radicals, causing a modification of the adhesion properties.

1.3.1 Adhesive bonding failure

The importance of surface preparation has been covered, as there are several factors that may affect an adhesively bonded joint. Other kinds of phenomena that lead to adhesive failure may include the degradation by means of sun exposure, or the presence of solvents that deteriorate the adhesive integrity. Otherwise, adhesive bonds may also fail due to mechanical stresses present that may separate the surfaces.
When a high enough load is applied to a bonded joint, debonding will occur; this fracture can manifest in several ways including:

- **Adhesive failure**: also known as interfacial fracture, this kind of failure is present when the adhesion is not as strong as the bulk material from the substrates, and the crack propagates at the interface.

- **Cohesive failure**: this kind of failure means that the adhesive bond is strong enough to hold the substrates together, but due to the lower strength of the adhesive employed compared to the bulk material of the substrates, the fracture propagates through the adhesive layer.

- **Substrate failure**: this happens when the adhesive bond is very strong, and the adhesive is tougher than the bulk material of the substrates. In this case, the crack may extend from the adhesive layer to the substrate.

These different kinds of failure are represented above on Figure 1.3.
1.4 Pulsed laser ablation as a reliable means for surface preparation

PLA is a promising alternative which holds the premise of improved repeatability, costs reduction, and waste minimization. PLA relies on the use of highly focused laser beams which leads to material removal and redistribution on the target surface.

Another positive aspect is that PLA enables micro-patterning of materials, cleaning off surfaces from contaminant layers and particulates, and it is currently employed in a wide range of applications in biotechnology and medicine [14]. On top of this, PLA is also prone to automation.

Figure 1.4: Example of laser ablation being carried on a Carbon Fiber Reinforced Polymer (CFRP) sample using the facilities available at KAUST.
1.5 Interfaces with heterogeneous surface properties

Recent research on bio-inspired surfaces with adhesive enhancement properties reveals that nature relies on dispersive mechanisms of adhesion (by the means of adsorption). However, these mechanisms usually consist of van der Waals forces which act on a very small scale and are not very strong compared to other methods of adhesion (i.e. covalent bonding).

Nature achieves remarkable adhesion properties by focusing on the contact area. Van der Waals forces are not particularly strong by themselves, but if the area is increased, then the number of van der Waals interactions will rapidly increase.

One way to do this is by introducing roughness into the surface. Nature excels at this, as it provides surfaces based on hierarchical structures, in which a structural element is conformed by structures itself. This allows for a greatly increased surface area compared to a neat surface. The use of structures on different length scales allows for an increased contact area, and thus provides robust adhesion properties.

These kinds of structures are not only abundantly present in nature, but in some man-made structures as well.

The inclusion of discontinuities at the substrate, or at the interface for adhesion, promotes local stress concentration, crack nucleation/arrest, and in turn enhance energy dissipation. These heterogeneous surfaces may induce sequential events of crack arrest and propagation thereby having a leveraging effect on the dissipation mechanisms (e.g. plastic dissipation). Overall, if the dissipation increases when severing the substrates, then the toughness of the joint increased.

Only a few works have focused on the study of interfacial discontinuities and revealed the basic features. Most of them focus on micro-scale samples fabricated using standard lithographic techniques; such techniques are time consuming [15, 16, 17].
Due to the nature of these techniques, and the material systems which are usually flexible adherents such as Polydimethylsiloxane (PDMS), they cannot be easily extended to large scale applications. Previous related works will now be detailed, in order showcase the expected behavior, and the possible underlying mechanisms that different authors present as a solution to their respective research problems.

In the work of Xia, et al. [18], the authors refer to biological systems, such as the gecko, which achieves an adhesion enhancement by 3D features; but they propose that such complex microstructures may not be necessarily required, and explore benefits in adhesion by simple thin film peeling patterning. They analyzed how a variation in the elastic properties at the microscale can significantly affect the effective peeling behavior of the adhesive at the macroscale.

They present results for the measured force required to peel a tape of alternating bending stiffness, compared to an homogeneous tape. The authors introduce an important term known as the effective peel force. They recognize that in order to peel the tape, the effective force that is required to peel any significant length of tape is equal to the average load of these peaks, as one needs to overcome this load in order to propagate the crack.

When the authors acknowledged the potential of this technique, they decided to experiment with a different material system, using PDMS and periodic arrays of ink features, to create a controlled heterogeneous tape. With this, they are able to create tailored surfaces and exploit this behavior.

They present this by making a direction-sensitive pattern, which consists of an asymmetric geometry. The test they propose involves the peeling of a patterned surface. The pattern remains the same, but at half the length of the test, the pattern is flipped. The evidence is clear when they present the deformed crack front, and the corresponding mechanical response.

Other authors such as Chan, et al. [15] covered a wider range of patterns and
identify the increase in the contact line during separation as the mechanism responsible for increases in the load. They recognize the pinning of the contact line, as it requires additional energy to propagate the crack.

The authors have identified that there is a variation in the mechanical response that comes from different area fractions. Given that they work with a single film that has a variation in the pattern in one direction, they refer to the area fraction as line fraction.

They present their test results by describing the adhesion energy normalized with respect to samples with an homogeneous interface. It is evident that the response of these samples does not solely depend on the treated area fraction. This article is, however, limited to the effects of the area fraction, as the authors do not consider the effect of area splitting. Although they do consider different shapes.

The enhancements in the peel energy are attributed to the pinning of the crack front in the areas with a higher toughness contrast. They present the different expected behavior of the crack front as it accommodates the different shapes, and it shows that there is an effect of the shape of the pattern.

Authors such as Ranade, et al. [16] have investigated the interaction of a propagating crack with weakened interfaces, as opposed to tougher regions. They utilize a technique that uses physical vapor deposition to create weaker regions of copper on an acid treated aluminium substrate. The samples are then tested under the DCB configuration.

They claim that the local weak interfaces influence the fracture energy over a close distance around the weak regions. They found that the minimum values of the fracture energy agree with the rule of mixture, for the contrast between the fracture energies of the aluminium base, and the weakened copper interface.

This study explores the extent of using laser ablation to generate interfaces with heterogeneous surface properties. Laser ablation can follow precise geometry accord-
ing to controllable design and specifications. It also creates a repeatable surface topology, critical to the quality of the bond. This allows to reproduce bio-inspired designs on interfaces as simplified patterns.

Unlike previous studies that rely on flexible adherents, laser ablation is an advantageous process. It enables the use of adhesively bonded metals and composite materials, which can be used for structural applications. It is also favorable, as it can treat large areas in a relatively short time.

This study will focus on the discovery of the mechanisms at play, and understanding the behavior, being able to exploit this technique for enhanced adhesion.

1.6 Thesis outline

This study has been categorized under 4 different chapters for a straightforward progression detailing the research progress. The first chapter presents a summary of the theories involved in the research. Furthermore, it discusses the literature and tries to establish a link between existing research and the intent of this study.

A second chapter covers the material selection, and focuses on the extent of laser ablation with the available resources, for the specific material system. It also encompasses mechanical and chemical surface analyses that help quantify the degree of interaction and ultimately the enhancements compared to other more traditional methods.

A third chapter centers on an initial study with homogeneously treated samples, in order to determine the best working conditions. It involves an initial calibration of the system to find the laser system working parameters, and a few other variables, such as the atmospheric conditions during processing.

A last chapter focuses on heterogeneously treated substrates. The design of the patterns is detailed, and an analysis of the results obtained is covered. This chap-
ter outlines the different effects that arise with surface patterning, and presents the mechanisms enabled due to the discontinuities in the surface.

Finally, a conclusions summary is included alongside possible directions for future work related to this research topic.
Chapter 2

Laser based surface modification of CuZn40

This section will cover the selection of the material system, as well as the results of surface modification via laser ablation using SEM, and XPS techniques.

In the case of the substrates material, there was no preference for any material in specific. The purpose of the study was to identify a combination of substrate, and adhesive that was compatible; and to further analyze the effect of laser ablation on the substrates. That said, thin copper plates were used as substrates as they were readily available. And besides being able to be processed with the laser system, the laser system was also capable of cutting the plates to any determined dimensions.

2.1 Materials

The material employed as substrates for adhesive bonding was provided by Metal Industries Technology Co. in Saudi Arabia which has identified it as Copper/Brass H62 (also known as ASTM C28000, and ISO CuZn40). The CuZn40 has favorable mechanical, thermal, corrosion and electrical properties. The good formability of
the alloy has led to a vast number of applications\(^1\) in several industries. However difficulties arise concerning joining, because traditional fusion welding is strongly affected by the presence of zinc, which evaporates during welding with a detrimental effect on the joint microstructure\(^2\). It follows that the fabrication of high-quality and reliable joints demands alternative joining techniques.

The adhesive selected for the fabrication of joints is a two component (resin+hardener) room temperature curing epoxy (Araldite 420 A/B, Huntsman, Salt Lake City, UT, USA). It is a structural adhesive with high shear and peel strength which bonds a wide array of materials, such as metals, composites, and thermoplastics. The basic mechanical properties of the adhesive provided by the manufacturer through tensile tests are as follows: Young’s modulus, \(E=1.5\ \text{GPa}\); elongation at break \(\epsilon_f=4.6\ \%\); tensile strength, \(\sigma_f=29\ \text{MPa}\).

The substrates consisted of thin copper foils (CuZn40) with nominal thickness equal to \(t=0.5\ \text{mm}\). CuZn40 copper alloy usually contains 59\%–63\% in weight of Cu, Pb<0.3\%, Fe<0.3\% and Zn (balance). The mechanical properties of the alloy were determined through dedicated tensile tests which are described in the next section.

\subsection*{2.1.1 Tensile tests and characterization}

To determine the mechanical properties of the material, a few tensile dog-bone samples were created by laser cutting, as can be seen in Figure 2.1, and tested in the machine Instron 5882 with the help of the video-extensometer that records the strain accurately.

\(^1\)e.g. pipe fitting, domestic taps, radiator valves, gas appliances, window and door furniture, architectural panel sheets, large nuts and bolts, condenser plates and heat exchangers

\(^2\)porous and weak layers of copper and copper oxide
The load-extension response and the stress-strain curves are shown in Figure 2.2. From this information it was possible to estimate the material’s mechanical properties: Young’s modulus $E=90$ GPa; elongation at break, $\epsilon_f=12.5$%; yielding stress $\sigma_y=85$ MPa.

Since the obtained mechanical properties will be later used for computational simulation purposes, the data was converted from engineering stress and strain to true stress and true strain. The engineering stress-strain curve is given in Figure 2.2.

Figure 2.1: Dimensions in millimeters for tensile test samples.

Figure 2.2: Tensile test results for the tested copper samples: engineering stress-strain curves.
The stress-strain datapoints that will be used later in FE simulations are shown in Figure 2.3.

![Figure 2.3: Calculated true stress vs. true strain for the copper samples tested.](image)

**2.2 Basic concepts of pulsed laser ablation (PLA)**

Typically pulsed laser ablation is used in medical and biotechnology applications, for example in the thermal ablation of soft-tissue tumors. But lasers are also available for industrial purposes, they focus on the removal of conductive and metalized layers from flexible substrates without damaging the carrier substrate.

In PLA there is a strong spatial and temporal localization of laser-material interaction which gives very large heating/cooling rates, and small material volumes subjected to the thermal induced defects [13]. Therefore, a strongly localized area is heated by the laser pulses, while the surrounding area is basically unaffected.
Surface modifications are imparted by controlling adjustable laser process parameters; of particular importance is the selection of pulse fluence ($F_p$). An adequate depiction of the pulse fluence is given in Figure 2.4. In fact, the actual depth achieved for the ablated material depends mostly on the fluence which is transmitted to the target surface. The fluence can be calculated as follows:

\[ I_p = \frac{W}{A_s} \tag{2.1} \]
\[ F_p = I_p \cdot t_p = \frac{W}{f \cdot A_s} \tag{2.2} \]

where $I_p$ represents the laser irradiance, $t_p$ is the laser pulse duration, $f$ the pulse frequency and $A_s$ is the spot size.

Using adjustable laser processing parameters such as laser average output power ($W$), speed of the beam relative to the substrate ($v$), and spacing or laser pitch, a variety of textures can be imparted to treated surfaces, as it will be shown later.

### 2.3 Description of the laser system available at KAUST

Fiber lasers, such as the one found at KAUST, use single emitter diodes to excite the lasing medium. These generally require less power and have a long lifetime cycle
that eliminates maintenance. The large surface area of the medium makes it easy to cool with air. Fiber lasers are also known to experience fewer power losses because the light source is completely sealed. Consequently, fiber lasers are more efficient and reliable than Neodymium doped yttrium aluminium garnet (YAG) lasers.

KAUST contains most of the tools needed for PLA, the most important being a 1.06 μm ytterbium, fiber laser (PLS6MW Multi-wavelength Laser Platform by Universal Laser Systems, NY, USA).

The laser system is required to be linked to different equipment to guarantee its proper operation; the layout of the laser is shown in Figure 2.6, where the various components can be appreciated. This specific laser machine is able to handle three distinct kinds of laser types, 1.06 μm fiber, 9.3, and 10.6 μm CO₂, each with different wavelengths, which favor the interaction with certain materials better than others. The fiber laser is the best option for interacting with metals, such as stainless steel, titanium, brass, copper, and aluminium. Not to mention, the laser can mark metals and even cut metal foils.

![Laser configuration displaying the z-axis displacement and beam focus. Where \( d_s \) corresponds to the diameter of the laser beam spot.](Figure 2.5)

The depth of penetration, the interaction within the material, and in turn the Heat Affected Zone (HAZ) (See Figure 2.5) depend on optical and thermal penetration
depths.

The actual penetration and the rate of vaporized, or ablated material depends on the laser fluency transmitted to the target surface. Materials with a high thermal conductivity require very short pulse times for high quality surfaces. For dielectric materials the optical penetration depth dominates, and it is a strong function of laser wavelength. For metals the optical penetration depth is negligible and the thermal depth dominates.

The lateral dimension (i.e. laser spot size) does not match with the diameter of the processed ablated zone, this is because the edges of the beam may act in an unwanted way causing thermal damage. For a high quality surface a smaller beam is preferable; but sharp beams may affect the laser induced plasma near the ablation front. Reduction of the laser pulse duration, beam diameter and pulse energy are expected to decrease the volume of the affected material, this can be exploited to improve accuracy. Very short pulse durations are required for precise patterning and micro-drilling.

Figure 2.6: Layout of laser system where (a) is the exhaust fan, (b) is the working surface of the laser machine, (c) is the computer that functions as a control unit, and (d) is the service inlet gas.

The exhaust system, as shown in Figure 2.6(a), is useful when cutting polymers, given that the fumes produced during processing could be toxic. The laser working
area is 813 x 457 mm, while the motorized Z-axis lifting capacity is 18 kg and the maximum part height is 229 mm. The laser system has interchangeable lasers, and focus lenses.

Additionally, the laser supports a service gas inlet, shown in Figure 2.6(d), that provides a continuous pressurized flow through the nozzle of the laser, thus blowing away any debris formed during processing, and cooling the treated area.

Lastly, the laser system is controlled via computer with a software extension for CorelDraw X7 provided by the manufacturer of the laser system.

2.3.1 Estimating laser scanning speed

Since the speed of the system was not disclosed, an estimation was made. For this, a large rectangle of a precise size was created and it was to be ablated by the laser system. The time it takes for the system to complete each side was then measured, as it is easy to observe when the laser head changes direction; this becomes complicated as the laser starts traveling faster, and a bigger error is introduced.

![Graph showing the relation of laser speeds and measured laser speeds.](image)

Figure 2.7: Relation of the laser machine speeds (in %), and the measured laser speeds.
The results for this analysis can be seen in Figure 2.7. In summary, 10% corresponds to 50 mm/s, 50% to 250 mm/s, and 100% corresponds to 500 mm/s. These results show that the nominal speed values that the system is able to produced, were obtained with fairly good accuracy, and with relative ease and without the need for a more sophisticated method.

The available laser processing parameters are summarized in Table 2.1.

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser wavelength</td>
<td>1064 nm</td>
</tr>
<tr>
<td>Focal distance</td>
<td>46 mm</td>
</tr>
<tr>
<td>Spot diameter ($d_s$)</td>
<td>25 μm</td>
</tr>
<tr>
<td>Pulse repetition rate</td>
<td>(30/76/145/230/250) kHz</td>
</tr>
<tr>
<td>Pulse duration (FWHM)</td>
<td>&gt;10 ns</td>
</tr>
<tr>
<td>Pulse energy (max)</td>
<td>2.0 mJ</td>
</tr>
<tr>
<td>Max average power</td>
<td>30 W</td>
</tr>
<tr>
<td>Max Laser speed</td>
<td>500 mm/s</td>
</tr>
</tbody>
</table>

FWHM: Full width at half maximum

It is worth noting that besides the laser system, there are only but a few tools required for the processing, and all of them are easily available at COHMAS Lab or at the Core Labs. These tools have been included in the Appendix B.

2.4 Laser irradiation of copper substrates

2.4.1 Calibration

In order to find the working conditions of the laser system that would create a favorable interaction with the selected materials in this study, a calibration procedure had to be carried on; this procedure helps in finding the optimal laser input parameters.

It was found that the laser spot size depends mostly on the laser speed, rather than the variation in the z-level (for the investigated range close to the surface=±0.30 mm). The estimated smallest spot area then occurs at higher speeds. Increasing the speed might reduce the effect of laser irradiation on the surface morphology.
If the frequency increases, there is an overall decrease in the spot size; this is expected since the fluence decreases. In subsequent analyses, it was established to keep the frequency constant and equal to 30 kHz.

Therefore, the laser processing parameters were set as follows: maximum power, and minimum frequency (i.e. maximum fluence), in order to analyze the effect of the laser speed; while the z-distance has been set such that the laser is in focus on the sample surface.

In order to ablate the entire surface, it was decided to ablate parallel lines close to each other. For this, the spacing was set as the smallest spot area that was measured (30 μm). The length of the lines and the number of lines can be adjusted, in order to cover a specific area.

2.5 Analysis of surface morphology and chemistry

A Scanning Electron Microscope (FEI Quanta 200) was used to analyze surface morphological modifications. In addition, backscattered electron analysis was also carried out to probe the fractured surfaces. Surface chemistry was monitored through X-ray photoelectron spectroscopy (XPS) carried out using a Kratos AXIS Ultra DLD spectrometer (KRATOS Analytical, Wharfside, UK) equipped with a monochromatic Al-Kα anode emitting X-ray source of photon energy $h\nu=1486.6$ eV. Measurements were performed at power of radiation beam equal to 150 W and the system was provided with a multichannel plate and delay line detector under a vacuum ($10^{-9}$ mbar). Measurements were performed in hybrid mode using electrostatic and magnetic lenses. All spectra were recorded using an aperture slot of 300 μm x 700 μm. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively. Samples were mounted in floating mode in order to avoid differential charging. Charge neutralization was required for all samples.
Binding energies were referenced to the C 1s peak of (C-C, C-H) bond which was set at 285.0 eV. Measurements were made at an angle of photoelectron emission of 0°, which corresponds to the average 10 nm examined thickness.

2.5.1 High resolution SEM imaging

SEM analyses of copper substrates as produced, and with a sanded surface are reported for comparison in Figure 2.8. The surface of as produced copper substrates is almost flat, see Figure 2.8(a), however after sanding random ridges and grooves were produced, as shown in Figs. 2.8(b–d), which can promote an increase in surface area and roughness.

![High resolution SEM images of (a) as received and (b to d) sanded CuZn40 substrates at different magnification levels.](image)

Using laser irradiation a fraction of the laser beam energy is absorbed by the material, thus promoting material melting and vaporization which ultimately leads to modifications in surface morphology and chemistry. A comparison among the SEM pictures as reported in Figure 2.9 demonstrates the effects of PLA, which were
carried out at maximum fluence and for varying speed levels. The laser speed had an important effect on the resulting morphology, i.e. the degree of modifications substantially increased as the laser speed decreased, see Figure 2.9. Moreover, the presence of recast material, a multitude of sharp asperities and metallic particles can be also observed. Spherical particles are likely to be originated by the rapid condensation of the expanding gas or plasma during cooling [4].

Figure 2.9: High resolution SEM images of laser treated CuZn40 substrates at power $W=30$ W and speed $v=50$ mm/s (a to c), $250$ mm/s (d to f), and $500$ mm/s (g to i).

The so obtained porous layer can increase contact surface, and may enhance mechanical interlocking since the cavities are able to retain the adhesive and resist debonding. On the other hand, surface asperities may adversely affect wetting because of capillarity forces and adhesive viscosity, especially when using cold cur-
ing adhesives [19]. High resolution SEM images reported in Figure 2.9(c), (f) and (i) indicated substantial differences in the surface features displayed by the treated substrates. Apparently, a structured oxide layer was formed that seems to have sub-micron scale features. The layer occasionally shows cracks and delamination, see Figs. 2.9(b) and (e), that may be related to the thermal process carried out in ambient atmosphere. For this reason, oxide adhesion to the bulk alloy may be lower than its adhesion to the adhesive thereby representing a critical factor able to trigger interfacial failure. Such an issue was already observed on laser textured titanium surfaces [5].

2.5.2 XPS measurements

A small copper substrate was subjected to surface treatment via PLA with different parameters that result in 6 different processing conditions. Three different speeds of the laser were investigated (50 mm/s, 250 mm/s, and 500 mm/s), on two atmospheric conditions (while air, or nitrogen, is being injected through the laser nozzle); this sample can be observed in Figure 2.10. The modification of the surface chemistry was analyzed with an XPS analysis.

Figure 2.10: Laser ablated copper substrate with laser test parameters.
On Figure 2.11, the XPS spectra for Cu2p is shown. Where the largest peak at the right side appears through the superposition of three different compounds. The largest peak signal was identified to belong to metallic copper, even though its binding energy is very similar to Cu$_2$O (cuprous oxide), and it is very hard to distinguish them from the Cu2p spectrum [20].

Figure 2.11: Cu2p XPS survey spectra of laser treated CuZn40 for various set of processing parameters.

The presence of the satellite peak signals, as indicated on the figure shifted from the large peak, belong to Cu$^{2+}$, and points towards CuO (Cupric oxide) being present on the probed sample. Another compound also identified to be present was Cu(OH)$_2$ (copper hydroxide).

It is worth noting that the spectra that were probed in air and nitrogen, do not change significantly, and that the peak intensity for metallic copper increases with laser speed. This implies that a higher intensity of laser ablation contributes to the removal of metallic Cu, and/or Cu$_2$O). With this information, it is not expected for
the nitrogen gas to play a significant role on the surface chemistry, and so, on the overall mechanical response of the joints.

Figure 2.12: Expanded view of the O1s region pertaining to laser treated CuZn40 for a various set of processing parameters.

To investigate the surface oxidation, the spectra corresponding to O1s is shown in Figure 2.12. The analysis of this portion of the spectra confirms the existence of CuO, and Cu(OH)$_2$, which can be seen as the two peaks present in the figure.

Reviewing the results, it is clear that the Cu(OH)$_2$ content on the surface is decreasing as the laser speed decreases, while the content of CuO prevails. This may be explained by considering that the local temperature increases as the laser speed is decreased; the formation of CuO is promoted at high temperatures (400$^\circ$C – 600$^\circ$C) [21]. This agrees with the observations from the SEM, which shows a progression of the oxide morphology at the sub-micron scale as the speed increases.

It has been demonstrated that the formation of CuO has a beneficial effect on the strength of adhesive joints; as it improves wettability, and in turn, increases the level
of interfacial contact with the adhesive, thus enabling mechanical interlocking [21].

Figure 2.13: Atomic percent abundance of copper, oxygen, nitrogen and carbon as determined through the analysis of XPS scan survey spectra.

In Figure 2.13, the elemental composition probed (atomic percentage) is shown as a function of the laser speed. It can be observed that the oxygen present increases after laser processing, but does not change that much between the different speeds; as does the copper content, which decreases slightly with laser speed. Regardless of this, the carbon present is influenced by several impurities, which could be related to dust from atmospheric contamination [22].

Considering the results obtained from the surface morphology, the surface chemistry, and significant thermal distortions as substrate warping that occurred after laser processing at 50 mm/s, as can be seen in Figure B.1. Subsequent experiments were carried out at 250 mm/s and 500 mm/s.
Chapter 3

Improving the adhesion of CuZn40/epoxy joints through laser surface irradiation

3.1 Sample fabrication and testing

For sample fabrication, CuZn40 plates (100 x 100 mm) were laser ablated over a 60 x 100 mm area; grit and debris formed during the processing was cleaned from the surface by exposing it to a compressed air flow. After surface pretreatment (sanding or PLA) the plates were cut down into 15 x 100 mm substrates, degreased with acetone, and subsequently bonded using the epoxy adhesive. The adhesive layer thickness was controlled using 250 μm thick optical fibers deployed in the longitudinal direction (*i.e.* x-direction in Figure 3.1). Weights were placed to hold the substrates in place and squeeze out any excess of adhesive.

After curing at room temperature for 24 hours, the adherents were bent by wedge splitting so that to confer the desired T-shape to the joint. To facilitate bending, a release film (A6000 Release Film, Richmond Aerovac, USA) was deployed over 40 mm of the total overlap length (100 mm). Special care was taken in order to ensure
a proper alignment of the bent portions, which were then coupled with the grips of an electro-mechanic tensile testing machine.

![Figure 3.1: T-peel test configuration and characteristic geometrical dimensions (H=80 mm; L=60 mm; B=15 mm).](image)

The overall dimensions of the fabricated T-peel joints are given in Figure 3.1(a). Since substrates warping and/or distortions occasionally led to a variable adhesive layer thickness, all samples were probed through optical microscopy and those showing substantial deviations from the nominal thickness ($\geq 10\%$) were not employed in mechanical tests.

Five batches of T-peel joints were prepared. One batch was fabricated by using sanding as surface preparation, and four batches with laser treated substrates so that to analyze the effect of laser speed (250 mm/s and 500 mm/s) and process gas (air and nitrogen). Sanded samples were used as baseline to analyze the subsequent improvements associated to PLA.

### 3.1.1 Mechanical testing of the samples

Mechanical testing of the joint was carried out using the T-peel test coupon. The T-peel test is an adhesion test involving large adherent deflections. Adherents are relatively flexible, bonded together and loaded in peel. The geometry has been standardized by ISO, ASTM and BSI [3].
Since it involves the propagation of a crack it is also considered to be a fracture test. It was chosen as it is very convenient for comparative analysis (i.e. surface treatments, processing, aging, etc...)

The apparent peel energy may also include plastic dissipation, therefore it depends on the thickness and yielding stress of the substrates.

The mechanical testing was carried out using an electro-mechanic tensile testing machine (Instron 5944, Norwood, Massachusetts, USA) equipped with a 2 kN load cell.

This machine has pneumatic grips that facilitates the clamping of the substrates. Use of the machine is greatly automated by being able to create a specific program, or “Method” for the machine to follow, the initial loading rates were defined as follows: 1mm/min for the pre-crack section, from the beginning of the test, to 5 mm/min for the subsequent crack propagation. Notice that the ablation pattern lines were orthogonal to the direction of crack propagation since laser scanning was made in the z-direction (cfr. Figure 3.1(a)).

Some of the features of this machine include the specimen protection control, where the machine automatically corrects the displacement to prevent unwanted applied forces at the time of clamping the sample. It also provides a function to automatically stop the tests after a certain extension has been reached.

3.1.2 Fracture mechanics interpretation of the T-peel test

The deformation of the T-peel samples is strongly affected by the thickness, and the yield strength of the substrates, as well as on the level of adhesion. The deformed samples can assume two configurations during testing, and the assumed one will affect the results obtained in terms of load-displacement response.

If the fracture process zone is of a constant size, and there is no stick-slip during crack propagation, then the distance from the line of action of the applied load to
the crack front \((d)\) will remain constant during the crack propagation. This is known as *self-similar (or steady state) debonding*. However, if the sample does not achieve self-similar debonding, then the distance will increase as the crack propagates [3].

The deformed configurations which describe the above situations are shown in the schematic reported in Figure 3.2(a), and (b); when self-similar debonding is achieved, it is possible to consider the *T-peel strength* as the average force after the peak \((P_{ave})\) divided by the width of the sample (Figure 3.1):

\[
\frac{P_{ave}}{B} \quad (3.1)
\]

While the apparent peel energy (or modified adhesion) is given by:

\[
\frac{2P_{ave}}{B} \quad (3.2)
\]

It is worth noting that the apparent peel energy will match the fracture toughness of the joint, for cases where there is no plastic dissipation in the substrates [3]. In addition, the area under the load-displacement response curve is the total absorbed energy.
If there are plastic deformations on the metal substrates, then this plastic dissipation will contribute to the apparent peel energy, in some cases it can be as high as one or two orders of magnitude higher than the fracture energy of the adhesive. This plastic dissipation partially comes from straightening the substrates to achieve self-similar debonding.

In cases like this, advanced computational techniques can be used to model the bond, and segregate the plasticity from the total dissipation, and obtain the bond toughness [19, 8, 9].

It will be shown later that the use of a cohesive model will allow to identify the toughness of the bond.
## 3.2 Mechanical response of homogeneous interfaces

A comparison of the load extension responses for laser treated and sanded samples are reported in Figure 3.3. A typical response curve from the T-peel test consists of an initiation stage which evolves until it reaches self-similar debonding. This steady state behavior indicates that the peeling force has reached a constant value.

Once self-similar debonding is obtained, and the distance from the line of action of the applied load to the crack front \( d \) becomes constant, then the crack tip will propagate at a rate corresponding to approximately half of the moving cross-head. This means that the load acting on the moving cross head (the recorded extension) will move twice the distance (cfr. Figure 3.1).

![Figure 3.3](image)

Figure 3.3: Comparison among the load-extension responses of sanded and laser treated T-peel joints. Self similar debonding was achieved in both cases.

All of the treated samples reached self-similar debonding, and while a small asym-
metry was present in the deformed configuration, it was attributed to the crack path, as it traveled closed to any one of the interfaces. Visual inspection of the fractured surfaces suggest that PLA enabled a higher degree of adhesion, which allowed the transition from adhesive interfacial failure to cohesive failure.

By comparing the global responses, it is evident that PLA enhanced significantly the apparent peel energy. It can be observed that the deformation present in the bonded joint is greatly affected by the level of adhesion. Where the weak adhesion limited the forces required to debond the sample with little influence on the plastic behavior. Nonetheless, as the adhesion was increased, larger forces were necessary, and bending moments induced plastic bending which increased the energy dissipation associated with the substrates yielding.

In order to draw quantitative conclusions, a summary of the whole set of experimental results, including processing at 500 mm/s and the use of nitrogen, is given by the bar diagrams reported in Figure 3.4. The diagram displays and compares the peak force, the average force after the peak, the T-peel strength, and the total absorbed energy\(^1\) per unit bonding area.

---

\(^1\)The total area under the load-extension curve represents the absorbed energy during the process.
Figure 3.4: T-peel tests results summary. All quantities are normalized with respect to samples treated in air at 250 mm/s speed. (a) Peak force ($P_{\text{peak}}$) recorded during the tests; (b) Average force after the peak ($P_{\text{ave}}$) achieved in the plateau region; (c) T-peel strength as defined in the ASTM D1876-08; (d) Total energy absorbed (per unit bonded area) during the tests. Notice that the quoted numbers represent averaged data over a minimum of five tests. The error bar represent the corresponding standard deviation.

All quantities show major increases after laser ablation. Note that the quoted values have been normalized with respect to samples treated at 250 mm/s in air, that provided the best response in mechanical tests, i.e. $P_{\text{peak}}=143$ N, $P_{\text{ave}}=87$ N, T-peel strength=5.8 N/mm, total energy per bonded area=5.7 kJ/m$^2$. The results also show that laser processing using nitrogen as service gas did not bring any significant difference with respect to samples treated in air.

Therefore, the improvement in adhesive bonding after PLA is attributed to the increase in surface area, the generation of surface features, also of sub-micron scale, which improved wetting and acted as locking sites enabling mechanical interlocking [4, 5, 23, 19].
It has been observed in previous related work that all these effects combined may also lead to the formation of a composite interfacial region \(i.e\). adhesive interlocked within substrates asperities) able to enhance the mechanical behavior [6].

### 3.3 Analysis of failed surfaces

The analysis of fractured surface though SEM can be an extremely useful tool in determining whether the failure was due to either a weak boundary layer or improper surface preparation. SEM pictures reported in Figure 3.5 show the appearance of fracture surfaces taken from the mating substrates which were treated at \(W=30\) W and \(v=250\) mm/s.
Cohesive failure occurred for laser treated samples, while sanded ones, not shown here for conciseness, failed in apparent interfacial fashion. Therefore, laser processing enabled the occurrence of cohesive fracture within the adhesive layer. However, the crack path was always closer to one of the mating substrate. Occasionally the adhesive was cleaved from patterns resulting in near interfacial decohesion.

It is shown in Figure 3.5(a) that the adhesive interlocked within the cavity created by the ablation process and the magnified view given in Figure 3.5(b) shows that oc-
casionally the adhesive was cleaved from the patterns resulting in apparent interfacial
decohesion. Figure 3.5(c) is the back scattered version of Figure 3.5(b) and demon-
strates the ability of the adhesive to interlock with the microscopic surface features
generated by PLA. Figure 3.5(d), which shows the fracture surfaces from the opposite
substrates, demonstrates that more adhesive was retained by one of the substrates
and the magnification given in Figure 3.5(e) shows an highly strained region where
cohesive failure occurred. The corresponding back scattered version, Figure 3.5(f),
highlights that portions of copper oxide were detached from the substrate.

Therefore, the backscattered images illustrate that the adhesive was able to inter-
lock within the surface features of the substrates, however the oxide layer was often
detached from the mating surface. This feature is also highlighted in Figure 3.5(g)
where a typical patch of oxide layer detached from the mating surface is reported.
It is possible to note from Figures 3.5(h) and (i) that the surface morphology of the
oxide layer closely resemble the one observed in the SEM pictures reported earlier in
the paper. Notice that failure of the laser treated surface was also observed in [5].

3.3.1 Segregation of the bond toughness from the apparent
peel energy

The apparent peel energy, as determined in mechanical tests, includes plastic dissipa-
tions occurring in the metal substrates, as a result the actual bond toughness of the
joint should be considerably lower. In order to segregate the bond toughness from
the apparent peel energy, finite element simulations based on the use of the Cohesive
Zone Model (CZM) of fracture were carried out. The CZM lends itself to the analysis
of plastically deforming adhesive joints because it allows to make a partition between
the energy required to advance the crack and that required by the plastic deformation
of the bonded substrates [9, 24, 25].

In the CZM approach, material failure is characterized by a traction-separation
relation which links the cohesive traction and the relative displacement across cohesive surfaces. The peak stress and the area enclosed by the traction-separation relation are referred to as the cohesive strength and cohesive energy, respectively. The debonding process was herein analyzed through a finite-element model of the sample where the adhesive layer is replaced by a single row of cohesive elements with finite thickness equal to the adhesive thickness. It is then assumed that the role of the adhesive is to provide a traction-separation relation across the interface between the substrates [26].

The stiffness matrix and the load vector of the cohesive elements are assembled in a user defined subroutine within the commercial code ABAQUS/Standard. The cohesive model employed herein to mimic the response of the adhesive layer is schematically shown in the insert of Figure 3.6. The evolution of cohesive interaction depends on a few parameters, which include the cohesive strength, $\sigma_{max}$, the shape parameters, $\lambda_1$ and $\lambda_2$, which allow to control the initial slope (i.e. the stiffness), the extension and position of the plateau, and the final opening width, $\delta_f$, after which the material is no longer able to sustain any load. Finally, the area under the traction-separation relation, $\Phi$, is the cohesive fracture energy or the bond toughness.
Figure 3.6: Comparison among experiments and simulations in the plateau region of the global response pertaining to laser treated samples. The insert shows the traction separation relation employed in the simulations along the main input parameters.

Although there are four independent cohesive parameters that fully define the cohesive interaction ($\phi_n$, $\sigma_{max}$, $\lambda_1$, $\lambda_2$), previous related works [8, 9] have shown that the simulated global load-extension curve in T-peel tests is mostly sensitive to the cohesive energy and cohesive stress, and that basic curve fitting in the plateau region allow to assess in a fairly reliable fashion the cohesive energy. A similar procedure has been employed in the present work. The analysis was restricted to laser treated samples at 250 mm/s speed, that displayed the best performance in mechanical tests.

A comparison among experiments and simulations in the plateau region is given in Figure 3.6. Notice that $\lambda_1$ and $\lambda_2$ were set equal to 0.01 and 0.5 for all simulations, while cohesive strength was estimated from tensile tests carried out on the adhesive and set equal to 29 MPa. Therefore, iterations were carried out to tune
cohesive energy. The input value that allowed to fit the experiments lies in the range \(2.20 \pm 0.60 \text{ kJ/m}^2\). A similar procedure also allowed to extract the bond toughness of the sanded samples, which was shown to be significantly lower and lying in the range \(0.12 \pm 0.03 \text{ kJ/m}^2\). It should be noted that, since a flat substrate/adhesive interface is assumed, the modeling approach undertaken herein neglects the microscopic morphological details of laser irradiated surfaces; moreover, all the dissipation occurring in the adhesive layer (\(i.e\). bulk plasticity) is lumped in the cohesive zone model and is included in the cohesive energy (\(i.e\). bond toughness). However, finite element simulations and experiments display a fairly good agreement with the force plateau region.
Chapter 4

Effective peel resistance of adhesive bonded substrates with heterogeneous surface properties

4.1 Design of heterogeneous interfaces

In order to design patterned samples, a representative surface area was selected considering the full width of the sample. The size was 15 x 15 mm, and 1, 4, 9, and 25 features (circular areas) were subsequently micro-machined using PLA with the following processing parameters: $W=30$ W, $v=250$ mm/s, and $f=30$ kHz.
A schematic is shown in Figure 4.1. An initial assessment was made considering patterns with constant area fraction. Afterwards, besides changing the number of interfacial features, the area fraction will also be modified.

It is expected that while testing, the samples with a lesser number of features present will have a load-extension response able to better highlight the individual contribution of single features, and in particular the effect of the feature’s shape. The intention of this section is to study this in more detail, as will be explained next.

### 4.2 Surface patterning

In order to design the features, we have to rely on geometry to obtain the size of the features as a function of other parameters. We can consider the area fraction as the starting point, it can be calculated as the ratio of the treated and untreated areas. The number of features may also increase, therefore it must be accounted for. This can be adapted in the equation as follows:
\[
A_f = \frac{\pi r^2}{\left(\frac{B}{n}\right)^2}
\]  

Where \(A_f\) is the area fraction, \(B\) is the width of the sample, and \(n\) is the number of features per side. For convenience we can define:

\[
b = \frac{B}{n}
\]

and so, the equation can be solved to find the radius as a function of the side of the square, and of the area fraction:

\[
r = \frac{B}{n} \sqrt{\frac{A_f}{\pi}} = b \sqrt{\frac{A_f}{\pi}}
\]

Naturally, these patterns can be treated on the surface either supplementary, on the inside part of the circle, or the complementary part on the outside (Figure 4.2). As a pre-requisite it has been established that all the surfaces must be sanded before treatment. It can be assumed that the untreated portion will have the same properties as the ones probed for the homogeneously sanded samples, that were analyzed earlier and whose fracture toughness has been determined using the CZM.
To create the desired patterns, it is only necessary to use the design software to create the circular geometry and then use the “trim” tool, to remove the parallel lines on either side of the circles. Removing the circles is necessary, otherwise the software may also unnecessarily ablate them on the substrate; this can be done by changing the color in the software (Appendix B).

The main advantage of processing the samples with parallel lines is due to the direct baseline comparison against samples with a homogeneously treated area. For this, the processing conditions remain unchanged, while a variation of the area fraction, and a variation of the geometrical pattern are introduced.

Another option would be to make an offset of the geometry of the pattern (i.e. concentric circles), as shown in Figure 4.3. This was tested at first, but the substrates suffered from excessive thermal distortion.
4.3 Load extension response of T-peel joints with heterogeneous interface

The mechanical response of the samples with heterogeneous surface properties is fundamentally different; using the same criteria as in previous experiments to analyze their behavior (such as average force after the peak, peak force, among others), is not convenient for a detailed analysis between patterned samples. In the following sections, the proposed methodology to study these effects will be presented.

4.3.1 Circular patterns: analysis of interfacial splitting for constant area fraction

An initial study was carried for constant area fraction, which was set equal to 50%. Circular features were treated initially following the supplementary, or inside area
approach, as detailed on Figure 4.1. Other configurations were also tested and will be explained later on. It was important to determine if there was any significant difference in the mechanical behavior arising from the different geometries proposed, while maintaining the area fraction constant.

The different responses for samples under different processing parameters can be seen on Figure 4.4. From this, it is possible to highlight that the number of features affects the response, and the overall behavior. It can be seen from this figure that the patterned interfaces provide a crack front trapping effect, achieved by the tougher regions where an increased load is required to re-initiate the crack propagation. This enhanced work of fracture can be introduced as the concept of the effective peel force, which is the maximum force needed to continue the crack propagation, and to debond
the samples.

The enhancement of the average effective peel force as the number features is increased, can be referred to as the effect of area splitting; where there is a substantial increase in the total dissipated energy with C3 and C5 splitting. All this is achieved with a relatively small treated area of only 50%, compared to a homogeneously treated substrate.

The effective peel load increased as the number of features increased. It is speculated that the increase in the effective peel load depends not only on the trapping effect, but also on the size of the circular feature. It is believed that smaller features fail at lower loads. This provides an evident link between the treated areas and the peaks achieved in the mechanical response of the joints.

This variation from the increased area splitting can be attributed to the processing conditions to some degree, but mainly to the warping that the thin plate experiences under prolonged laser exposure. From this it can be concluded that there is a definite number of features that will “saturate” the possible enhancements that can be achieved through patterning, thus creating a large scatter in the results. For this particular material system, and sample dimensions, the saturation effect was reached when the area splitting reached 25 features per unit reference area. This point will be further explored later in the thesis through the analysis of crack front morphology.

4.3.2 Complementary patterns with 50% area fraction

In addition to this, samples that have been treated with a complementary (i.e. the treated area that is outside of the circular features) approach have also been tested. It is worth noting that these specific kinds of patterns did not yield consistent results, due to thermal warping by prolonged laser exposure. However, the results can be compared against those of the supplementary treated samples.
Figure 4.5: Total energy absorbed (per unit bonding area) obtained during the tests of supplementary, and complementary treated patterns. All quantities are normalized with respect to homogeneously treated samples.

As it is shown in Figure 4.5, there is a trend in the total absorbed energy per unit bonded area; this trend shows an increase, as the degree of area splitting is increased. Beyond a certain number of features there is a decrease that points towards the homogeneously treated samples. It seems that this kind of metric follows a parabolic kind of tendency; however it is only useful for the overall behavior. The mechanisms that are enabled during patterning, and that are responsible for the enhancement of the effective peel force will be covered later.

Taking into account the increased variability in the results from complementary treated samples, it was established to solely work with samples treated with the supplementary approach.

It is worth mentioning that the issues present with these processing conditions are only associated to the specific material system, and sample dimensions, that have been probed; and will not necessarily happen with a different material, or a different substrate, or adhesive, thickness.
4.3.3 Effect of area fraction

Another important aspect to take into consideration is the effect of the area fraction that is being treated. Besides considering 50% treated area fraction, the response of samples treated under 25%, and 75% treated area fraction was also tested. It is easy to find an appropriate radius for the features using equation (4.3).

Figure 4.6: Total energy absorbed per unit bonding area obtained from samples tested with a variation in the area fraction. All quantities are normalized with respect to homogeneously treated samples.

As can be seen from Figure 4.6, it is clear that the area fraction plays a significant role on the overall dissipation achieved. It may be worth pointing out that the best results were obtained with a 50% treated area fraction, and three features.
4.4 Results analysis

4.4.1 Distance between peak loads

Analyzing the overall behavior of the different responses, a periodical regime is distinguishable; the behavior of which is dictated by the characteristics of the geometrical pattern.

It becomes apparent that the different peaks follow approximately the same frequency for the same number of features, regardless of the treated area fraction. An aspect to analyze, besides the overall behavior, is the characterization of the peaks. The presence of clear peaks provides a good reference to inspect whether a self-similar configuration is achieved during testing (See Figure 3.2).

Consequently, this entails that the extension recorded during testing, should be approximately twice the bonded length of the sample (2 x 60 mm=120 mm). To verify if this condition is fulfilled, the position of the effective peel force is obtained from the load-extension response. The distance between the peaks can be found by performing a subtraction.

A comparison was performed with respect to the expected nominal values. In this case, the expected value is equal to the distance between centers of the circular features (\(\lambda\)).
If this assumption holds true, then a value of two times this distance (2\(\lambda\)) will be measured on the response curves. This can be tested for the different degrees of area splittings.

The results of this analysis are shown in Figure 4.7, where the assumption is confirmed, even for patterns with a greater degree of area splitting. The different values of the feature radius and lambda can be seen in Table 4.1.

Table 4.1: Circular feature size for 50% area fraction, and spacing (\(\lambda\))

<table>
<thead>
<tr>
<th>n</th>
<th>(r ) (mm)</th>
<th>(\lambda ) (mm)</th>
<th>2(\lambda) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.984134</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>2.992067</td>
<td>7.5</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>1.994711</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.196827</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>

4.4.2 Effective peel force analysis

Another aspect that can be analyzed from the heterogeneous interfaces, is the effective peel force. As it has been shown in Figure 4.4, the value of the effective peel force
will change depending on the degree of area splitting that is present. To properly characterize this behavior, it is possible to extract information about the average effective peel force (also known as the average peak load).

From Figure 4.8, it is evident that the average effective peel force always reaches a maximum when the area fraction is approximately 50%, and this is independent from the number of features present. It can be seen that the maximum effective peel force is achieved with three area splittings, and that the contrast between maximum and minimum forces is always higher when the area fraction is 50%.
Heterogeneous interface mechanism: crack front visualization

Previous results presented show that the response of joints with heterogeneous interfaces cannot be simply described in terms of the area fraction that is being treated. To determine the mechanism that allows the effective peel force to increase, which leads to an enhancement in the macroscopic energy absorption, a simple technique has been utilized.

It was suspected that these enhancements are related to a lengthening of the crack front, which comes from the contact line pinning that the laser treated areas provide [17, 15, 18]. However, the material system that is being used is not transparent as the ones previously presented; some limitations can be expected.

In order to visualize if the crack front deforms as it encounters the pinning zones, ink can be sprayed near the crack front while testing. For this, the current t-peel test was paused and the ink was sprayed with a syringe promptly. A few minutes were allowed for the ink to dry, and to prevent the ink from flowing into the re-initiated crack by capillarity.

![Figure 4.9: Optical microscope images showing the crack front evolution for two different samples with three area splittings, and two area fractions: 50%, and 75.](image)

In Figure 4.9, the crack evolution path has been highlighted in white. It can be seen that there is a severe distortion of the crack front as it encounters the laser treated areas. This pinning of the crack front leads to the lengthening of the contact
line. Additional energy must be supplied in order to drive the crack forward; this has a leveraging effect on the total dissipation.

Figure 4.10: Proposed crack evolution diagram for three different area fractions.

In the interest of finding an explanation for the effect of the area fraction, besides the area splitting, the crack evolution can be analyzed for samples that have been treated with different area fractions. In Figure 4.10, the crack front is presented initially as a straight line, that extends to accommodate the different crack pinning zones.

For the smaller treated area fraction at 25%, there is an effective crack trapping effect present. However, the features are too small, and the extension in the crack front is not effective. While for the higher treated area fraction at 75%, the crack trapping effect loses efficiency, as the features are so large that it resembles a homogeneously treated interface. In this case, a treated area fraction of 50%, presents the best compromise between both ends of the spectrum. Offering a well spaced pattern, and a feature size large enough that they provide effective crack trapping that lead to greater load overshoots.

This also offers an explanation to the decrease in the total absorbed energy from samples with a higher degree of area splitting. This “saturation” in the enhancement of the effective peel force is dependent on factors such as the dimensions of the sample, but also on the mechanical properties of the substrates and the adhesive itself.
4.5 Issues and limitations

Processing time limitation

One of the main issues with the processing conditions, is the use of parallel lines to cover the entire area (Appendix A); while this works for the homogeneously treated samples, the software instead of processing the lines in one direction, has to stop and ablate each line that belongs to a pattern individually.

This results in an increase in the treatment time; if a pattern with a single feature is being treated, it will take approximately twice the time as if the area was being treated homogeneously. If the pattern has 4 features, then it will take approximately four times.

Alongside the notable increase in processing time, the laser irradiation must also
be considered. As the process is being carried on, the software determines the path to follow to complete the pattern. This may result in a geometrical imbalance, or asymmetry, while treating the surface. This effect combined with the prolonged laser exposure favors the warping of the substrates from thermal distortion, in some cases very severe.

**Substrate failure**

In the case of the samples with lesser number of patterned features, a very high load was reached. The appearance of sudden peaks recorded in the load-extension response suggest the phenomenon of crack arrest is present.

As has been previously shown, some of the samples with an intermediate number of features have recorded a remarkably high effective peel force. While this contributes to the overall dissipation, this sudden behavior is also liable of substrate failure for some of the samples, as can be seen in Figure 4.12.

![Figura 4.12: Samples where substrate failure was present, either partially, or completely.](image)

This kind of failure, while exceptional, is not useful for the proposed comparative
analysis with the purpose of studying the effect of different patterns; therefore they will be excluded from the current analyses. The cause of this is yet unclear, although it is suspected to be related to the laser processing, which may enable an interaction with the material which affects its bending stiffness. These effects could be due to the thermal warping on plates with a high laser exposure; which creates residual stresses on the plates, that must be overcome while bonding, but will manifest themselves when the t-peel joints are being tested.

Under scrutinous visual inspection, a very light marking of the pattern can be appreciated on the backside of the treated surfaces. This may be due to the varying conditions that the plate is subjected to. As a thermal warping of the substrate may be present, the focal distance of the laser also changes; thus allowing for a concentrated focus of the laser in specific areas.

This kind of behavior was not experienced with plates that were treated homogeneously, as this possible effect may present itself throughout the whole surface instead of in specific areas.
Chapter 5

Concluding Remarks

5.1 Summary

The present work reports the effects of heterogeneous interfaces in adhesive bonding; by performing pulsed laser ablation on copper substrates that have been bonded using an epoxy adhesive.

This work consists of four chapters which detail different stages of the study. On the initial chapter, the discussion of the proposed research works is included because it is important to know the scope of their obtained knowledge, and how it can be improved upon. As it is explained, most of the materials that have been used in order to demonstrate the benefits of heterogeneous interfaces is done with flexible substrates or thin elastic films. These kinds of materials are hardly relevant when dealing with structures; and yet, the use of composite materials in mechanical structures has steadily increased over the years. It is possible that some of the advantages that such materials can potentially provide may be neglected if traditional coupling techniques such as mechanical fasteners, or even harmful as in the cases of acids for surface preparation, are still being used.

It is clear that industry requires new fabrication techniques, more adept to the applications in mind. This study aims to provide a bridge between novel techniques still under research, and their industrial application, by providing a procedure for
reliable design analysis and dependable mechanical performance.

In chapter 2, the extents of PLA are analyzed from the mechanical and chemical points of view. SEM, and XPS analyses were carried out, and it was found that the procedure imparts a significant modification of the surface topography, and the surface chemistry alike. In the interest of determining if these modifications favor the interaction of the material with the adhesive, bonded joints were fabricated to observe macroscopic effects in the adhesive bond performance.

The next chapter introduces the mechanical testing of adhesively bonded joints, it details the test coupon that was selected, and the data that it provides. The mechanics of the test are included; as it is explained, the configuration that the samples assume during testing will affect the results, and it is necessary then to provide this information. An initial analysis of substrates with homogeneously treated surfaces is also presented. An array of different processing parameters is studied and considered to establish the best working parameters.

The last chapter exploits the benefits found through laser processing, by adapting them on a new analysis of heterogeneously treated interfaces. An extensive range of proposed control variables were explored, such as the area splitting, and the area fraction, in order to observe their intrinsic effect. The mechanical performance results are discussed alongside those of homogeneously treated surfaces. Once the advantages of heterogeneous interfaces become evident from the results, the underlying mechanism was investigated, as it was found that the extent of the effect of the heterogeneities depends on certain factors. Finally, some of the limitations and issues encountered during the processing are explained.
5.2 Future Research Work

Most of the issues that arise due to processing can be associated to the specific material system, and sample dimensions, that were selected for this study. Also, the extent of pulsed laser ablation on different materials depends on the laser system that is available, and a particular system may be optimal for a specific material.

The selection of the material depends on the application in mind, and a laser system with the required criteria to provide satisfactory treatment conditions must be selected accordingly. It would also be of great interest to analyze the degree of interaction, and the capabilities that can be attained with other materials and thicknesses for both substrate, and adhesive layer.

Another aspect that is not covered in this work is the possible effect of heterogeneous interfaces with different shapes other than a circle. It is proposed that the bond performance is analyzed while using different shapes.

A sensible initial approach would be to work only with the best parameters found in previous sections; as is the case of the laser parameters (at $W=30$ W, $f=30$ kHz, and $v=250$ mm/s). The best conditions for working with patterns could also be used, as is the case of 50% area fraction, and working with 3 features; however this might not be the case, as will be explained.

It is evident that geometrical dissimilarities exist between different shapes; one of the consequences of this is the maximum, or critical, area fraction that can be achieved with each geometrical shape. To illustrate this, a circular feature can be considered. The radius of the circle can increase, covering a larger area until eventually the circumference is tangent to the sides of the representative unit square.
After the circular feature reaches this critical area fraction, the equation to calculate the area changes. It can be seen from Figure 5.1, how this quadratic behavior is reversed completely; changing from a positive quadratic tendency to a negative quadratic behavior until the area of the circle has complete coverage of the initial representative square area.

![Figure 5.1: Plot of the area fraction as a function of a circle’s radius.](image)

It is then expected for different geometries to have different parameters as is the critical area fraction. To verify this, four basic shapes are proposed: circle, rhombus, hexagon, and ellipse. The way these different figures are constructed can be see in Figure 5.2. Note that in the case of the ellipse, one side has been set of equal length to the square that holds it. From this figure it is possible to see already that all
proposed geometries will reach the critical area fraction when $a = \frac{b}{2}$.

![Plot of the area fraction as a function of the variable geometry length normalized with respect to the representative square area.](image)

**Figure 5.3:** Plot of the area fraction as a function of the variable geometry length normalized with respect to the representative square area.

From Figure 5.3, it is possible to see the evolution of the area fraction by incrementing the length variable $a$, for the different geometries. As can be seen, all four proposed geometries reach different critical area fractions, the lowest being the rhombus at 50%. And naturally both, the rhombus and the circle, reach the same critical area fraction, when they both become a circle that is tangent to all sides of the square.
A plot of the rest of the geometries interaction with the area fraction can be seen in Figure 5.4. While the complementary part of this plot does not have any significant meaning, it is possible to see that some geometries will reach a full area coverage before others, as in the case of the circle. Other geometries, as in the case of the ellipse, will only achieve full area coverage as $a$ tends to infinity. This can be seen in Figure 5.5.
Figure 5.5: Evolving features as the variable length increases. (a) represents the shapes for $a < b/2$, (b) represents the shapes when they reach the critical area fraction $a = b/2$, and (c) represents the shapes for $a > b/2$.

It is notable to observe that in the case of the hexagon, the curve will experience an additional change in tendency. First as the corner of the hexagon reaches the side of the square, and then as the side also reaches the square.

This analysis might point to a dissimilar behavior of different shapes and their corresponding area fractions. From this it may be understood, that it is likely that the best parameters that work for circular features may not be the same ones for different shapes. This is inconclusive with the data that has been gathered so far, and further analyses are required, such as the crack front visualization for different shapes. Some of the preliminary results can be seen in Appendix C.

The new proposed shapes can be also tested by changing the orientation of the geometry. One can change the orientation of the hexagon, and the ellipse, by rotating them. A rotation of the rhombus to form a square can also be considered, but was not tested. The rotations of the shapes may not be so different from one another, as is
the case of the hexagon which does not change too much, to the ellipse which changes greatly, thus predicting a largely dissimilar behavior which allow us to further tailor the response with a direction dependency.

These are only some of the proposed analyses that can be investigated further.
REFERENCES


APPENDICES
A PLS6MW Laser system guide for laser ablation and cutting

A.1 Protocols and tools

In this section the protocols that are required to perform PLA will be covered, specifically with the aid of the PLS6MW available at KAUST, and the steps describing the process.

Beginning with an introduction to the laser control parameters, including the different ablation procedures, and cutting. Finally, the procedure will be described step-by-step, to emphasize some of the aspects that need to be considered.

A.1.1 Control panel settings

An understanding of the laser system is required before beginning the step-by-step procedure. The settings control panel of the laser system will be discussed as it will be referenced in the future.
Figure A.1: Laser settings control panel screen for the PLS6MW.

In the screen displayed in Figure A.1, there is a list with different colors. These colors represent a set of working parameters for the laser. On this screen, the following conditions can be controlled:

- **Mode**: This represents which colors that can be used for the processing (On: Rast/Vect, Off: Skip). It allows for the possibility to create a design with multiple colors, and therefore perform laser ablation with multiple parameters (such as power, speed, and frequency) on a single run.

- **Power**: Linear variation of power in percentage.

- **Speed**: Linear variation of speed in percentage. Note that higher speeds produce less intensity on the material’s surface, generally leading to a lighter mark.

- **Waveform and frequency (kHz)**: These parameters are linked; by changing the value in the Waveform drop-down menu, as different frequencies are selected, the waveform adapts to the newly selected frequency.
Higher Waveform and Frequency values generally correspond to lighter marks.

- **Z-Axis**: Given that the laser is calibrated so that it is always in focus when the work surface is at z-height of 0, the height of the substrate must be accounted for, and compensated accordingly. This also applied for any additional protective plate, so that it is always as close to being focused on the surface as possible.

Note: The controls are inconvenient at times, so the settings must be changed individually, otherwise by selecting more than one, when the button “Set” is clicked, all the selected colors will store the values that have been selected last. It is important to always click “Set” after the parameters have been selected, and “OK” to exit. If “Enter (Return)” key is pressed on the keyboard, the control panel will exit without saving the changes.

### A.1.2 Sample preparation

Materials to be used as substrate can be obtained from the workshop at KAUST, some of them may come with a protective film coating on the surface. This protective film can be removed and additionally to remove the naturally forming oxides, a grinding paper can be used to remove the surface layer.

**Positioning and alignment**

The next step is placing the sample on the laser machine working surface. If the sample surface is being treated, but cutting will also be performed, then a thin metal sheet, or plate can be placed between the sample and the laser working base to protect the working surface.

If many samples have to be treated, then it is preferable to fix this protective plate to the laser working base, and then mark/ablate the shape of the samples on
the protective plate. This provides an easy reference for positioning and aligning the samples.

A sensible initial guess for the parameters to mark the protective plate would be to use:

- $W = 50\%$, $v = 100\%$, Z-Axis level would equal the thickness of the protective plate.

It is safe to start with a low value of power at the highest speed, as this achieves the least fluence. The frequency would have to be selected according to the material that is being treated. Consult the manufacturer’s User Guide [27]. Setting the Z-axis level to the thickness of the plate means that the laser will be focused at the top surface of the plate.

Afterwards the substrates can be fixed to the plate, or the working surface. If ablation is being performed, it is recommended to apply tape or double-sided tape underneath the plate, apart from taping the front to the base, to avoid problems with substrate warping, but this depends on area that will be covered.

**Design**

The next step will be sketching the design that will be treated, this includes the treated areas and the cutting processes. On the laptop computer, CorelDraw X7 has to be initiated, the software automatically loads with the laser system extension.

For an easier visualization, it is suggested to draw the outline, or shape, of the sample. Next the features to be ablated, or cut can be added. It is preferable to set them with different colors, as they will be performed under their own processing parameters.
A.1.3 Cover area options and procedures

The machine follows a linear path, therefore to cover an area there are several options, which will be explained along with the different procedures required for each option.

![Image of CorelDraw X7 interface with labeled areas]

Figure A.2: New document screen in CorelDraw X7. Where (a) is the size of the sheet which should match the laser working surface, (b) are the Horizontal and Vertical offset boxes on the Property bar, (c) is the Uniform area fill settings, and (d) is the line color settings.

Uniform area fill

The software allows for an uniform area fill function, in which the laser machine will automatically define the parameters necessary to achieve this. The result is a neat and constant fluence all across the area.

To achieve this in CorelDraw, while selecting the feature to fill, double-click the area fill settings icon, as shown in Figure A.2(c). A small pop-up window will appear where a filling color can be selected, said color should correspond to the laser parameters that can be defined.
Line Patterning (Hatch)

This method consists of creating parallel lines that are so close to each other that the target area is ablated entirely. It is of significance to know that this is dependent on the precision of the laser machine. It is necessary to assess that the machine capabilities will meet the requirements beforehand.

A previous test consisting of ablating lines with different laser parameters, and measuring the width of the ablated canal might be necessary. After this a pitch for the line pattern can be established based on the results, this hatch can be done with parallel lines in any orientation, or crosswise.

For the calibration of this technique, it is recommended to perform a test beforehand on a piece of the same material that can be scrapped. A pattern of parallel lines can be created and set with different colors, which will represent the same power, the same speed, and the same frequency, while varying the Z-axis level.

Afterwards optical microscopy can be employed to identify the width of the lines that were ablated. Identifying the most suitable one and then creating the design based on this line pitch.

**Note:** To duplicate a line, the spacing can be defined on the offset boxes, shown in Figure A.2(b). Then the line to duplicate has to be selected and use the command Ctrl+d as many times as needed. It was found in SEM analyses that there is a vibration when the lines are parallel to the vertical direction. Thus, introducing a wobble to the ablated canal.

**Text**

The laser system is also able to ablate text, depending on the width of the font chosen it may follow curves, or perform an area fill.
A.1.4 Ablation and cutting

To perform the ablation, the design that has been created has to be printed. There are a few options for printing, some of them include only printing a determined selection of features.

In the command dialog box that appears, the following options can be selected: Current document (default), and Selection, as shown in Figure A.3(c).

It is essential that the PLS6MW is selected as a printer (Figure A.3(a)). Afterwards, the treatment parameters can be defined by clicking on “Preferences...”, as shown in Figure A.3(b), the laser system settings control panel will appear.

![Figure A.3: Print dialog box. Where (a) designates the laser system as the print destination, (b) leads to the laser settings control panel, (c) displays the print range, and (d) shows the number of copies, or repetitions.](image)

The sample can be then cut into individual pieces, either once the laser ablation has been carried out, or before processing. Depending on the thickness of the sample, it might be required to use multiple passes as the laser cuts deeper into the sample.
For this, it is suggested that the user duplicate the cutting layout, change the colors, and overlap the curves into the same position. Additionally, the number of prints can be modified, as shown in Figure A.3(d) to process the same program multiple times, this way the machine does multi-runs faster by skipping the homing process.

The commands in the laser processing window can be used, as shown in Figure A.8, to align out samples and also move the laser around the working area with the available tools.

Note: It is recommended that every time after the laser system has had a startup, the Homing operation is performed. This is achieved by clicking “Home xy”; the process does not take longer than 2 minutes and it will prevent any problems in the future caused by misalignment.

If the outline of the substrate was included in the printed program, there is an additional opportunity to disable it by going into the Settings from this window and modifying the parameters. All that remains is to click the “Play” button and the program will run in the machine. The flow of the inlet gas must be turned off.

A.1.5 Procedure

Now that the basics have been covered the workings of the operation of the laser system have been explained, the steps required to complete the procedure will be described.
1. Start laser machine, and computer:
   
   (a) The switch of the laser machine can be found at the lower right side below the table of the computer, next to a fan, and the power cable. The laser machine will go into a warm-up mode that will take about 2 minutes.
   
   (b) The computer should be on, if the lid is closed, it should start up when opening the display.

2. CorelDraw X7 can be initiated on the computer, in most cases it will already be open on the welcome screen shown in Figure A.4.

3. A new document can be created, otherwise it is possible to open a document that has been created previously. Notice that when opening a new document, the size of the Sheet will match the working area dimensions (813 x 457 mm), as shown in Figure A.2(a).
4. Files from different formats can be imported, including Adobe Illustrator (AI), AutoCAD (DWG, and DXF), Images (JPG, PNG, BMP), among many others. While importing it is important to remember the scale of the drawing, as it might change units while importing, see Figure A.5.

5. The tools in CorelDraw can be used to design a path to be treated. To make this process easier, it is recommended to start by the outline of the sample itself. Looking at the Laser control panel settings, the order of the colors that is shown in Figure A.1 must be followed. After the outline has been created, then the different colors available can be used for the different features that will be treated.
All the lines must be set with the width as “Wireframe”, if the lines are set with a thicker width, the laser will perform an area filling function.

6. Before proceeding to treatment and processing, the sample has to be aligned to the table. This can be done either manually, or using the protective plate method, as described later.

Note: Wait at least 2 minutes after start up. As the laser head might start moving for a calibration/homing operation.

When the door of the laser is open, the laser head will produce a visible laser pointer, this helps in the alignment process (See Figure A.6).

Once the plate is fixed to the working surface, the shape, or outline of the sample can be aligned on the plate. On the drawing in CorelDraw, the design can be moved to be roughly in the same position as the protective plate. It is not needed to be precise about this, as it can be changed later.
Figure A.6: Alignment of the laser head with the protective plate.

7. The next step consists of “printing” the design, there are a few options available for this (See Figure A.3(c)); the entire document may be printed, or if preferred, only a selection of features defined before entering the print dialog box.

Note: The laser machine can also do a certain number of repetitions of the same pattern, which is very useful for laser cutting, this can be done by changing the value of the “Number of copies” also found in the print dialog box, in Figure A.3(d).
Figure A.7: Access to laser control screen via task-bar icon.

8. There is an option to define the laser working parameters before and after printing, but it is recommended to always set them before printing the design. For this, click on “Preferences”. The Laser settings control panel from Figure A.1 will appear.

Figure A.8: Laser control screen with “Focus View” tool selected for positioning and alignment of the sample.

The laser will follow the order of the colors in this window as a rule, but some
of the colors can be turned ON or OFF; this is useful for large designs, as it may be useful not to print some features.

9. Once Ok is pressed in the print dialog box, it will close and return to the drawing screen. To enter the laser control screen click the Red icon that appears at the right side of the Windows task-bar, next to the clock (See Figure A.7).

10. The Laser control screen will appear, and the alignment procedure can begin. Always calibrate the laser machine by pressing “Home xy” (See Figure A.8)

For this, use the “Zoom” tool to focus on the sample outline. Afterwards use the “Focus View” command, when clicked, lines that follow the mouse position will appear on the display area. By clicking anywhere on the screen while using this command, the laser head will position itself there.

Make sure there is nothing on the working surface that can collide with the laser head before clicking. Then proceed to make the necessary adjustments in the position on CorelDraw, and printing to make sure the design is inside the protective plate.
11. Afterwards the outline of the sample can be marked on the protective plate by clicking “Play”. For this, print only the required color(s).

   This marking provides the best guiding reference for positioning samples, as shown in Figure A.9.

12. Fix the sample to the protective plate, aligning it with the markings just made. Then print all the features that need to be ablated, or cut. Remember to turn the pressurized gas flow on if processing, or cutting. This is done simply by opening the valve on the wall behind the computer.

   Note: Any treatment that is currently in process can be paused with the option to resume, or start from zero. However, A process cannot be stopped to perform another, and then resume with the first one. It is good to remember that the “Resume” button will replace the “Pause” button, while the “Play” button will start the job from zero.

   Once the required laser treatments have completed, simply close the computer and turn off the laser machine.
B Sample fabrication best practices

While trying to find a reliable way for sample fabrication, several processes that introduced errors were encountered. These vary from performing sanding adequately, up to the fabrication of an alignment jig for the bonding procedure. These tools and procedures will be next described in order to alert the reader to probable sources of preventable variability in the final results.

B.1 Sample fabrication tools

Before starting with the sample fabrication, it is a requisite to think about the expected bond performance which comes from the laser treatment layout. Simple things such as a fixture for laser treatment will reduce the likelihood of experiencing a poor treatment due to unwanted bending of the plate being treated from thermal distortion, or even a poor alignment during bonding that leads to unbalanced joints.

To avoid these common issues, a guide has been included that lists the possible tools that might be needed in order to create the best possible samples.

Sanding

As a requirement, only the treatment of a specific area may be needed, as is the case for patterning. Or in order to evaluate bond performance, a comparative analysis can be carried out against sanded samples as a traditional means for surface preparation.
The following tools can be used:

- Masking or electrical tape.
- Sanding paper with a grit size as required by the user.

**Laser ablation**

While performing laser ablation, it is expected to obtain large heating and cooling rates, and small material volumes subjected to the thermal induced defects; this might warp, or bend the substrate away from the focal length of the laser, as it is shown in Figure B.1.

![Image of laser ablation effect](image)

Figure B.1: Thermal distortion on a copper substrate induced by high laser irradiation intensity; it can be seen that the warping was severe in the lower portion, which caused the surface to be out of the laser’s focus.

Fixing the substrate to the base adequately is necessary. The following tools can be used:

- Transparent tape, and Double-sided tape
- Protective laser tape which can be found on the laser system workbench.
- Scissors, or utility knife.
Laser cutting

Depending on the laser machine, and the material, some laser systems are able to cut metals from thin metal foils up to sheet metal.

In this case, if it is needed to cut metal plates, it is good practice to use a protective metal sheet, or plate, that sits flush on the laser working area. This prevents the laser from marking, or damaging the base.

Surface preparation

After laser ablation, some residue in the form of dust will have deposited over the laser machine working area, and the sample itself. This happens as the material vaporizes and the inlet flow of gas blows it away. After the treatment has been done, the surface can be cleaned of any particles by injecting pressurized gas directly to the surface.

Additionally, degreasing is recommended immediately preceding the bonding procedure. For this, a solvent may be needed, such as ethanol, or acetone to remove any grease or lubricant present in the surface.
Bonding

To prepare the samples for bonding, the following items can be used:

- **Release film**: covering specific surfaces will prevent the adhesive from bonding in unwanted areas.
- **Masking tape**: besides holding the release film in place, it will protect the backside of the sample, preventing any squeezed adhesive to bond to the back of the sample.
- **Spacers**: only if necessary, they will ensure a constant adhesive thickness all along the bond.
- **Alignment jig**: a proper fixture is needed to guarantee the alignment of the samples during the adhesive curing process. It will include the use of weights to constrain the adhesive thickness.

B.2 Sample fabrication procedures

Some of the first attempts at sample fabrication helped to find an improved method that would reduce the inconsistencies in the procedure while avoiding common issues found along the way. This iterative method helps refine the technique multiple times until the typical sample fabrication defects were able to be quantitatively classified. The different steps taken will be explained.

The first attempt at sample processing was using untreated samples, in this case the procedure was as shown in Figure B.3.
First, the bi-component epoxy adhesive is mixed as seen in Figure B.3(1), trying to prevent the formation of air bubbles during mixing (It is worth noting that the adhesive used was expired). The substrates were degreased with solvent using acetone. Next, the adhesive was spread over the surface with a wood stick, an anti-sticking film was used to reproduce the initial debonded area (Figures B.3(2a, and 2b)). The substrate surfaces are placed together manually and pressure was applied with clamps, no spacers were employed to secure the thickness of the adhesive layer (Figures B.3(3, and 4)). After curing, the substrates in the debonded portion were bent to the 90 degree shape using only pliers (Figure B.3(5)).

These preliminary tests were carried out in order to answer a few basic questions:

- Is the selected length for the bonded portion able to provide a stabilized load?
- Is the material system able to provide nominal interfacial failure?

A system that fails at the interface is needed in order to probe the effect of surface treatment on the interface, as can be seen in Figure 1.3.

A very weak bonding strength was found as testified by the reduced sample deformation, low failure loads, and interfacial fracture. Not using spacers, adversely
affected the mechanical behavior of the joint, as the bond line is very thin with very little adhesive present. This problem was exacerbated by the use of clamps.

Some of the improvements implemented afterwards were the precise alignment of the bonding area by using pins on a specific base. The use of spacers also ensured a constant adhesive thickness of 250 microns. Weights were used to squeeze the excess adhesive. This method is illustrated in Figure B.4.

Figure B.4: Improved sample fabrication procedure for bonding.

For the bending, a vice was used to generate a full clamping of the bonded portion and subsequent bending to 90 degrees was carried out with a wedge, and a hammer, as can be seen in Figure B.5.

Figure B.5: Improved fabrication procedure for bending the samples to 90 degrees.
Some of the typical fabrication defects, as illustrated in Figure B.6, include:

- Twisting of the bent portions, which may cause out of plane bending on the bond line
- Misalignment of the substrates, this results in the 90 degree angle not preserved.
- Non constant adhesive layer thickness, which comes from slightly bent substrates due to the laser processing; after bonding, the samples tend to "spring" back and this leads to a non-uniform bond line.

![Figure B.6: Typically encountered fabrication defects, where (a) shows the twisting of the bent portions, and (b) shows the 90 degree deviation.](image)

On preliminary tests, the adhesive was placed only on one side; there was not enough weight placed on the samples leading to a non-uniform bond line which caused an oscillation in the load. However, self similar debonding was achieved with strong plastic dissipation and cohesive failure near the interface. Detailed observation suggests that there is mechanical interlocking present, this is another aspect that has been analyzed in this study.
Some of the main outcomes from the preliminary tests were the updated final directions for fabrication, as can be seen in Figure B.4. The final improvements include:

- The use of weights in order to prevent the substrates from springing during the adhesive curing process.
- The use of spacers along the longitudinal direction, this prevents the added weight to induce unwanted bending and modify the bond line thickness.
- Careful sample area alignment with the use of pins and a base to prevent twisting of the sample arms.
- Cutting of the samples should be done with additional steps in order to facilitate their separation without inducing any distortion of the substrates.
C  T-peel test results

C.1 Results for homogeneously treated samples

In this section, the load-displacement responses for all the samples that were tested can be found according to their corresponding specifications. For the homogeneously treated samples see Figure C.1.
Figure C.1: Load-displacement responses for the homogeneously treated samples under different processing conditions. (a): Samples processed at 250 mm/s in air, (b): samples processed at 500 mm/s in air, (c): samples processed at 250 mm/s in nitrogen, (d): samples processed at 500 mm/s in nitrogen, and (e) samples with no laser treatment, and a sanded surface.
C.2 Results for heterogeneously treated samples

This section will present the load-displacement response for the heterogeneously treated samples.

For the patterned circles with area fraction of 50%, with supplementary and complementary treated areas see Figure C.2.

For the patterned circles with a treated area fraction of 25%, see Figure C.3; and with a treated area fraction 75%, see C.4.

For the samples tested with a different shape pattern: for the rhombus see Figure C.5, for the hexagons see Figure C.6, and for the ellipse see Figure C.7.
Figure C.2: Load-displacement responses for heterogeneously treated samples with a circular pattern and constant area fraction of 50%. (a),(c),(e),(g): correspond to 1, 4, 9, and 25 area splittings with a supplementary treated area. (b),(d),(f),(g): correspond to 1, 4, 9, and 25 areas splittings with a complementary treated area.
Figure C.3: Results for patterned circles with area fraction of 25%. (a),(b),(c),(d): correspond to 1, 4, 9, and 25 area splittings respectively.
Figure C.4: Results for patterned circles with area fraction of 75%. (a),(b),(c),(d): correspond to 1, 4, 9, and 25 area splittings respectively.
Figure C.5: Results for patterned rhombus shape with area fraction of 50%. (a), (b), (c): correspond to 1, 4, and 9 area splittings respectively.
Figure C.6: Results for patterned hexagon shape with area fraction of 50%. (a): corresponds to the single hexagon, while (b): corresponds to a rotated single hexagon. Note there is no significant difference between either. (c),(d): correspond to 4, and 9 area splittings respectively, of the rotated hexagon shape.
Figure C.7: Results for patterned ellipse shape. (a),(c): correspond to 1, and 9 area splittings of the ellipse, while (b),(d): correspond to 1, and 9 area splittings of a rotated ellipse.
D Papers Submitted and Under Preparation
