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**An investigation into the surface pre-treatment
of CFRPs prior to adhesive bonding**

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Declaration of originality

I declare that this thesis, **“An investigation into the surface pre-treatment of CFRPs prior to adhesive bonding”**, is entirely my own work under the supervision of Prof. Bamber Blackman with the co-supervision of Dr. Zhusheng Shi and Prof. Jianguo Lin. The information derived from any published or unpublished work has been acknowledged in the text and references are given in the list of sources. This work has not been previously submitted, in whole or in part, to any other academic institution for a degree or any other qualification.

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Abstract

This thesis aims to develop guidelines for designers to select adherend materials and surface pre-treatment methods/parameters for adhesive joints in aerospace applications. Academic issues in the research field of adhesive/adhesion concerning composite interface, adhesion theory, and failure mechanism are also explored.

Firstly, state-of-art technologies of surface pre-treatment have been reviewed. As oxygen plasma treatment is environmentally friendly and is an effective pre-treatment method on composites, it has been the focus of this study. Acetone cleaning and grit blasting are also employed for comparison.

Secondly, in the experiments conducted, aerospace-grade carbon fibre reinforced polymer (CFRP) composites were prepared and employed as adherends, i.e., two thermosetting CFRPs made of similar preregs but manufactured via different techniques, and three thermoplastic CFRPs made of different preregs. An aerospace epoxy-film adhesive was used to join two pre-treated adherends. Both CFRP/CFRP and CFRP/aluminium alloy joints were investigated.

Thirdly, interfacial characterisation was studied by the techniques of SEM, EDX, XPS and contact angle analysis. These results show that plasma treatment is highly effective on the different CFRPs, due to the removal of surface contamination, the development of an appropriate surface topography, the activation of the surface chemistry, and the improved interfacial wetting. Furthermore, thermoplastic matrix composites usually exhibited slower erosion of the surface by the plasma treatment than thermosetting ones.

Finally, it is proposed that the dissimilarity of the two adherends in a hybrid joint can influence the joint performance. For example, a patterned surface created by autoclave processing can realise a high specific surface area of exposure to plasma, strengthening the effect of plasma and leading to higher joint strengths; however, the uneven surface can exacerbate air retention during the preparation of hybrid joints (when an uneven composite surface is adhesively bonded to a relatively-flat aluminium alloy surface), reducing the joint strength.

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“A hamster’s cheeks can hold a quarter of its body weight.”

Adapted from BBC Earth (2019)

Publications during PhD programme

Journal paper

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Nomenclature

Symbol

τ	single-lap-shear strength
F_{max}	maximum load before failure during single-lap-shear testing
X_{max}	maximum displacement before failure during single-lap-shear testing
A_0	overlap area in single-lap-shear testing
G_{IC}	mode I (opening mode) fracture toughness

Chemical

Element:

C	carbon (element)
O	oxygen (element)
F	fluorine (element)
Na	sodium (element)
Mg	magnesium (element)
Al	aluminium (element)
Si	silicon (element)
S	sulphur (element)
Cl	chlorine (element)
K	potassium (element)
Ca	calcium (element)
Ti	titanium (element)
Mn	manganese (element)
Fe	iron (element)
Cu	copper (element)
Zn	zinc (element)

Bond or functional group:

$C-C$	carbon-carbon bond (especially carbon-carbon single bond)
$C-O$	carbon-oxygen single bond
$C-O-C$	carbon-oxygen single bond or ether bond
$C=O$	carbon-oxygen double bond or part of carbonyl group
$O-C=O$	carbon-oxygen double bond or part of ester group
$-Si-O-$	alkoxy group
$-OH$	hydroxyl group
$-NH_2$	amidogen group
$-COOH$	carboxyl group

Inorganic gas or solid:

N_2	nitrogen (gas)
O_2	oxygen (gas)

CO	carbon monoxide
CO_2	carbon dioxide
SiC	silicon carbide
Al_2O_3	aluminium oxide
Al_2O_3	aluminium oxide
Al_xO_y	compound(s) containing aluminium and oxygen
Cu_xO_y	compound(s) containing copper and oxygen

Inorganic acid, alkaline, or salt:

HF	hydrofluoric acid
HNO_3	nitric acid
H_2SO_4	sulphuric acid
H_3PO_4	phosphoric acid
H_2CrO_4	chromic acid
H_2O	<i>water</i>
H_2O_2	hydrogen peroxide
$NaOH$	sodium hydroxide
$Al(OH)_3$	aluminium hydroxide
OH^-	hydroxide ion
$Na_2Cr_2O_7$	sodium dichromate
$KMnO_4$	potassium permanganate
AlO_2^-	meta-aluminate ion

Organic or polymeric substance:

$DMSO$	Dimethyl sulfoxide
IPA	Isopropanol
MEK	Methyl ethyl ketone
$PAEK$	Polyaryletherketone
PE	Polyethylene
$PEEK$	Polyether ether ketone
PU	polyurethane
TCE	trichloro ethylene
γ -MPS	γ -methacryloxypropyltrimethoxy silane
γ -APS	γ -aminopropyltriethoxy silane

Model of materials

The model of raw materials used in this study:

AA2014	an aerospace-grade aluminium alloy
AF163-2	an aerospace-grade adhesive film
AS7	an aerospace T700 grade carbon fibre
SYT49S	an aerospace T700 grade carbon fibre
SYT55S	an aerospace T800S grade carbon fibre

Grade of carbon fibre:

<i>T300</i>	tensile strength ≥ 3500 MPa
<i>T700</i>	tensile strength ≥ 4900 MPa
<i>T800</i>	tensile strength ≥ 5500 MPa
<i>T800S</i>	tensile strength around 5900 MPa (a specific high-level T800 grade)

Standard code**Prefix code of a standard:**

<i>ISO</i>	standard formulated by International Organisation for Standardisation
<i>BS</i>	standard formulated by Britain Standard Institute
<i>GB, GB/T</i>	standard formulated by Standardisation Administration of China
<i>ASTM</i>	standard formulated by American Society for Testing and Materials
<i>EN</i>	European standard
<i>HB</i>	China aviation industry standard

The title of the standard code:

<i>ISO 4587</i>	Adhesives-Determination of tensile lap-shear strength of rigid-to-rigid bonded assemblies
<i>GB/T 33334</i>	Test method for strength properties of adhesives in shear by tension loading of single-lap-joint laminated assemblies (composite and composite)
<i>ASTM D3039</i>	Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials
<i>ASTM D6641</i>	Standard Test Method for Compressive Properties of Polymer Matrix Composite Materials Using a Combined Loading Compression (CLC) Test Fixture
<i>ASTM D7264</i>	Standard Test Method for Flexural Properties of Polymer Matrix Composite Materials
<i>ASTM D2344</i>	Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates
<i>ASTM D7137</i>	Standard Test Method for Compressive Residual Strength Properties of Damaged Polymer Matrix Composite Plates
<i>BS EN 6033</i>	Aerospace series. Carbon fibre reinforced plastics. Test method. Determination of interlaminar fracture toughness energy. Mode I. G_{IC}
<i>HB 7402</i>	Test method for mode I interlaminar fracture toughness G_{IC} of carbon fibre reinforced composite laminates

Other abbreviations

<i>AC</i>	acetone cleaned or the acetone cleaning performed in this study
<i>AFM</i>	atomic force microscope
<i>Al/Al</i>	homogenous joint of Al alloys: two same Al adherends bonded together
<i>APPT</i>	atmospheric-pressure plasma treatment
<i>CA</i>	contact angle

<i>CFRP</i>	carbon fibre reinforced polymer
<i>CFRP/Al</i>	hybrid joint: a CFRP adherend bonded to an aluminium alloy
<i>CFRP/CFRP</i>	homogenous joint of CFRPs: two same CFRP adherends bonded together
<i>COVID-19</i>	the worldwide coronavirus disease starting from 2019
<i>DCB</i>	double cantilever beam
<i>EDX, EDS</i>	energy dispersive X-ray spectroscopy
<i>FRP</i>	fibre reinforced polymer
<i>GB</i>	grit blasted or the grit blasting performed in this study
<i>GFRP</i>	glass fibre reinforced polymer
<i>IR</i>	Infrared ray
<i>LOD</i>	limit of detection
<i>LPPT</i>	low-pressure plasma treatment
<i>PL</i>	plasma treated or the plasma treatment (LPPT) performed in this study
<i>SA</i>	silane agent treated or silane agent treatment
<i>SEM</i>	scanning electron microscope
<i>SLS</i>	single-lap-shear
<i>UV</i>	ultraviolet
<i>XPS</i>	X-ray photoelectron spectroscopy

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Chapter 1: Introduction

1.1 Background

1.1.1 Adhesive bonding

To minimise fuel consumption and raise the carrying capacity of aircraft, cars or ships, designers employ materials with high strength which are also lightweight. The designers tend to employ aluminium alloys, titanium alloys, glass fibre reinforced polymer (GFRP) composites and especially carbon fibre reinforced polymer (CFRP) composites [1-3]. A modern component often requires the inclusion of diverse materials or structures. It is the joining of similar materials or the joining of composites to metallic materials that not only realises complex structures but also contributes to the weight reduction [4,5].

The use of adhesive bonding is a developing technology in the pursuit of these goals. There are some alternative joining techniques. For instance, riveting, bolting, and welding techniques are frequently utilised to join similar or dissimilar materials in modern industry [6,7]. However, riveting and bolting usually require hole-drilling during the manufacturing, which gives rise to stress concentration and lower sealing capacity, which shortens the fatigue life of the joined structure [6-8]. Such effects worsen if the raw material is a fibre reinforced polymer composite (FRP) as damage (e.g. cracking or/and delamination) can occur when the internal structure is drilled [9,10]. Welding techniques include fusion welding [11,12], pressure welding (among which diffusion welding is often studied for hybrid joining) [13,14], soldering and brazing [15]. All of these will introduce heat affected zones, where inappropriate hardness or embrittlement may take place during or after the cooling process. When it comes to adhesive bonding, the adhesives are capable of maintaining the integrity as well as maintaining the original mechanical properties of the substrates [16,17].

Furthermore, the adhesive layer is also able to prevent crevice corrosion and galvanic corrosion when used to form a hybrid joint [18]. The non-conducting adhesive electrically isolates the two adherends, preventing corrosion from occurring.

In addition, adhesive bonding can be useful in developing modern aerospace structures using thermoplastic polymers or composites. In the last decade, the technologies related to thermoplastic matrix fibre composites have developed rapidly. Thermoplastic composites offer advantages in processability, toughness and high impact resistance [19,20] compared to fibre composites based upon thermosetting matrices, and as a result they have captured the attention of researchers and engineers [21]. Although the thermoplastic materials can be reused or reprocessed, they usually need to be heated to a relatively high temperature (e.g., over 350 °C to produce some thermoplastic CFRPs) for several hours or/and in a high-pressure environment [22,23]. Also, many complex structures are difficult to realise by one-piece manufacturing. Hence, the secondary adhesive bonding is still necessary for joining, which is flexible and only requires a relatively low heating temperature for short time to cure the adhesive [24]. For example, heating to 100-150 °C for 1-2 hours or 80 °C for 2-3 hours can cure most epoxy-based adhesives.

The mechanisms of adhesion have been widely explored over recent decades. The proposed theories have concentrated on adsorption, diffusion, chemical bonding, electrostatic force, mechanical interlocking, or removing weak boundary layers [25,26]. No single theory describes all the different categories of adhesive bonding. However, it is acknowledged that the attainment of intimate interaction between the adhesive and the surfaces to be joined is vital for successful adhesive bonding. The surface should have a desirable chemical composition, wettability, roughness, or other chemical, physical, and mechanical properties prior to bonding. Hence surface pre-treatment, which aims to prepare the adherends for joining, is undoubtedly a key requirement prior to bonding [6,25-29]. In addition, surface pre-treatment is beneficial to prevent or remove the weak boundary layers. Such layers hinder close contact between the adhesive and adherend molecules/atoms, leaving a layer with little adhesion, which may cause stress relaxation or even cracking of the interface after

bonding [25,30]. In contrast to joining the same or similar materials, joining a FRP to an alloy involves distinguishing treatments for both adherends.

1.1.2 Pre-treating CFRPs

In terms of pre-treating CFRPs, diverse methods have been developed. When manufacturing CFRPs via vacuum autoclave, additional peel plies are frequently employed on the surface of the composite part which, upon removal prior to bonding, control surface topography and protect the surface from additional contamination [31,32]. Some wet peel plies, which are impregnated with a resin, can affect the surface chemistry by controlling the volatilization of superficial resin during CFRP manufacturing. To further adjust the surface roughness, polishing or blasting is employed. Recently, more advanced pre-treatment technologies have been investigated which utilise high-energy impact upon the surface, e.g., laser ablation [33-37], UV irradiation [38-40], or plasma treatment [41-46].

Previous studies have provided valuable information concerning pre-treating CFRPs. For example, an abrasion process should be carefully designed as it may lead to interlaminar fracture or fibre breakage, which is detrimental to the materials and their subsequent joining. In terms of plasma treatment, this technique causes significant changes in wettability and surface chemical composition, with gentle changes in the surface topography [47,48]. The activated gas (plasma) cleans the surface, and active functional groups which contain e.g. the oxygen or nitrogen element may appear at the surface [49,50]. The surface also becomes more hydrophilic and attains higher surface energy [48,50].

1.1.3 Challenges

Some topics concerning pre-treating CFRPs for adhesive bonding remain under explored. Firstly, most of the previous findings [36,43,51-55] in 2010s were not based on joints with a very high joint performance, e.g., the single lap shearing strength of the joints was usually in the range of 5-27 MPa. Higher-performance materials for aerospace bonding using aerospace film adhesives lacks detailed investigation.

Secondly, as for adhesive bonding associated with fibre reinforced polymers, the effects of fibre factors (e.g., fibre type, unidirectional/woven/discontinuous, strength and modulus,) or matrix resin factors (e.g., chemical compatibility of matrix resin to adhesives) have been studied [49,52,56]. However, the influence of the manufacturing process has not been evaluated in detail. Industrial manufacturing process can significantly affect the chemistry and topography of CFPR surfaces, leading to practical problems. For example, the effectiveness of surface pre-treatment will be affected, finally influencing the joint performance.

Thirdly, most previous studies have focused on thermosetting composites (e.g., carbon fibre reinforced epoxy resin). For example, how the processing parameters in plasma treatment affect the surface conditions and the joint performance of the thermosetting CFRPs has been thoroughly explored [57-64]. However, thermoplastic CFRPs have not been investigated in as much detail. Recently, some technologies related to thermoplastic materials, especially the production of, for example, aerospace-grade high-impact-resistance polyether ether ketone (PEEK), have been developed [19,20,65]. The thermoplastic CFRPs, having a processability and chemical composition very different from the thermosetting based CFRPs, should respond to plasma treatment differently. Hence, how plasma affects the thermoplastic CFRPs needs to be carefully investigated. Also, a wider understanding of how the adhesive bonding of thermosetting and thermoplastic based CFRPs differ can be gained.

Finally, the development of adhesion theories is ongoing, and faces underlying challenges. Early studies frequently investigated the bonding of similar materials while several recent studies [36,54,66] have moved their focus onto hybrid bonding. However, rarely have both similar and dissimilar joints been included into a single investigation for detailed comparison. Without such a comparison, it is difficult to evaluate the mechanisms of adhesive bonding, especially in the context of hybrid joining. In addition, by comparing the conclusions from various different previous studies, it is evident that some controversy still exists in some specific areas. For example, there is no consensus on whether removing the superficial matrix resin of FRPs to expose some fibres can improve adhesion or not. Although the different

experimental results can be explained by the various current adhesion theories, they are still disputed.

Therefore, it is necessary to set up a, not only detailed but also comprehensive, study with comparative analysis covering diverse CFRP adherends, different surface pre-treatment methods, and both hybrid and homogenous joints.

1.2 Aims and objectives

The aim of this research project is to develop guidelines for designers to select adherend materials and surface pre-treatment methods/parameters for adhesively bonded joints in aerospace applications. The research in this thesis will also contribute to solving the problems in the academic community and in industry as outlined in subsection 1.1.3.

All adherends and adhesives employed in this research are of aerospace grade. Five different types of unidirectional CFRPs are investigated, including i) two thermosetting CFRPs made using the same carbon fibre and epoxy-based matrix but formed into the composite material using different manufacturing techniques, and ii) three thermoplastic CFRPs, in which the carbon fibre is either T700 grade or T800S grade (see detailed datasheet in Chapter 3) and the matrix resin is either polyether-etherketone (PEEK) or polyaryl-etheretherketone (PAEK). In terms of surface pre-treatments, acetone cleaning, grit blasting, and plasma treatment following different processing parameters are employed. Homogeneous bonding of two CFRPs (i.e., CFRP/CFRP joints) are studied, and the hybrid bonding of CFRP to an aerospace-grade aluminium alloy (i.e., CFRP/Al joints) are also studied and compared.

The following objectives have been defined:

1. To investigate the effects of the manufacturing process (i.e., compression moulding versus autoclave moulding) on subsequent surface pre-treatment and joint performance in thermosetting matrix CFRPs.
2. To investigate how the pre-treatments affect the surface properties (e.g., topography, chemistry, and wettability) of thermosetting and thermoplastic

matrix CFRPs. To investigate how these factors influence the mechanical performance of adhesive joints.

3. To compare the effects of surface pre-treatments on thermosetting and thermoplastic matrix CFRPs.
4. To evaluate how the dissimilarities in surface conditions affect the adhesive bonding through comparing the homogenous joining and the hybrid joining.

1.3 Contents of each chapter

This PhD thesis investigates the surface pre-treatment of CFRPs prior to adhesive bonding. Figure 1-1 briefly shows the structure and the contents of this PhD thesis.

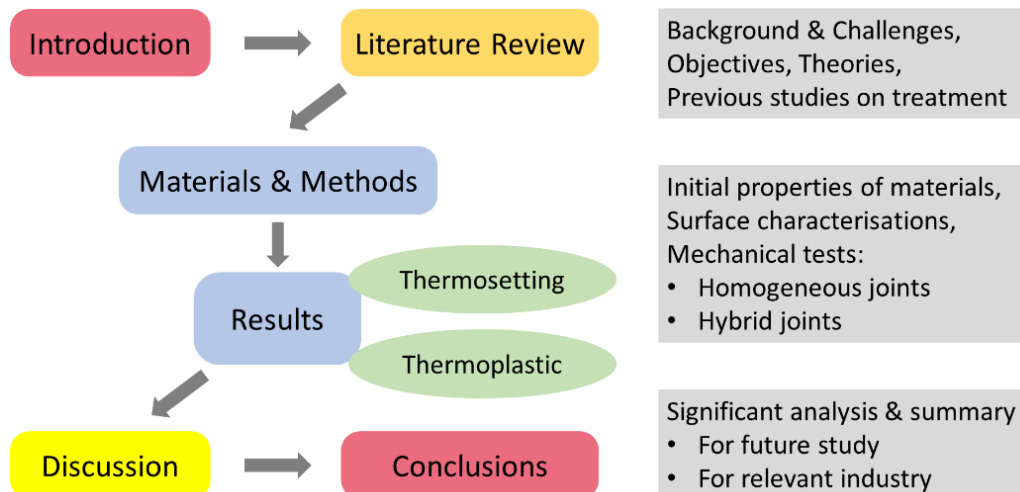


Figure 1-1. The structure and contents of this PhD thesis

Chapter 1 (Introduction) briefly introduces the background of the research field of adhesion and adhesives, especially in the aerospace industry. The progress and problems encountered in the surface pre-treatment of CFRPs prior to adhesive bonding are highlighted. Also, the aims objectives of the research presented in this thesis are introduced.

Chapter 2 (A review on adhesive bonding: theories, surface pre-treatments for composites, and joint performance) presents a literature review focusing on recent progress in surface pre-treatment methods prior to adhesive bonding. Diverse treatment methods for the composites (especially CFRPs) are introduced, including

solvent cleaning, chemical treatment, abrasion (hand sanding and grit blasting), peel-ply method, plasma treatment, and laser ablation. Relevant studies on these methods are reviewed and summarised. The effectiveness, compatibility, economy, and environmental concerns of these methods are analysed and compared.

Chapter 3 (Materials & methods) describes in detail the materials investigated and all experiments performed. The details of the five different CFRPs studied are firstly introduced, including the suppliers and types of the carbon fibres and matrix resins of the CFRP preregs employed. The processing parameters for manufacturing the CFRPs are also described and discussed, e.g., the proportion of fibres and resin in the prepreg, and the details of compression moulding or autoclave processing of prepreg to produce CFRPs. Subsequently, the surface pre-treatments for the CFRP adherends and the aluminium adherends prior to adhesive bonding are introduced, i.e., acetone cleaning, grit blasting and plasma treatment for both types of adherend, and silane agent treatment for aluminium adherends. Then the application and curing of the adhesive are introduced. The single-lap-shear (SLS) test is described in detail. Finally, the description of other tests employed and the interfacial characterisation methods are included, e.g., universal mechanical tests for the as-prepared CFRPs, the characterisation of surface topography after a treatment via optical microscopy or scanning electron microscopy, the characterisation of surface chemistry after a treatment via X-ray photoelectron spectroscopy (XPS) or energy dispersive X-ray spectroscopy (EDX), the measurement of water contact angle on surface after a treatment, and the characterisation of the fracture surfaces of the fractured joints after SLS testing is presented.

Chapter 4 (Results of the surface property and joint performance for the thermosetting CFRPs) presents the results of the investigation into the effects of the manufacturing process (i.e., compression moulding versus autoclave moulding) on subsequent surface pre-treatment and joint performance in thermosetting matrix CFRPs. Firstly, the material properties which were measured for the composites forming the adherends are presented. Secondly, the results of surface topography, chemistry, and wettability after the different surface treatments were performed, are

presented. Finally, the results from the single lap shear tests including the stress-displacement curves, SLS strength, and interface appearance after failure in terms of SLS joints of CFRP/CFRP or CFRP/Al are presented.

Chapter 5 (Results of the surface property and joint performance for the thermoplastic CFRPs) presents the results of the investigation into the effects of surface pre-treatments on thermoplastic matrix CFRPs. Firstly, the material properties of the CFRP adherend materials are presented. Secondly, the results of the studies into surface topography, chemistry, and wettability before and after plasma treatment (with various levels of treatment applied) are presented. Finally, the results from the single lap shear tests including the stress-displacement curves, SLS strength, and interface appearance after failure in terms of SLS joints of CFRP/CFRP or CFRP/Al are presented. The results for the 3 different CFRPs are compared.

Chapter 6 (Discussion of results) is a discussion of the results presented in chapters 4 and 5. Firstly, the effects of the CFRP manufacturing process for the thermosetting based CFRPs are discussed. Secondly, the effectiveness of the different surface treatment methods or processing parameters on the different materials are further analysed and discussed. The discussion then establishes comparative illustrations between the thermosetting and the thermoplastic matrix CFRPs highlighting the effects of the plasma treatment parameters and the resulting SLS strength of the bonded joints. The comparison with materials in other studies are also included. Finally, the contrast between homogenous and hybrid joining is discussed. The presence of one aluminium alloy adherend in combination with a CFRP adherend introduces some complexities into the results which required detailed consideration. Some new mechanisms important for hybrid joining are proposed to explain the experimental results.

Chapter 7 (Conclusions and recommendations for future work) presents the conclusions of this PhD research study and proposes recommendations for future work in this area. These recommendations are both for researchers and for industry where the fields of surfaces & interfaces, adhesion & adhesives, and aerospace composites, are important.

Chapter 2: A review on adhesive bonding: theories, surface pre-treatments for composites, and joint performance

2.1 Introduction to the review

Aerospace structures usually require joining of lightweight high-performance materials, e.g., aluminium alloys [67-69] and CFRPs [70-72]. Metallic alloys usually have a relatively high surface energy which is an advantage for adhesive bonding. To pre-treat the metallic alloys, chemical treatment is one of the most common methods used in industry. This method can remove contaminants and simultaneously etches or anodises the surface. Chromic acid (H_2CrO_4), sulphuric acid (H_2SO_4), sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) or silane agents are usually used to treat the aluminium alloys in laboratory research or industrial production. By contrast, fibre reinforced polymers (FRPs) usually have low surface energies which makes their surfaces difficult to wet by adhesives. Surface pre-treatment for FRPs prior to applying an adhesive firstly aims to enhance the wettability i.e., enabling the adhesives to spread on their surfaces. At the same time, a roughened topography, a protective layer, and/or polar functional groups will be generated on the surface which can generate stronger interaction with the adhesive. However, some traditional surface pre-treatment methods are not applicable or not effective when applied to FRPs.

Recently, researchers have been paying more attention to the surface pre-treatment methods for FRPs as the surface pre-treatment of metals is more

established. In this chapter, diverse surface pre-treatment methods for FRPs prior to adhesive bonding are reviewed, including solvent cleaning, chemical treatment, abrasion, the peel-ply method, plasma treatment, and laser ablation. The theories of adhesion and the experimental techniques developed to evaluate the pre-treatment methods and/or the final joint performance are introduced. The advantages and disadvantages of these methods are summarised. This review concentrates mainly on adhesive joints concerning carbon fibre reinforced epoxy resins using epoxy-based adhesives, except those with special instructions.

2.2 Adhesion theories

Adhesion is a complicated concept [73,74] and there are still many disagreements among researchers from different fields about how adhesion is attained. As mentioned in chapter 1, many theories concerning adhesion and adhesive bonding have been proposed. Some adhesion theories only relate to the cohesion of an adhesive rather than considering the adherend surface or the interface between the adhesive and the adherends. In this section, the theories which consider the adherend are introduced. Adhesion theories usually consider physical, mechanical, or chemical aspects. Table 2-1 summarises the adhesion theories [75-80] based upon adsorption, diffusion, electrostatic force, chemical bond, mechanical interlocking, and the weak boundary layer theory.

Table 2-1. A brief summary of adhesion theories based on absorption, diffusion, electrostatic force, chemical bond, mechanical interlock, or weak boundary layer.

Theory	Standpoint	Reason for adhesion	Adherend factors in adhesion
Adsorption	Molecular	Intermolecular forces	Roughness, surface chemistry
Diffusion	Molecular	Interdiffusion, solution	Wettability
Electrostatic force	Atomic	Charge transfer reaction	Surface chemistry
Chemical bond	Atomic	Chemical reaction	Surface chemistry, wettability
Mechanical interlock	Mechanical	Frictional force	Surface topography
Weak boundary layer	Mechanical	Not discussed	Impurities, air retention, non-uniformity

2.2.1 Adsorption theory

Adsorption theory attributes the adhesion to intermolecular forces, which is associated with the mutual attraction between the adherend molecules and the adhesive molecules [81]. The adsorption can be physical or/and chemical. Physical adsorption, usually derived by van der Waals force (as shown in Figure 2-1a), is fundamental in adhesive bonding [81,82].

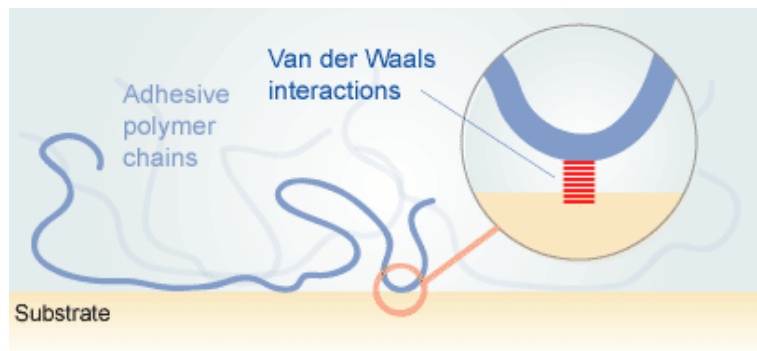


Figure 2-1. Sketch illustrations of adsorption theory [76,77].

Firstly, the adhesive molecules can move to the surface of the adherend due to Brownian motion [83]. Increasing the temperature/pressure or reducing the viscosity of the adhesive can improve this process. Secondly, when the distance between the adhesive molecules and the adherend molecules becomes lower than 1 nm, van der Waals forces are established so that the adhesive molecules are adsorbed at the surface of the adherend [84]. This process gives rise to the adhesion. In some cases, chemical absorption takes place when ionic bond or covalent bond forms, increasing the joint strength.

According to the adsorption theory, the specific surface area of the adherend is significant in adhesive bonding. The chemical composition of the adherend surface can also affect the adhesion.

2.2.2 Diffusion theory

The diffusion theory proposes that the adhesion between polymers arises due to the interdiffusion of polymeric molecules across their mutual interface. In many cases

of adhesive bonding, the adhesive is a polymer and the adherends are also polymeric or polymeric composites. As the formation of a joint often requires it to be heated (to cure the adhesive) then there is the possibility that the adhesive molecules and the adherend molecules could diffuse into each other as in a solution [85], as shown in Figure 2-2. This interdiffusion could induce a new interfacial region or even a new phase (sometimes in the form of a copolymer). During the curing process of adhesive joining, the heating temperature and duration can affect the adhesion.

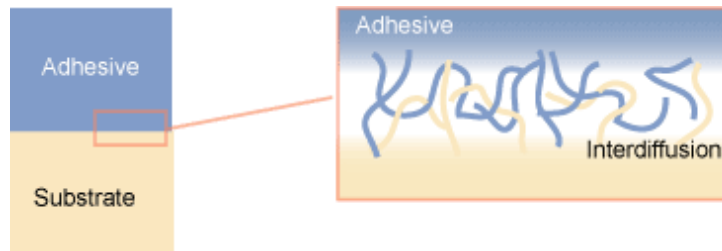


Figure 2-2. Sketch illustrations of diffusion theory [76,77].

According to this theory, the interdiffusion is influenced not only by the molecular mass or the molecular structure, but also by the factors related to the contact between the polymeric adhesive and the polymeric adherends [86,87]. For example, wettability (on the surface of the adherend, quantified by contact angle) is a significant indicator.

2.2.3 Electrostatic theory

If the adhesive material and the adherend material have remarkable difference in electronegativity, a charge transfer reaction will take place at the interface as shown in Figure 2-3. This theory proposes that the resultant electrostatic force between the charge donator and the charge acceptor can affect the adhesion [88,89].

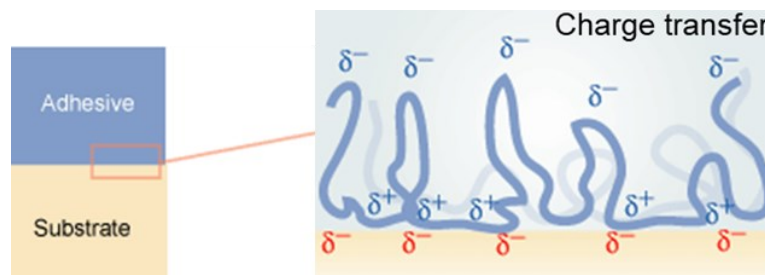


Figure 2-3. Sketch illustrations of electrostatic theory [76,77].

The electrostatic theory is sometimes useful to explain some observations during

separation of the adherends (joint failure). For example, at a lower peeling rate, the adhesion seems to be weaker [90] (i.e., for peeling, less work is needed or smaller forces can be used). According to the electrostatic theory, the decrease of work of adhesion can be explained by the decrease of electrostatic force: at lower peeling rate, more charges can escape in separating two materials.

However, in making adhesive joints, the contribution of electrostatic force is usually not obvious. Even when the joints are made of common metallic adherends (as charge donator) with polymeric adhesives (as charge acceptor), the electrostatic force can usually be ignored in comparison to other forces/interaction that affects the adhesive bonding.

2.2.4 Chemical bonding theory

In the chemical bonding theory, specific chemical reactions take place at the contact area between the adhesive and the adherends [91,92], in accordance with the quantum mechanics of molecular orbitals [93]. As shown in Figure 2-4, chemical bonds will form between the molecules. The chemical bonds can be ionic bonds, covalent bonds, or coordinate covalent bond. For example, ionic bonds can form between an inorganic adhesive and the surface of inorganic adherends. Covalent bonds can form when the adhesive is organic.

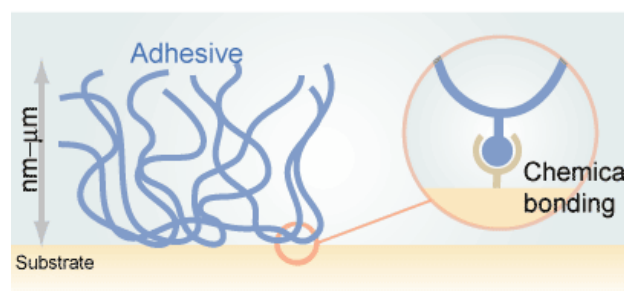


Figure 2-4. Sketch illustrations of chemical bond theory [76,77].

In comparison to a van der Waals force (bond), a chemical bond is much stronger. However, the effect of van der Waals forces in an adhesive joint is usually more significant than the chemical bond. This is because the van der Waals forces are much more frequently occurring than the chemical bonds, which are only significant in

certain situations. To form a chemical bond, many quantum-chemistry conditions should be met [93].

Considering the chemical bonding theory, the importance of many modern surface pre-treatments can be explained. For example, surface treatments often optimise the wettability or surface chemistry of the adherends. A better wettability of an adherend can increase the contact area with the adhesive so that more chemical bonding can occur [94], which is beneficial to adhesive bonding. Modifying the surface chemistry of the adherends can affect the adhesion by changing the reactant and influencing the bond energy.

2.2.5 Mechanical interlocking theory

On the surface of porous or rough adherends, a liquid adhesive can penetrate into the pores or cavities and can displace the trapped air at the surface or interface. Then after the adhesive is cured, the liquid solidifies to a rigid solid and the adhesive/adherend takes on a lock-key system (Figure 2-5), namely the mechanical interlocking effect [95,96].

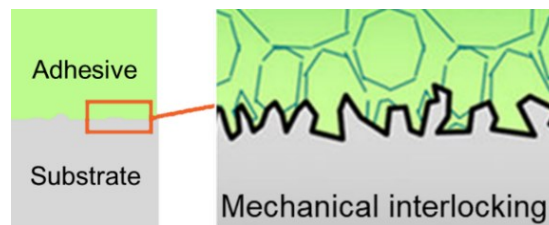


Figure 2-5. Sketch illustrations of mechanical interlocking theory [75].

Mechanical interlocking theory cannot explain the bonding mechanism of some perfectly smooth materials (such as glass). It applies on porous and rough adherends. In terms of these adherends, the mechanical interlocking theory proposes that the adhesion is enhanced as the mechanical interlocking impedes the separation of adhesive from the adherend (e.g., in the form of a frictional force) [97,98]. According to this theory, a rough surface topography introduced to the adherends should lead to a significant improvement in adhesive bonding.

2.2.6 Weak boundary layer theory

In practical adhesive joining, the distribution of the strength usually cannot be uniform. Weak points (with lower adhesion than the surrounding) exist in the system of adherend/adhesive/adherend, and this theory proposes that the bond failure takes place due to a weak boundary layer [99,100]. For example, weak boundary layers can occur in the adhesive, adherend, or the interface where trapped air or moisture and surface contamination or the impurities concentrate to form a weak attachment as shown in Figure 2-6.

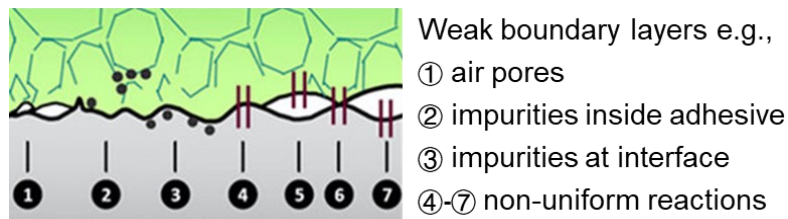


Figure 2-6. Sketch illustrations of weak boundary layer theory [75].

Weak boundary layer theory is useful in analysing the fracture surface (e.g., the reason for the failure mode as shown in the appearance of a fracture surface) after mechanical testing. According to this theory, to achieve a high joint strength or high fracture toughness, any weak boundary layers should be removed or prevented. To prevent these weak boundary layers, surface pre-treatments should be applied.

2.2.7 Summary of the adhesion theories

Since diverse types of adherends and adhesives can be employed in adhesive bonding, no single theory can describe all the different categories of adhesion. It is suggested that the physical, chemical, or even mechanical effects in adhesion cannot be completely isolated from one another. The surface chemistry, surface topography, and wettability usually can remarkably affect the performance of adhesively bonded joints. Hence, in the study of adhesive bonding, these surface properties should be carefully characterised to evaluate the effect of surface pre-treatment methods. The interfacial characterisation avenues to assess these surface properties are introduced in section 2.3.

2.3 Interfacial characterisation

Interfacial characterisation techniques have been developed to analyse the effect of surface treatment methods. Specifically, they are employed to investigate the surface topography, chemistry, and wettability.

Table 2-2. Common interfacial characterisation techniques to evaluate surface treatments.

Apparatus	Output information
Optical microscope	Surface microstructure
Scanning electron microscope (SEM)	Surface micro/nano-structure
Atomic force microscope (AFM)	Surface micro/nano-structure, roughness
Profilometer	Surface roughness
X-ray photoelectron spectroscopy (XPS)	Elementary composition, chemical bond
Energy dispersive X-ray spectroscopy (EDX)	Elementary composition and distribution
Infrared spectroscopy (IR)	Molecular functional group
Contact angle goniometer	Contact angle to show the wettability

Different microscopes can be used to observe the surface topography, e.g., an optical microscope, a scanning electron microscope (SEM), or an atomic force microscope (AFM). These observations show the morphological effect [96] of the treatment method. Additionally, to access the data of surface roughness, a profile meter or an AFM software can be employed.

In terms of the surface chemistry, an Energy dispersive X-ray spectroscopy (EDX, or EDS) can be connected to a microscope for in-site detection. EDX characterises the composition of the chemical elements at the surface. Other avenues can access more detailed information of the surface chemistry. X-ray photoelectron spectroscopy (XPS) can identify the chemical bonds (e.g., C-O, C=O) by peak deconvolution. Infrared-ray (IR) spectroscopy characterises the functional groups. Characterisations before and after a treatment show how the method affects the surface chemistry. For example, Mund et al. [101] used SEM to observe the surface of CFRPs with different surface topography and used EDX to analyse their surface chemistry. By comparing the results of these characterisations and the results of mechanical testing of adhesively bonded

joints, they discussed the remarkable influence of the surface topography and the release agent residue on bonding strength.

Contact angle (CA) measurement is a quantitative characterisation of wettability (i.e., the wetting of a solid surface by a liquid) [102]. The CA is measured at which a liquid-vapour interface meets a solid surface, as shown in Figure 2-7. A lower CA means that the surface is more easily wetted by the liquid.

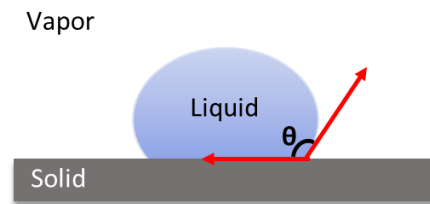


Figure 2-7. Sketch diagrams of the wettability measurement.

These characterisations are usually employed together to show the changes in any surface properties caused by a surface pre-treatment. For example, Hu et al. [103] reported the result of SEM, XPS, and CA characterisations on an aluminium adherend before and after alkaline etching and resin pre-coating. Taking advantage of these characterisations, they attribute the improvement in CFRP/Al bonding strength to the beneficial changes in surface topography, surface chemistry and wettability on the aluminium adherends following the surface pre-treatments.

2.4 Mechanical testing

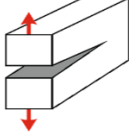
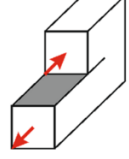
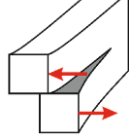
2.4.1 Fracture mechanics testing

In fracture mechanics testing, a crack is inserted in the bondline and the joints are loaded to initiate and propagate the crack so that the fracture toughness is measured. Loading the joints in different ways generates the different fracture modes, including the opening mode (mode I fracture), sliding mode (mode II fracture), and shearing mode (mode III fracture) [76,77,104], as shown in Table 2-3.

For example, double-cantilever-beam (DCB) testing measures mode I fracture toughness (G_{Ic}). In DCB tests, the tensile opening forces are applied to opposite sides

of the joint. When the two adherends are made of the same material and are of equal thickness, with the crack at the mid-thickness, the fracture mode is pure mode I [105].

Table 2-3. A brief summary of mode I (opening) fracture, mode II (sliding) fracture, and mode III (shearing) fracture.

Fracture	Applied stress	Sketch diagram [104]
Mode I	Tensile opening, namely opening	
Mode II	In-plane shearing, namely sliding	
Mode III	Anti-plane shearing, namely shearing or tearing	

2.4.2 Single lap shear testing

Single lap shear (SLS) tests show the ability of a lap-joint to withstand external shear forces which pull the two adherends in opposite directions, as shown in Figure 2-8. To break the SLS joint, a mixture of mode I and mode II fracture occurs [106,107]. The loading is mostly mode II in the central area of the SLS overlap, while at the edge of the overlap, mode I loading plays a more significant role. Although the fracture of a SLS joint is usually not in a pure mode, SLS tests are commonly employed in industry and in academic research to evaluate the joint performance as it is a simple test to perform [108]. The result of a SLS test, i.e., the SLS strength, is a simple measure to evaluate the effectiveness of adhesive bonding.

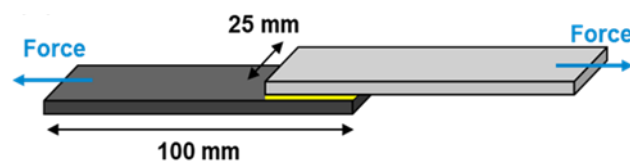


Figure 2-8. Sketch diagram of SLS testing.

2.4.3 Failure mode

To evaluate the performance of the adhesive joints and also to evaluate the effectiveness of surface pre-treatments applied prior to bonding, the failure mode of the joints is investigated. To investigate the failure mode, the appearance of the fracture surfaces after the failure of the joint in the mechanical test is observed. The fracture surfaces can be photographed using a digital camera [109-111] or by using a diverse range of microscopes [112-114]). Depending on the location of the failure (i.e., the failure loci), the failure modes can be divided into three categories, i.e., interfacial failure (namely adhesive failure) on the adherend surface or between the adherend and the adhesive, cohesive failure within the adhesive, and failure within the adherend (e.g., interlaminar fracture in a fibre composite material). Figure 2-9 shows the sketch diagram of these failure modes. It is possible also that combinations of these failure modes can occur in a single joint.

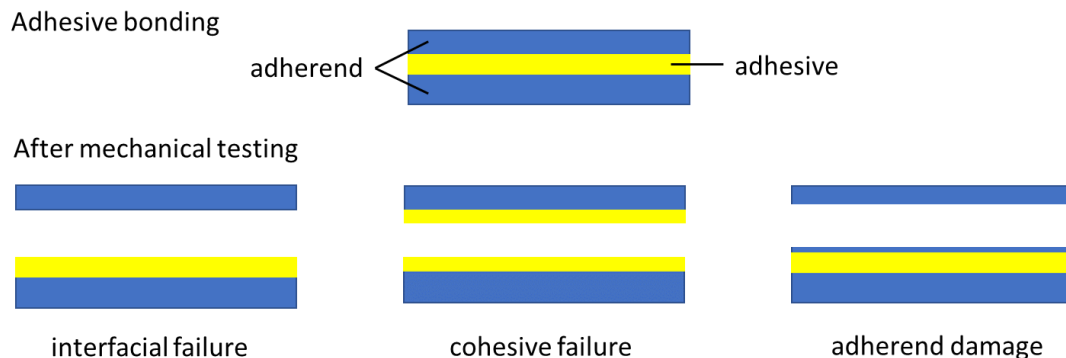


Figure 2-9. Sketch diagrams of the different failure modes. (a) interfacial failure; (b) cohesive failure; (c) adherend failure.

An interfacial failure is usually associated with a relatively poor joint performance, and may also indicate that the surface pre-treatment prior to adhesive bonding was not effective. When the failure mode is observed to be cohesive failure, the surface pre-treatment is deemed to be sufficient [115-117]. If the damage to the adherend is observed, then either i) the surface pre-treatment is sufficient and the strength of the adhesive is higher than the local adherend, or ii) the surface pre-treatment is excessive and has caused damage to the adherend which leads to adherend failure.

2.5 Surface pre-treatments

Various surface pre-treatments have been developed to optimise the surface topography, chemistry, and wettability prior to adhesive bonding. Taking advantage of these surface pre-treatments, joint strength or fracture toughness are increased. In this section, the various surface pre-treatments for FRPs are reviewed.

2.5.1 Solvent cleaning

Solvent cleaning aims to remove the contamination that is soluble or/and can be washed away, i.e., dust, residual processing agents, and grease. It is usually an essential step in any multi-stage surface pre-treatment. One of the most frequently-used chemical substances to clean polymers and FRPs is acetone [118-120]. Methyl ethyl ketone (MEK), isopropanol (IPA), ethanol, trichloro ethylene (TCE), and deionised water are also sometimes used as cleaning solvents at different stages of a surface pre-treatment for FRPs. A drying step frequently follows solvent cleaning to prevent any liquid residues or secondary pollution from occurring.

The choice between solvent wiping, washing, immersing, ultrasonic bathing, or solvent vapour degreasing depends on the degree of contamination as well as the size and type of materials being treated. Wingfield [121] suggested that solvent wiping sometimes just spreads the contaminations over the surface rather than removing the contamination. Yudhanto et al. [122] reported that the joint strength or fracture toughness usually cannot be effectively improved simply by solvent cleaning. For example, they commented that it is difficult to fully remove fluorine contamination left after the manufacturing of thermosetting composites. They suggested that solvent cleaning is considered to be a supporting treatment which can be employed before and/or after other treatments.

2.5.2 Chemical treatment

Chemical treatment has a similar effect to solvent cleaning, but the chemical treatment mainly aims to remove some of the adherend surface material by etching. It

uses a solution, e.g., usually an acid (especially oxidising) or alkaline solution, to clean the surface and sculpture or modify the surface. Such treatment applies to metallic or polymeric composites, but most literature relates to metallic alloys as noted in section 2.1. Here chemical treatment for FRPs is reviewed.

Menningen et al. [123] etched CFRPs using potassium permanganate (KMnO_4) solution and obtained a uniformly rough surface which enhanced the mechanical interlocking mechanism. It was reported that hydrofluoric acid (HF), phosphoric acid (H_3PO_4), hydrogen peroxide (H_2O_2) could also etch some FRPs for other purposes [124-127], but whether their etching can effectively improve the strength or durability of adhesive joints remains to be studied. Martínez-Landeros et al. [55] studied the effect of nitric acid (HNO_3) or sodium hydroxide (NaOH) solution etching on CFRPs, as shown in Figure 2-10. They found that the acid etching led to lower contact angle and mild modification (Figure 2-10b) which benefited adhesive bonding. However, the surface showed local variations (Figure 2-10c) after alkaline etching, which reduced the stability and resulted in a lower fracture toughness.

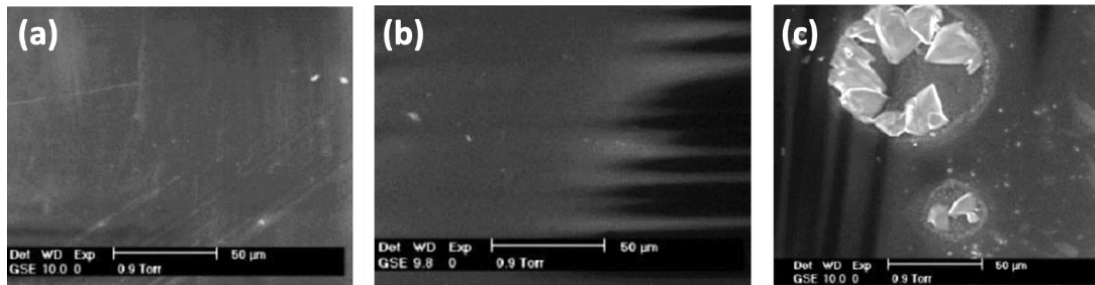


Figure 2-10. Surface topography of CFRPs. (a) after IPA cleaning: mild modification; (b) after IPA cleaning+ HNO_3 etching, mild modification with further activation of surface functional groups; (c) after IPA cleaning + NaOH etching: local variations. [55]

Silane coupling agents, e.g., γ -MPS (γ -methacryloxypropyltrimethoxy silane) and γ -APS (γ -aminopropyltriethoxy silane) are also used for treatment. Silane treatment (or silane agent treatment, SA) has frequently been used to pre-treat some metallic materials or GFRPs for hybrid joining [128-130]. Kim et al. [131] demonstrated the effectiveness of silane agent treatments on aramid/epoxy composites. They also added a flame treatment using propane gas prior to the SA. The flame treatment plus SA achieved an improvement of 35% in SLS strength compared with the single SA.

The roughness or topography of a surface can be controlled by adjusting the concentration and composition of chemical solution. However, as FRPs are inactive to chemicals, chemical treatment has a limited effect. More powerful methods should be employed to achieve improved joint performance. Furthermore, chemical treatment for composites usually involves hazardous substances which can harm the environment and can be hazardous to health [132]. For example, H_2CrO_4 was widely employed in the industrial process to etch and activate the surface of polymers, polymeric composites, and metallic materials. However, it has led to serious problems with waste polluted water disposal so that some countries have restricted its usage [133]. As a consequence, research now usually gives priority to the other methods which are greener and more effective as will be introduced in the following sections.

2.5.3 Abrasion

Abrasion is a mechanical technique which is widely utilised in both laboratory research and in industrial production to optimise the surface roughness and surface area. Abrasion is also able to remove some solid contamination which is difficult to remove by solvent cleaning [134]. In terms of FRPs as opposed to metallic materials, over abrasion usually results in a reduction in the cohesive strength of the polymer matrix or results in the breakage of reinforcing fibres [133]. Hence, relatively mild abrasion is usually employed to treat FRPs.

A typical abrasion process for FRPs has the following steps. Firstly, the FRP adherend is cleaned by a solvent to remove contamination. This step is essential, without which detrimental contamination (e.g., mould releasing agents containing silicanes) may permeate through the surface during subsequent abrasive treatment. Secondly, after a drying process, the abrasive treatment, e.g., hand sanding or grit blasting [135] is carried out. Silicon carbide (SiC) or aluminium oxide (Al_2O_3) may be used as abrasive materials. In hand sanding, abrasive paper is used to rub the surface. In grit blasting, a gas at high pressure containing abrasive solid particles or a liquid flow that contains the abrasive solid is used for abrasion, e.g., a grit-blasting apparatus. A grit-blasting apparatus which combines grit with water to make a slurry that is then

blasted at the surface, namely the wet grit-blaster, tends to be softer on the surface compared with the high-pressure-gas grit blaster. The wet grit blaster is possibly better suited for polymer composites. Finally, the FRP is cleaned again by a dry, clean lint-free cloth or brush, washing solvent or gas to remove the residual particles or powder.

Contact angle values will depend on surface roughness in terms of abraded surfaces, and low values of CA are typically required for good joint performance. To improve joint performance, in most cases, an appropriate roughness for a lower CA is necessary. For example, Park et al. [136] used different grades of SiC abrasive paper for hand-sanding polyethylene & aramid fibre/vinyl ester resin. As shown in Figure 2-11a, surfaces with roughness in the range of 0.05 to 0.51 μm were achieved. When this FRP was treated to possess an average surface roughness of 0.23 μm , the smallest water CA and the best bonding performance were observed.

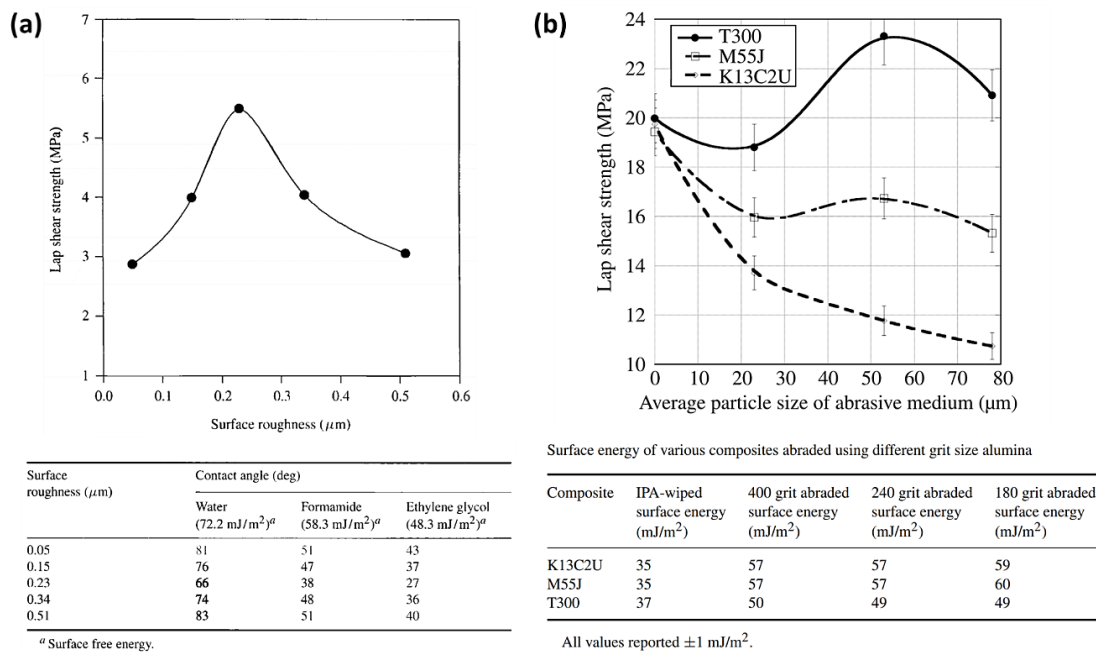


Figure 2-11. Correlation of CA, roughness and SLS strength using abrasion method. (a) on an AFRP [136]; (b) on CFRPs made respectively using carbon fibres of different modulus (T300 grade: around 230 GPa, M55J grade: around 540 GPa, K13C2U: around 900 GPa) [52].

However, since the over application of abrasion can damage the FRPs, a lower CA does not necessarily lead to an enhanced joint performance. Noticeable damage may occur on a sensitive material. Interlaminar failure of FRP may become the main failure mode during a mechanical test. Zaldivar et al. [52] carried out abrasion on a diverse

range of CFRPs using abrasive papers of different size. They found that large abrasive grit particles can cause a larger abrasion damage zone, which causes a reduction of SLS strength even if the surface energy of treated CFRPs is enhanced (see Figure 2-11b). They also found that the CFRP reinforced with lower-modulus carbon fibres was less affected by over abrading because lower-modulus fibres tend to couple more strongly to the matrix resin.

Many studies [27,55,123,137,138] have indicated that abrasion applied to FRPs contributes to a better joint performance than solvent cleaning and chemical treatment. It does not mean that mechanical interlocking is more important than chemical bonding because FRPs are inactive to chemicals. Other methods (e.g. plasma treatment [139], see section 2.5.6) which exert a greater influence on chemical activity but less influence on roughness can show a higher joint strength.

More significantly, the FRP is usually not chemically modified during an abrasive treatment. Different treatments can be combined if a greater joint performance is required [140]. For example, Del-Real et al. [138] performed a grit blasting plus silane treatment on a CFRP (bidirectional 0/90° carbon fibre plate with an epoxy matrix composite) and demonstrated that the techniques in combination led to a higher fracture toughness (G_{IC}) of joint being obtained after bonding with an acrylic adhesive.

Although abrasion is a simple and well-developed surface pre-treatment technique, it still has some intrinsic drawbacks. For example, the hand sanding method has low repeatability and is labour intensive: the manual nature of the process makes it difficult to treat the surface area evenly. Grit blasting is applicable for neither extra thin FRPs nor complex-shaped FRPs [141]. Abrasion is slow, which limits commercial production rates. Although abrasion is more friendly to the environment compared to chemical treatment, the dust pollutants generated can potentially cause air pollution and are hazardous to health. As a common and commercial method, researchers [27,30,53,142] have reported comparative studies between abrasion and alternative surface treatment methods to illustrate the effectiveness and superiority of other modern technologies (e.g., using plasma or using laser).

2.5.4 The use of Peel-ply

The peel-ply method was developed specially for composites to treat the surface prior to bonding. A peel ply is a removable fabric layer attached to a composite surface (as shown in Figure 2-12), which aims to protect and simultaneously modify the surface [143-145]. Covering the surface with such a protective layer makes the composite more resistant to environmental factors such as contaminations, moisture ingress, and temperature change, etc. After the layer is removed, the surface acquires the required roughness and chemical composition, which is ready for post processing.

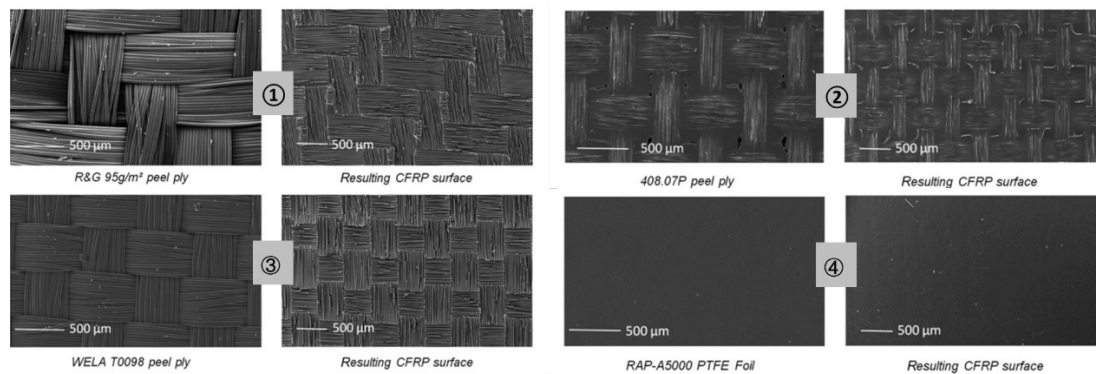


Figure 2-12. Different peel plies and the resulting CFRP surfaces [143].

Peel plies have been adopted commercially and commonly by aerospace manufacturers for over 10 years. They are a simple and cost-effective choice for industry [146]. Commercial peel plies are made of polyester, polyamide, or glass. Bénard et al. [147] reported that on the surfaces which have the same roughness, polar liquids (substance whose molecules have an uneven charge distribution, e.g. water, formamide, glycerol) presents a lower CA on polyamide peel ply treated GFRPs or CFRPs, but nonpolar liquids (e.g. diiodomethane) shows a lower CA on the polyester treated FRPs. Hence, it can be predicted that the chemical composition of adhesive (e.g., polar or nonpolar) may affect joint performance when different types of peel plies are used.

The peel plies for adhesive bonding can be either dry or wet. A dry peel ply will not bring about further contamination because there are no other coatings or impurities on such dry fabric. A wet peel ply, namely a tear ply, is fabricated by

impregnating suitable resin (the matrix resin of the FRP) onto a dry peel ply [148]. The two types may contribute to the same roughness, but the wet one is able to avoid the loss of superficial resin and even the bareness of reinforced fibre [144]. A wet peel ply should be used within the operational life-span, and the solidification should be completed before the end of mechanical property life-span [149].

Recently, a soft-layer method [150,151] has been developed, which has the same operations as the conventional peel-ply method. The initial purpose of such a soft-layer method is to enhance the electroconductivity of CFRPs by removing the superficial surface resin and deliberately causing the exposure of bare fibres [152]. Lee et al. [153] combined the principle of the peel-ply method with the methodology of the soft-layer process. They employed a reusable thermoplastic layer rather than the relatively costly peel ply to treat GFRPs and achieved a uniform exposure of woven glass fibres on the surface. GFRPs which had uniformly bare fibres showed a higher SLS strength after bonding. On a personal note, the uniform exposure of glass fibre without delamination and fibre breakage could be regarded as a positive adjustment of surface topography or/and wettability for adhesive bonding.

It has been reviewed or reported by numerous researchers [55,137,144,154-156] that alternative pre-treatment methods to peel-ply lead to superior joint performance (see examples in Figure 2-13). Kanerva and Saarela [144] reported that it is possible for contamination to be transferred from the peel ply to the composite surface. However, the majority of the industrial producers currently still choose peel-ply methods for treating FRPs. Arenas et al. [157] established a comparative illustration between sanding, grit blasting and peel-ply method using a multi-criteria decision analysis in terms of bonding CFRPs to aluminium alloys via polyurethane (PU) or epoxy adhesives. When various industrial factors (i.e., availability delays, safety, associated costs) were considered, the peel-ply method was the most satisfactory option even if it failed to achieve the highest joint strength [157].

The peel-ply method is satisfactory also on account of the fact that peel-ply can be designed to protect the surface from elevated temperature, moisture, and contamination. These environmental factors sometimes are deleterious to adhesive

bonding. As adhesives are not usually applied to FRP surface immediately after the pre-treatment in a discontinuous industrial production, these factors are inescapable when other methods are adopted [158-160]. Adding a protective layer, the materials can be stored for a relatively long time. A FRP covered with a peel ply is also a semi-product for sale because it can be further used for many purposes including but not limited to bonding after the layer is removed [149]. Furthermore, to achieve much higher bonding strength and durability, further surface activation treatment will be combined after the peel ply is removed if necessary [161].

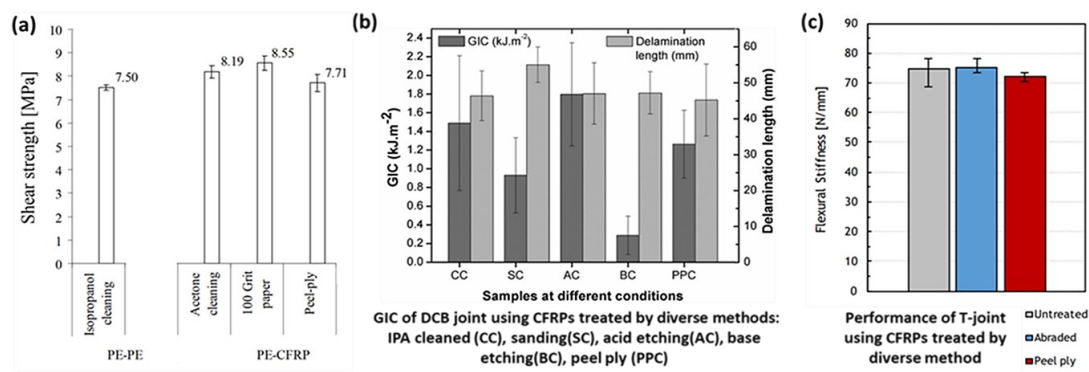


Figure 2-13. Other methods compared with peel ply. (a) Comparing SLS strength [137], (b) Comparing DCB testing results (G_{IC}) [55], (c) Comparing T-joint performance [156].

2.5.5 Laser ablation

Laser ablation uses a pulsating or continuous high-energy laser beam to impact the surface rapidly and locally. Classified by the wavelength, commercial laser equipment usually involves far-IR laser (10600 nm, e.g., CO₂ laser), near-IR laser (1064 nm), or ultraviolet laser (UV laser, 248-355 nm). Laser pre-treatment enhances the joint performance by removing contaminants, sculpturing the surface topography, and changing the chemical composition [30]. It can accurately construct a desirable microstructure on the surface because of the low processing linewidth [34,36].

As shown in Table 2-4, IR and UV lasers involve different processing theories. IR laser [162] vibrates the molecules of a small target surface (e.g., around 20 μm processing scope), where thermal effects cause the dissolution and volatilization of material. Due to the small processing scope, IR laser ablation minimises this drawback (i.e., heat affected zones, residual stresses) potentially caused by conventional heat

treatment [163]. A UV laser has a much higher photon energy so that it directly breaks down the chemical bonds of molecules on the surface [164]. The UV laser is not considered as a heat treatment principally.

Table 2-4. Comparison between the IR laser and UV laser.

	IR laser	UV laser
Wave-length	1064-10600 nm	248-355 nm
Linewidth	usually $\geq 20 \mu\text{m}$	around $10 \mu\text{m}$
Laser beam	Vibrating the molecules of small target surface	Having much higher photon energy than IR laser
Theory	Causing thermal effects: dissolution and volatilization of material	Directly breaking down the chemical bonds in molecules at surface

Akman et al. [33] found that a CO₂ laser and a UV laser contributed to similar surface roughness on CFRPs, but accumulated UV laser tended to increase -OH groups while the CO₂ laser had a reducing effect. Li et al. [35] concluded that a near-IR laser could remove the matrix resin of CFRPs to expose the carbon fibre. They found an approximate linear relationship which indicated the SLS strength increased as the remaining resin decreased. Schweizer et al. [142] found a similar trend when using UV laser. Palmieri et al. found that a UV laser removes silicones (Si) from the surface of CFRP and a low Si/C ratio or a low CA is the predictor of a high bonding performance. Li et al. [36] found that laser treatment optimised the surface topography and enhanced the wettability by increasing the presence of C=O and O-C=O bonds. They suggested that the chemical bonding, rather than mechanical interlocking, was the major reason for the improvement of CFRP/Al joint performance when laser treatment was applied to both substrates.

Some studies [36,142] have reported that near-IR laser is preferable to UV laser when the values of SLS strength are compared. Other studies [30,33,142] have indicated that laser ablation is superior to abrasion in terms of enhancing the joint performance. These studies are all based on pre-treatment for CFRPs. More research should be carried out to show its applicability to other composite materials and to compare it with alternative methods. Recently, some machining industries have taken

advantage of laser processing instead of the traditional heat treatment. However, as a powerful treatment for FRPs prior to adhesive bonding, laser processing parameters should be accurately studied and optimised to avoid fibre damage or the risk of delamination being induced before it is used in industrial production [33,34]. However, laser ablation is regarded as a promising method since it is effective, accurate, fast, and environmentally friendly.

2.5.6 Plasma treatment

Plasma treatment is a physicochemical method which uses activated gas to clean the surface and also to activate it chemically. Firstly, the processing gas is ionised into a plasma state by means of external power. Subsequently, the samples are exposed under the plasma environment where their surfaces are treated. Active functional groups which contain e.g. the oxygen or nitrogen elements appear at the surface [47,49,148,165]. Following the treatment, the surface becomes more hydrophilic and attains higher surface energy.

The low-pressure plasma treatment (LPPT) was developed recently. This technology employs a partial vacuum chamber, inside which the plasma is generated and the samples are treated. Pizzorni et al. [53] treated CFRPs using a vacuum cold-plasma technique and investigated the effect of plasma power (50 W, 100 W, 150 W) and exposure time (50 s, 100 s, 150 s) using different processing gases (air, O₂, argon, N₂), as shown in Figure 2-14a. XPS and IR analysis showed that the plasma treatment in all conditions resulted in an increase in the ratio of oxygen to carbon, i.e. the O/C ratio as well as an increase in polar groups at the surface, which improved the wettability of the surfaces. This result was most evident when the processing gas was O₂ (air was in second place). The samples after O₂-plasma treatment showed the highest SLS strength on average. Also, there was no evidence to indicate that there was a correlation between the SLS strength and the plasma power or the exposure time. The maximum SLS strength value was achieved when the power was 150 W and the time was 50 s using air as the processing gas.

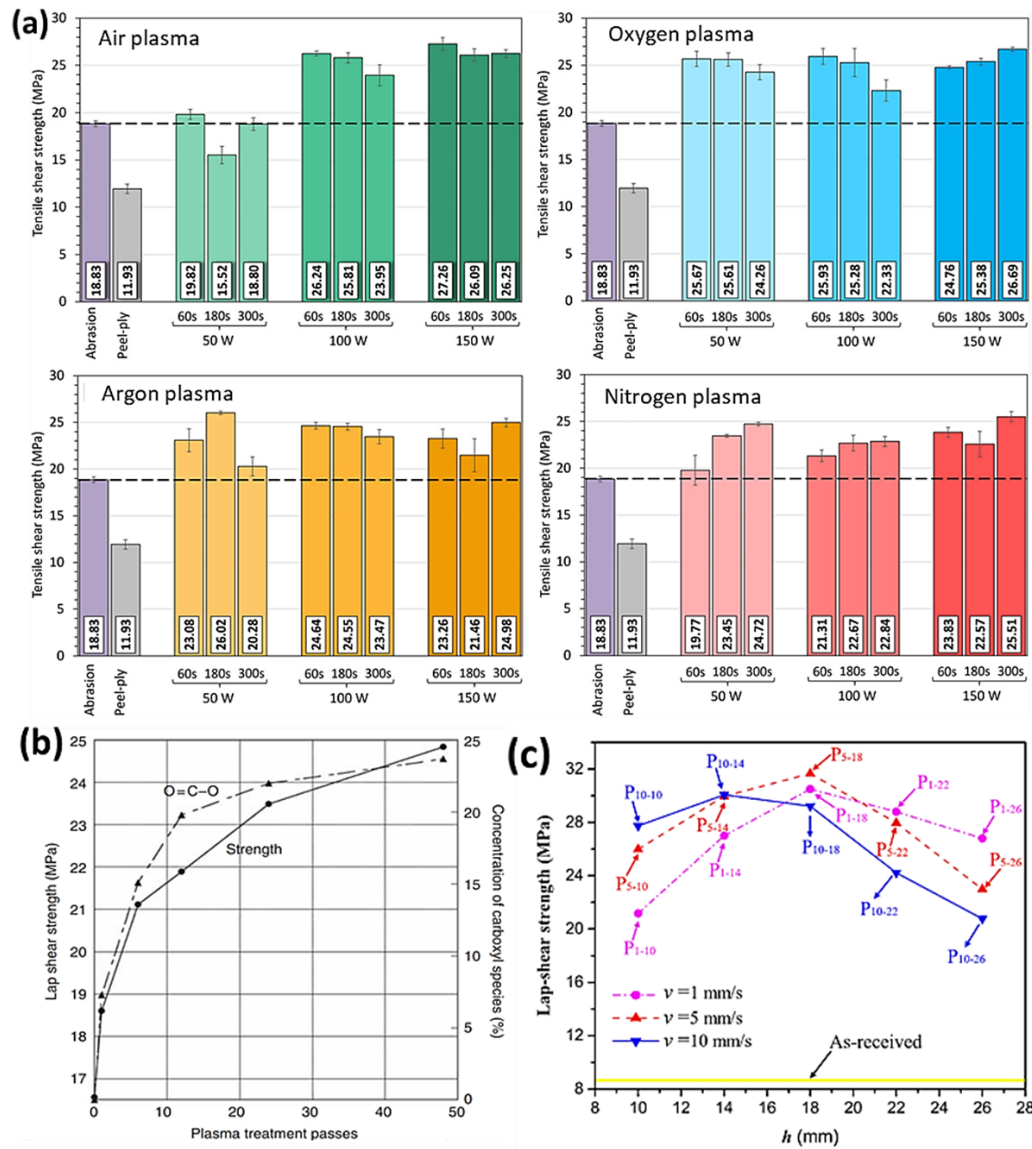


Figure 2-14. Effect of plasma treatment on joint performance of CFRPs. (a) Effect of processing gas, power, and duration of LPPT on SLS strength [53] ; (b) Effect on concentration of O=C=O on SLS strength [166] ; (c) Effect of nozzle distance and speed of APPT on SLS strength [43].

Plasma treatment can also be carried out under atmospheric pressure, i.e., the atmospheric pressure plasma treatment (APPT) [167,168]. This technology does not require a chamber, so samples with larger dimensions can be treated [169,170]. A robotic arm containing a nozzle, which scans the surface of the samples at constant speed, is used to transport the plasma source. The control unit uses an inert gas as a carrier, e.g., Helium and Argon.

Zaldivar et al. [166] found that the presence of C-O, C=O, and O-C=O bonds on CFRP surfaces increased sharply after O₂-plasma treatment. Furthermore, the change in the O-C=O bond percentage was positively correlated with the surface wettability as well as the SLS strength (see Figure 2-14b). Yoozbashizadeh et al. [44] reported that the increase of oxygen composition contributed to greater surface hydrophilicity and thus an increase of G_{Ic} . They also observed that by reducing the distance between surface and plasma nozzle (from 6 mm to 3 mm), or by increasing the exposure time (from 0.3 s to 50 s), or by increasing the processing gas flow rate, G_{Ic} could be controllably increased.

Sun et al. [43] carried out the APPT on CFRPs using air as activated processing gas. They found a decrease in Si, -CH₃ components and an increase in -OH, -NH₂, -COOH groups, which indicated the cleaning effect on the surface contaminants and the surface activation with increasing polar groups. This change consequently enhanced the wettability of surface and SLS strength of joint. They also reported how the nozzle distance (from 10 to 26 mm) and speed (1 mm/s, 5 mm/s, 10 mm/s) influenced the SLS, as shown in Figure 2-14c. Their results did not follow a monotonic function, which might indicate that greater levels of plasma treatment are harmful, possibly by causing fibre exposure and/or fibre breakage in FRP.

Zaldivar et al. [171] carried out the APPT on a carbon fibre reinforced cyanate ester resin using O₂, CO, and CO₂ as activated gases (see Figure 2-15a). They found a remarkable degradation as the carbonate group increased after O₂-plasma treatment. CO₂-plasma treatment had a similar but less powerful effect. CO-plasma treated samples did not have an evident increase of carbonate concentration, but the carbonyl groups sharply increased. They also suggested that whether one of these plasma-treated samples could have the highest joint strength was associated with the chemistry of the adhesive.

Besides the robust change in chemical composition and wettability, plasma treatment also gently changes the surface topography. It was speculated that plasma treatment initially made the composite surface smoother than the original substrate and then made it much rougher [53]. When only plasma treatment was used and when

the plasma treatment was not over applied, the lap-joint strength enhanced as the roughness increased [53,172]. Abrasion can result in a much higher roughness, but it is usually less effective in enhancing the SLS strength compared with plasma treatment [53,171]. On a personal note, this paradox indicates that the effect of surface chemical composition and wettability is vital in terms of the plasma treatment for adhesive bonding.

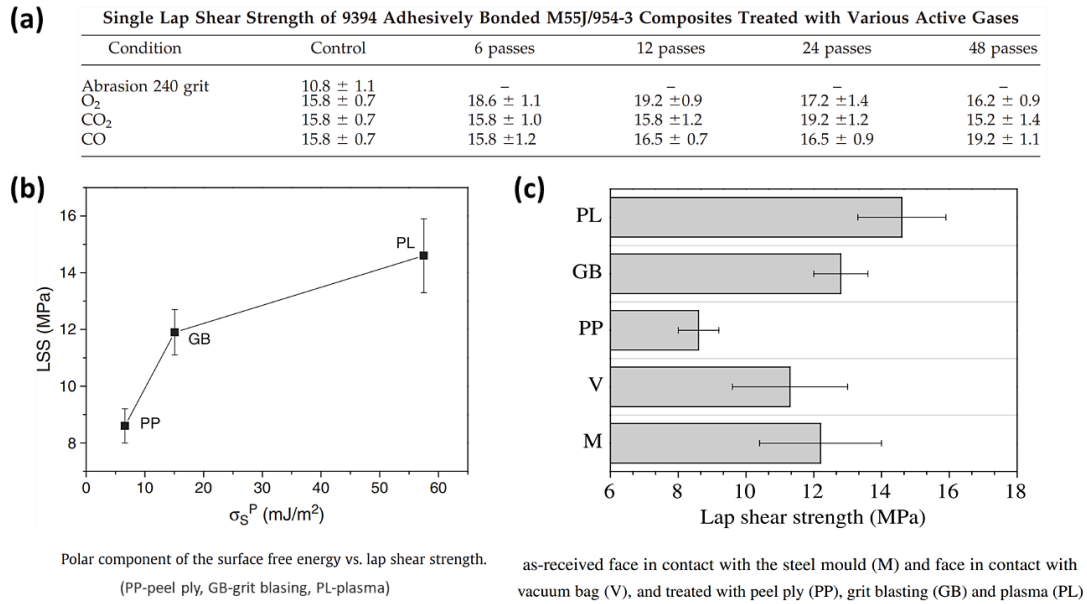


Figure 2-15. Better joint performance of CFRPs treated by APPT than other methods. (a) Effect of O₂, CO₂, or CO plasma on SLS strength in comparison to abrasion [171]; (b) Effect of plasma in increasing polar group and SLS strength in comparison to grit blasting and peel ply [154]; (c) Effect of plasma on SLS strength in comparison to other methods [155].

Most of the above studies concerning plasma treatment are based on bonding using an epoxy adhesive. In this case, plasma treatment can contribute to a better joint performance (see examples in Figure 2-14a, Figure 2-15) than the other methods as introduced above when the processing parameters of plasma treatment are optimised [27,53,154,155,160,171].

However, although plasma treatment is a powerful technique, it does have some drawbacks. For example, when a PU adhesive is used, plasma treatment has been shown to exert a limited effect or even an adversely effect upon the joint performance [42,173]. It was suggested that this might be because plasma induced micro-structures

fail to enhance the mechanical interlocking with PU adhesive as the PU is viscous. In addition, Encinas [27] et al. indicated that plasma treatment can be less effective than abrasion in terms of removing fluorine (F) contaminants from the GFRP surface.

Overall, plasma treatment is effective, fast, advanced and environment-friendly [174]. It has been recently employed in the aerospace industry and could find increased application in other industries if the cost can be reduced and/or the treatment could be scaled to larger manufacturing processes.

2.6 Summary

The surfaces of FRP composites are not chemically active in comparison with the surfaces of metallic materials, hence different and more advanced methods have been developed for pre-treating them. This chapter has reviewed the surface pre-treatment methods for FRPs prior to adhesive bonding. From the literature reviewed, the following conclusions can be drawn:

- 1) Chemical treatments are the most economic and common surface pre-treatment methods for many materials in large-scale industrial production, but they have limited effect on FRP surfaces (which tend to be chemically inert) and usually cause pollution to the environment. Abrasion and peel-ply methods are also cost-effective, easy to apply and are frequently used. Plasma treatment and laser treatments are relatively new and are advanced technologies that utilise high-energy impact, so are expensive but are highly effective and environmentally friendly.
- 2) Successful surface pre-treatment methods enable the surfaces to develop stronger interactions with adhesives. Relevant studies have investigated how the consequential change of surface roughness, surface chemistry and wettability affect the final joint performance. Additionally, in most surface pre-treatment methods, these factors are controllable by adjusting the processing parameters.
- 3) The literature also reveals that surface pre-treatments for composites prior to

adhesive bonding should be sufficient but not excessive. Over treating a FRP surface has been seen to cause cracking, delamination, and/or fibre breakage in the FRP, which is detrimental to subsequent adhesive bonding. Therefore, the processing parameters of a surface pre-treatment should be carefully designed.

In the experiments described in the next chapter of this thesis, the surface pre-treatments of oxygen plasma treatment for the CFRPs have been employed since it is powerful and environmentally friendly as mentioned in section 2.5. Acetone cleaning and grit blasting has also been employed for comparison. Since the surface chemistry, surface topography, and wettability on the adherends usually can remarkably affect the performance of adhesively bonded joints (as summarised in section 2.3), they are characterised to show the effect of the surface pre-treatments. Single-lap-shear tests are employed due to the advantages mentioned in section 2.4.

Chapter 3: Materials & methods

3.1 Introduction to the experiment

As discussed in Chapter 1, the study described in this thesis involved the comparisons between compression moulding and autoclave processing, between thermosetting and thermoplastic CFRPs, between hybrid joining and homogenous joining, and between different pre-treatment methods. To achieve this, five different types of CFRP prepregs were firstly obtained and which were further manufactured into the five different CFRP adherends. An aluminium alloy was employed as the material for the dissimilar adherend used in the study of hybrid joining.

In terms of the surface treatment methods, the study mainly concentrates on plasma treatment. As discussed in Chapter 2, plasma treatment is environmentally friendly and can be very effective on CFRPs. Since the low-pressure plasma treatment (LPPT) has been less investigated than the atmospheric plasma treatment in previous studies (especially on thermoplastic CFRPs, e.g., rarely has the research of LPPT on thermoplastic CFRPs been reported), the LPPT was used in the current research. The effect of using different processing parameters in the plasma treatment was also studied. Furthermore, the surface pre-treatment of acetone cleaning or grit blasting was also studied for comparison. Surface characterisation before and after a treatment as well as the mechanical testing of joints were carried out to evaluate these methods.

3.2 Materials

Two thermosetting CFRPs (termed, CFRP-1 and CFRP-2) and three thermoplastic CFRPs (termed, CFRP-3, CFRP-4, and CFRP-5) were studied. The details of these CFRP adherends are summarised in Table 3-1.

Table 3-1. Details of the 5 different CFRP adherends.

	CFRP-1	CFRP-2	CFRP-3	CFRP-4	CFRP-5
Carbon fibre	T700 grade ^a	T700 grade ^a	T700 grade	T700 grade ^a	T800S grade
Matrix resin	Epoxy resin	Epoxy resin	PEEK	PEEK ^b	PAEK
Resin %wt	-	-	36%	55%	38%
Fibre %vol	65%	65%	-	-	54%
After heating	Thermosetting	Thermosetting	Thermoplastic	Thermoplastic	Thermoplastic
Technology	Compression moulding	Autoclave processing	Compression moulding	Compression moulding	Compression moulding

^a CFRP-1, CFRP-2, CFRP-4 use the fibre of the same specification from the same company.

^b The carbon fibre/PEEK used for CFRP-4 is different from the one for CFRP-3.

Prepregs of thermosetting CFRP-1 and CFRP-2: The prepregs were made and provided by Zhongfu Shenying Carbon Fiber Co. Ltd (Lianyungang, China), in which the carbon fibres (SYT49S, aerospace T700 grade, see Table 3-2 for datasheet) were unidirectional and the fibre volume fraction (%vol) was 65%. The matrix was epoxy.

Prepregs of thermoplastic CFRP-3: The prepregs were obtained via commercial approach. They consisted of unidirectional T700 grade carbon fibres (HexTow-AS7 aerospace, see Table 3-2 for datasheet) from Hexcel Corporation (Stamford, USA) and aerospace-grade PEEK from Victrex plc (Lancashire, UK). The PEEK mass percentage (%wt) was around 36%.

Prepregs of thermoplastic CFRP-4: The prepregs were obtained via commercial approach. They consisted of unidirectional carbon fibres (SYT49S, aerospace T700 grade, see Table 3-2 for datasheet) from Zhongfu Shenying Carbon Fiber Co. Ltd (Lianyungang, China) and aerospace-grade PEEK from Junhua Co. Ltd (Jiangsu, China). The PEEK resin accounted for around 55 %wt.

Prepregs of thermoplastic CFRP-5: T800S grade carbon fibres (SYT55G, see Table 3-2 for datasheet) were manufactured by Zhongfu Shenying Carbon Fiber Co. Ltd (Lianyungang, China). The prepregs were prepared in Donghua University (Shanghai, China) consisting of unidirectional carbon fibres and a newly-developed PAEK resin (see details in Appendix A1) developed by the university. The resin %wt was 38% and the fibre %vol was around 54%.

Table 3-2. Datasheet of carbon fibre SYT49S, HexTow-AS7, and SYT55G. (SYT49S and SYT55G is from Zhongfu Shenyang Carbon Fiber Co. Ltd; HexTow-AS7 aerospace is from Hexcel Corporation.)

	SYT49S	HexTow-AS7	SYT55G
(In this study) made into	CFRP-1,2,4	CFRP-3	CFRP-5
Number of filaments	12 K	12 K	12 K
Carbon %wt	≥ 94	94	≥ 94
Strength (MPa)	≥ 4900	4930	6036
Modulus (GPa)	239	243	300
Ultimate elongation	1.8-2.1 %	1.8%	≥ 2.0%
Line density (g/m)	0.8	0.8	0.45
Density (g/cm ³)	1.79	1.79	1.79
Diameter of filament (μm)	7.0	6.9	5.1
Grade	T700	T700	T800S

Aluminium alloys: The aluminium alloy employed in this research (AA2014) was purchased from Smith Metal Centres Co., Ltd (London, UK). As shown in Table 3-3, the AA2014 is an aerospace grade. The chemical composition of the alloy is shown in Table A2-1 (see Appendix A2).

Table 3-3. Performance of the Aluminium adherend and the adhesive film. (Adapted from the datasheet from the corresponding manufacturers, all data based on tests at room temperature; the density of adhesive based on adhesive without curing, and the other data of adhesive based on curing 60 min at 121°C.)

	Aluminium adherend: AA2014	Adhesive: AF163-2 (OST Red)
Density (kg/m ³)	2820	1243
Young's modulus (GPa)	71	1.11
Yield stress (MPa)	370	36.2
Ultimate strength (GPa)	415	47.9
Thermal expansion (10 ⁻⁶ .°C ⁻¹)	90	23

Adhesive film: The adhesive (AF163-2 OST Red) was purchased from 3M Co., Ltd (Saint Paul, USA). It is an epoxy film adhesive for aerospace use, see Table 3-3 for its

performance. The adhesive is ‘carried’ on a fabric and the “OST” designates the film as being “one side tacky” meaning that the fabric is closer to one side (the non-tacky side, than the other. This is taken into account when making joints with multiple layers of adhesive.

3.3 Manufacturing of CFRPs

The plates of CFRP were manufactured in Zhongfu Shenying Carbon Fibre Co., Ltd (Lianyungang, China) assisted by the author and were then sent to Imperial College London for the further research. CFRP-1, CFRP3, CFRP-4, and CFRP-5 were manufactured via compression moulding (Figure 3-1a). These CFRP plates possessed a flat/plain surface morphology. The CFRP-2 plates were manufactured via a vacuum autoclave technique (Figure 3-1b), and possessed a patterned surface morphology due to the use of assistant materials in the autoclave during their manufacture.

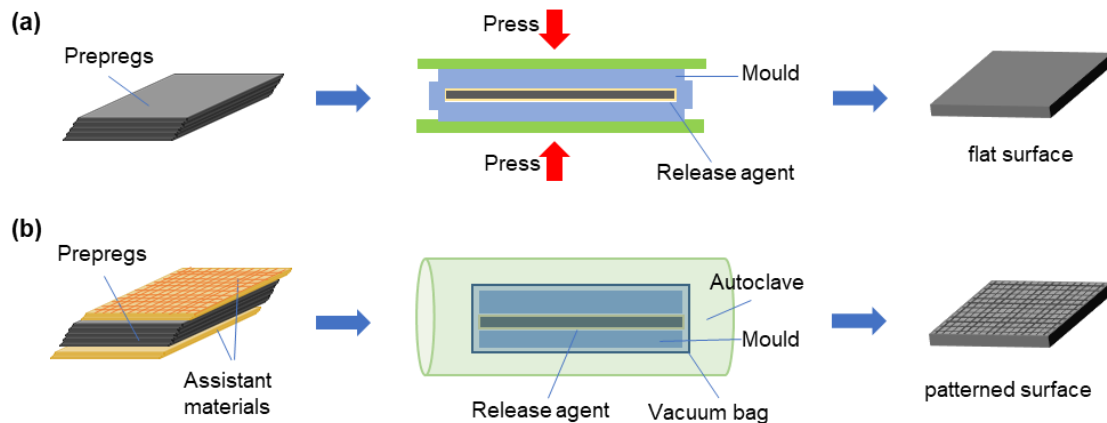


Figure 3-1. Manufacturing of CFRPs. (a) Compression moulding, resulting in a flat surface morphology; (b) Autoclave processing, resulting in a patterned surface morphology due to the use of the assistant materials in their manufacture.

3.3.1 Compression moulding

Thermosetting CFRP-1: Layered carbon fibre prepregs were placed into a mould which was firstly applied with fluoride-based release agent. The thickness of CFRP plates were nominally 2 mm (obtained by using about 13 layers of prepreg). The pressure was set to 0.6-1.0 MPa. As shown in Figure 3-2a, the temperature of the press

was raised to 80 °C in 40 min and was maintained at 80 °C for 30 min. The temperature was then raised to 130°C in 30 min and was maintained at 130 °C for 40 min. Finally, the mould was cooled to below 60 °C and the CFRP plates were removed from the mould.

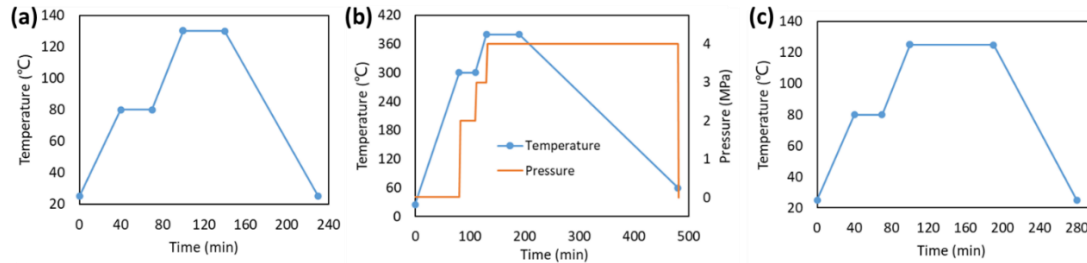


Figure 3-2. Temperature-time curve of the CFRP manufacturing. (a) Compression moulding of thermosetting CFRP-1; (b) Compression moulding of thermoplastic CFRP-3 (CFRP-4 and CFRPP-5 had a technique similar to CFRP-3); (c) Autoclave processing of thermosetting CFRP-2.

Thermoplastic CFRP-3: Firstly, silicon-based release agent was applied to the surfaces of the mould. Then to prepare CFRPs of approximately 2 mm thickness, 15 prepreg layers were placed inside the mould. Figure 3-2b shows the temperature and pressure at different stages of the compression moulding process in this research. Firstly, the temperature was raised from room temperature to 300 °C in 80 min, and the pressure at this stage was 0.01 MPa. Secondly, the pressure was raised to 2 MPa but the temperature was maintained at 300 °C for 30 min. Thirdly, the temperature was raised to 380 °C in 20 min and the pressure at this stage was 3 MPa. Fourthly, the temperature was kept at 380°C for 60 min and the pressure at this stage (i.e., the moulding pressure) was 4 MPa. Finally, the heating element was switched off but the pressure was maintained. The material was not removed from the mould until it had cooled to below 60 °C.

Thermoplastic CFRP-4, CFRP-5: The processing was similar to manufacturing CFRP-3 but some parameters were optimised to be compatible with the different prepreps. (Some of the processing details are commercially sensitive and were not revealed.)

3.3.2 Autoclave processing

Thermosetting CFRP-2: Layered carbon fibre preregs (nominally 13 layers to obtain a 2 mm thickness) were covered with assistant materials, including release fabric, bleeders, and sealing materials. The above materials were embedded in a mould which was firstly applied with a fluoride-based release agent and were then placed inside a vacuum bag inside the autoclave. Then, as shown in Figure 3-2c, the temperature of the autoclave was raised to 80 °C in 40 min and this was maintained at 80 °C for 30 min. The air pressure at this stage was 0.3 MPa. The temperature was then raised to 125 °C in 30 min and was maintained at 125 °C for 90 min. The air pressure at this stage was 0.6 MPa. Finally, the heating was switched off. The plates were removed from the autoclave after the temperature had fallen to room temperature.

3.4 Surface pre-treatments

Table 3-4 shows the surface-treatments employed in this study. Prior to adhesive bonding, acetone cleaning was firstly carried out. In terms of the CFRPs, grit blasting or plasma treatment was then performed. Plasma treatments with different processing parameters were investigated in this research. As for the AA2014, grit blasting, plasma treatment, or silane agent treatment was then carried out.

Table 3-4. A brief introduction of the procedures for acetone cleaned samples, grit blasted samples, plasma treated samples, and silane agent treated samples, and the applied materials in the experiment.

Samples	Treatment procedures	Materials
Acetone cleaned	Sprayed with acetone and wiped with acetone-infused cloth; no further treatments.	All CFRPs, Al
Grit blasted	1)Acetone cleaning, 2) grit blasting, 3) acetone cleaning.	CFRP-1, CFRP-2, Al
Plasma treated	1) Acetone cleaning, 2) plasma treatment	All CFRPs, Al
Silane agent treated	1)Acetone cleaning, 2) degreasing, 3) acetone cleaning, 4) silane agent treatment.	Al

3.4.1 Acetone cleaning

Acetone (analytical purity) was used in the present study as a cleaning solvent. All the CFRP or Aluminium alloy adherends were firstly acetone cleaned, i.e., sprayed using acetone and wiped with an acetone-infused cloth.

Then, the other treatment or further procedures were carried out after the acetone had evaporated. The samples on which only acetone cleaning was carried out (i.e., the acetone cleaned samples) were regarded as the control group since the acetone cleaning was applied to all the CFRP or Aluminium alloy adherends.

3.4.2 Grit blasting

Grit blasting was carried out after acetone cleaning using a grit blaster (Euroblast 6SF 507319, Guyson, UK) as shown in Figure 3-3. The grit used in the blasting was Al_2O_3 (180/220 μm mesh). The duration of the grit blasting was less than 50 s. For the AA2014, the compressed air pressure of grit blasting was approximately 75 psi. For all the CFRPs adherends, the pressure was 40 psi. The lower pressure was used when CFRPs were treated, to minimise the damage to the carbon fibres close to the adherend surface.

After the adherends were treated by the grit blaster, an acetone cleaning procedure was followed to remove the residual grit and contamination during blasting. The as-treated adherends were then labelled accordingly.

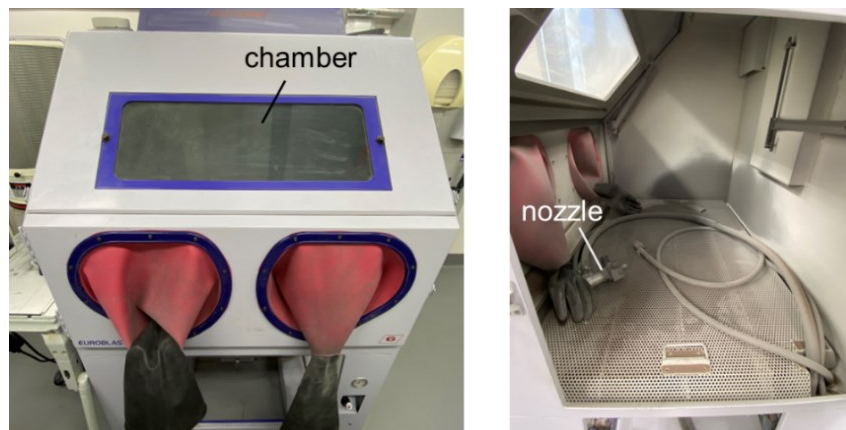


Figure 3-3. The apparatus for grit blasting.

3.4.3 Plasma treatment

Plasma treatment was carried out after acetone cleaning using the plasma-

surface-technology (PICO Q, Diener Electronic, Germany) treater as shown in Figure 3-4. The as-treated adherends were labelled accordingly. These plasma-treated samples were bonded or analysed within an hour following the treatment to avoid any secondary contamination.

The plasma treater employed a power of up to 200 W and an excitation frequency of 40 kHz. The plasma chamber was connected to a vacuum pump. The pump was activated to reduce the pressure to 0.4 mbar. When the pressure had fallen to this value, the processing gas used O₂ was admitted to the chamber and its flow rate was controlled by a float valve to be in the range 1.5-2 mL·min⁻¹. The plasma treatment then proceeded at approximately the same pressure.



Figure 3-4. The apparatus used for the plasma treatment.

In a typical plasma treatment process applied to adherends of thermosetting CFRP-1, CFRP-2 and AA2014, the power of the plasma treatment was 100 W and the duration was 1 min . Plasma treatments with different combinations of power and/or duration were investigated for comparison (see details in Chapter 4 and Chapter 6).

In terms of the thermoplastic adherends of CFRP-3, CFRP-4, and CFRP-5, plasma treatments of power (W)/duration (min) ranged from 100 W/0.5 min to 180 W/8 min (as shown in Table 3-5) were studied.

Table 3-5. Plasma treatment processing parameter for the thermoplastic CFRPs.

Plasma treatment	Processing parameter
------------------	----------------------

PL-1	100 W power, 0.5 min
PL-1.5	100 W power, 1 min
PL-2	100 W power, 2 min
PL-2.5	180 W power, 1 min
PL-3	180 W power, 2 min
PL-4	180 W power, 5 min
PL-5	180 W power, 8 min

3.4.4 Silane treatment

Silane treatment was carried out on some AA2014 samples at Chunlei Haoyu Environmental Protection Technology Co., Ltd. (Jiangsu, China). The degreasing agent (PV754) and the silane agent (CL-M5322, Table 3-6) employed during the treatment were from the same company. Firstly, acetone cleaned AA2014 was immersed into a degreasing solution at 20-30 °C for around 10 min. The solution was the mixture of 5:100 (mass) degreasing agent and deionised water. The degreased AA2014 was again cleaned by acetone to remove any residual degreasing agent or/and other contamination. Then the degreased and cleaned AA2014 was treated by a 2 %wt silane agent solution at 20-30 °C for at least 5 min.

Table 3-6. Physicochemical properties of the silane agent.

Model	Main composition	pH	Solubility	Colour
CL-M5322	Epoxy silane, organic silicon resin	9-10	Soluble in water	Transparent

3.5 Preparation of Joints

3.5.1 Joint geometry

After the surface pre-treatments had been performed, SLS joints were prepared for mechanical tests. The dimensions of the adherends used for the test specimens were selected according to the relevant standards GB/T 33334 (for composites) or ISO 4587 (for metals) i.e., a length × width × thickness of 100 mm × 25 mm × 2 mm. Also, the nominal joint overlap area was 12.5 mm × 25 mm and the gripped area for each adherend was 25 mm × 25 mm, as shown in Figure 3-5a.

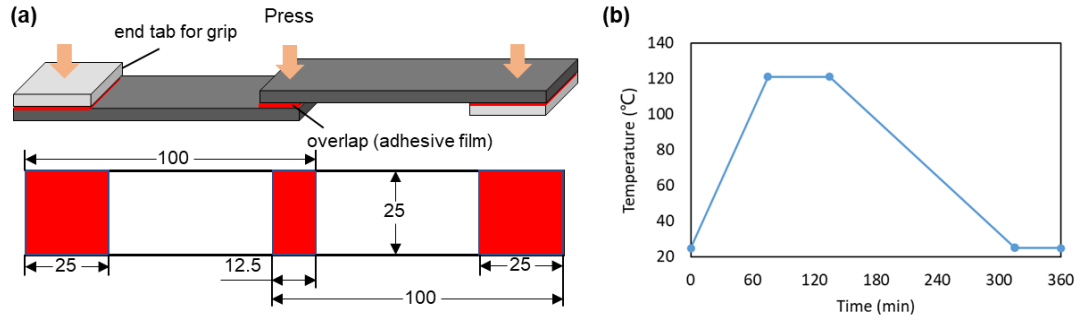


Figure 3-5. Preparation of the SLS joints. (a) SLS joint geometry; (b) Temperature-time curve of adhesive curing.

The adhesive roll of film was stored at -23°C in a freezer, and was removed from the freezer 12 hours prior to making the joint, to ensure it had reached ambient room temperature. Films were cut to size and two layers of adhesive film were used to form the adhesive layer in the overlap region of each joint. To control the bond-line thickness in the overlap, a 0.4 mm diameter copper wire was diagonally placed between the two plies of adhesive film. The films of adhesive were stacked with their non-tacky to tacky sides in contact, according to the instructions from the manufacturers.

3.5.2 Curing of adhesive

To cure the adhesive, the joints were placed in a jig (Figure 3-6a) and the jig was placed in an oven. Weights were placed on top of the jig (Figure 3-6b) during the entire curing process to minimise the trapped air. Additionally, rubber inserts were placed between the jig and the adherends to uniformly distribute the pressure (Figure 3-6c). A digital thermometer (RS Pro RS-41, RS, UK) was connected to the jig (Figure 3-6b) to monitor the temperature of the surrounding area close to the adhesive layer. As shown in Figure 3-5b, the temperature was raised to 121°C in approximately 75 min and was maintained at 121°C for 60 min. Then, the oven was switched off and the jig was left inside to cool down to room temperature. The joints were therefore removed from the jig when they had reached room temperature.

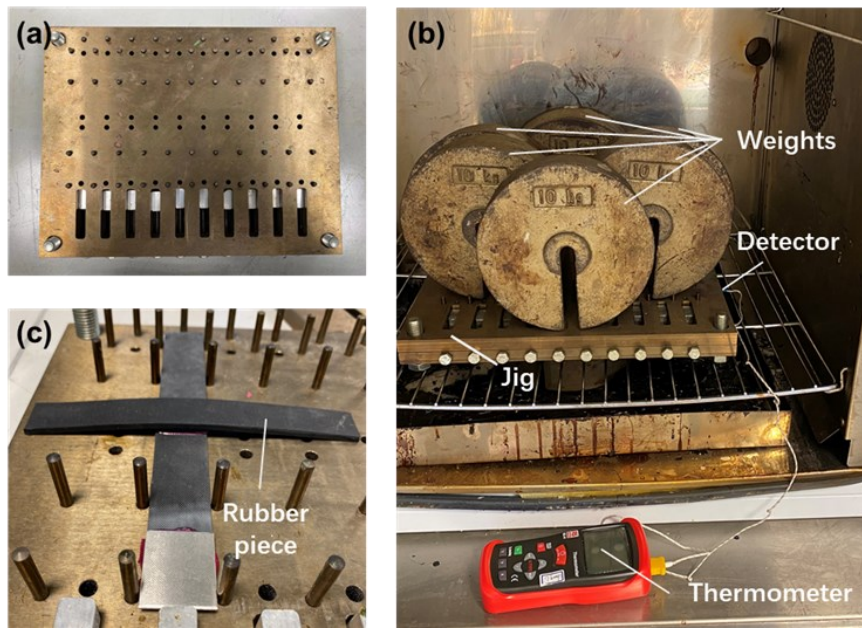


Figure 3-6. Items for the bonding operation and adhesive curing. (a) Jig; (b) Weights on the jig and a thermometer with detector connecting to the jig; (c) Rubber piece for uniform pressure distribution.

3.6 Mechanical testing

The mechanical tests employed a universal mechanical testing machine to measure the properties of the as-prepared CFRP adherends and to measure the SLS strength of the adhesive joints. All mechanical tests were carried out at room temperature (i.e., $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$). The majority of the tests were carried out by the author at Imperial College London. Some material property tests were carried out in Zhongfu Shenying Carbon Fibre Co., Ltd (Lianyungang, China) assisted by the author based on personal collaboration (these tests were not conducted at Imperial College as the labs were not always available/accessible during the COVID-19 lockdown).

3.6.1 Universal testing of CFRPs

A universal testing machine (5982, Instron, USA; or Autograph-xplus 100KN, Shimadzu, Japan) was used to measure the mechanical properties of the as-prepared CFRPs. Specifically, the tensile, compressive, bending, and interlaminar shear strength/modulus were measured according to the ASTM D3039, D6641, D7264,

D2344, accordingly. Each test was repeated a minimum of 6 times. Details of these tests and are shown in Table 3-7.

Table 3-7. Universal mechanical testing of CFRPs.

Testing	Standard	Dimensions (mm)	Displacement (mm/min)	Initial load (N)	Other details
Tensile strength/modulus	ASTM D3039	15 x250 x 1(0°) 25 x 175 x 2(90°)	2	250	Gauge: 50 mm; Extensometer scale: 2.5 mm
Compressive strength/modulus	ASTM D6641	12 x 140 x 2	1.3	20-50	Gauge: 5 mm; Extensometer strain: 20000 μ st
Bending strength/modulus	ASTM D7264	13 x 77 x 2	1	5	Span: 64 mm
Interlaminar shear strength	ASTM D2344	4 x 12 x 2	1	5	Span: 8 mm

3.6.2 SLS testing of joints

The setup for the SLS tests (in Chapter 4: 8801-100kN, Instron, UK; in Chapter 5: AG-XPWS, Shimadzu, Japan) is shown in Figure 3-7. At least 3 specimens for each SLS joint samples condition were tested as repeats.

The testing of the SLS joints with the same CFRP adherends (homogeneous joints) were carried out according to the standards GB/T 33334. The tests on the joints with dissimilar adherends (hybrid joining of CFRP to AA2014) also followed the above procedures, which enabled the further comparison. The tests were run in displacement control and the applied displacement rate was 1.3 mm/min. The maximum displacement (X_{max}) was recorded for each test. The SLS strength was calculated by the following equation [53,54]

$$\tau = \frac{F_{max}}{A_0} \quad (\text{Eq. 1})$$

where τ is the SLS strength, F_{max} is the maximum load, A_0 is the overlap area (312.5 mm² herein).

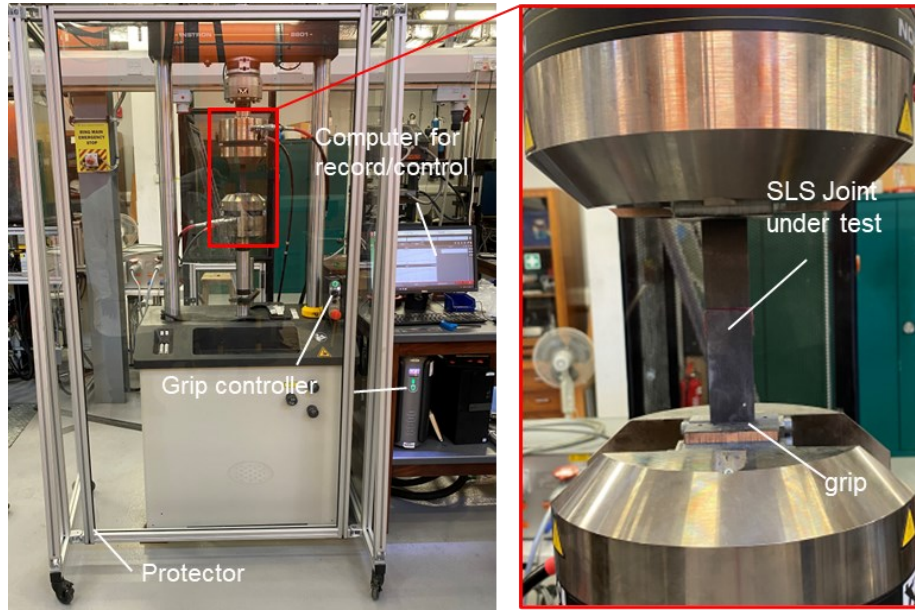


Figure 3-7. The Instron apparatus and samples placement for the SLS testing.

3.7 Interfacial characterisation

The characterisations performed before and after treatment were conducted to study the effect of the various surface pre-treatments on topography, chemistry and wettability. Experiments to assess the surface/interface properties were carried out at room temperature (i.e., $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$).

3.7.1 Topography: microscopes

To observe the surface topography, an optical microscope (Axio Scope.A1, Zeiss, Germany) was firstly used. A scanning electron microscope (SEM; Mira, Tescan, Czech Republic; or EVO10, Zeiss, Germany) was then used to obtain the images of local surfaces with a higher magnification or/and a higher resolution. CFRP specimens were sputter-coated (with gold or chrome) prior to SEM observation.

3.7.2 Chemistry: EDX or XPS

An energy dispersive X-ray detector (EDX; Essence, Tescan, Czech Republic; or X-MaxN, Oxford Instruments, UK) was connected to the SEM to analyse the change in surface chemistry after the different treatments (for CFRP-1, CFRP-2, and AA2014). The

EDX had been calibrated and the limit of detection (LOD) for a minor element was 0.1-0.2 % (weight percentage, the same hereinafter). For each surface condition, at least 6 points/areas on the surface were analysed. Typical mapping images for each surface condition were saved, and the value ranges of each element percentage were recorded.

An X-ray photoelectron spectroscope (XPS; Nexsa, ThermoFisher, USA) was used to detect the change in surface chemistry after different plasma treatments applied to the CFRP-3, CFRP-4, and CFRP-5 adherends. For these tests, the CFRP plates were cut into 5 mm × 5 mm sections using a milling machine before the surface pre-treatments. After being surface treated, the specimens were put into the vacuum chamber of the XPS machine. They were firstly held at the 'park position' for around 30 minutes and were then moved into the analyser chamber for 1 hour before testing. The minor element on CFRP surface (i.e., the impurities or containments) was analysed qualitatively. The carbon-carbon bond (C-C), carbon-oxygen single bond (C-O), and carbon-oxygen double bond (C=O) percentage was accessed by peak deconvolution. For each condition, at least 3 specimens were tested. A typical spectrum was saved for each condition, and the averaged values of the percentage of the chemical bonds were recorded.

3.7.3 Wettability: CA testing

A contact angle goniometer (100-00 230, Ramé-hart, USA) was used to measure the surface wettability of the CFRPs or the aluminium alloys before and after each surface pre-treatment. The apparatus consists of a specimen stage, a light source, a digital video camera, a micro-droplet pipette and dedicated image analysis PC software programme. For each condition, 3 specimens were tested and for each specimen 3 different locations were tested across its surface.

Figure 3-8 shows the goniometer for the contact angle measurement. Firstly, a liquid droplet was dropped through a syringe onto the surface of the material to be tested. In this study, the testing liquid was water and the volume of a liquid droplet was around 3-4 μL . Then, the digital camera of the goniometer took images of the droplet. The shape of the droplet was analysed by the computer software of the

goniometer to calculate the contact angle.

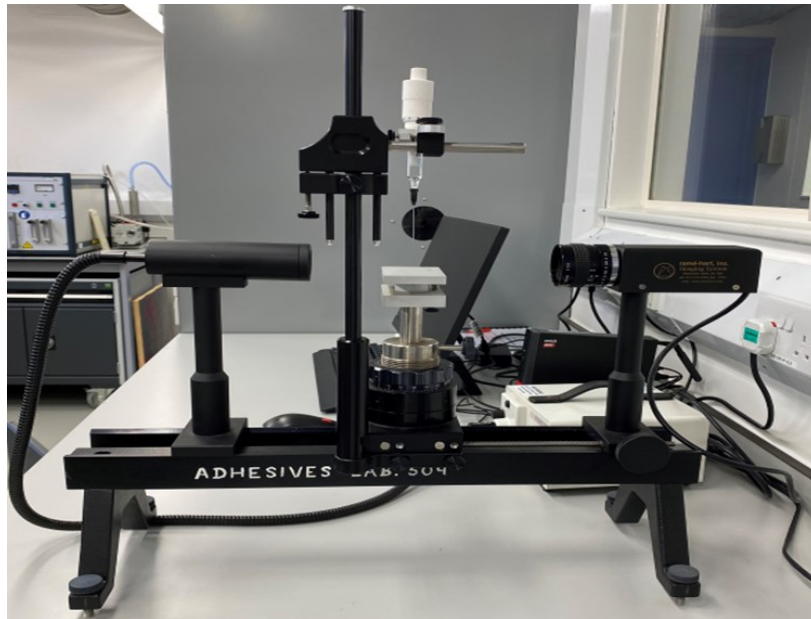


Figure 3-8. The apparatus for contact angle measurement.

3.7.4 Observing fracture interface

After the SLS tests, a high-resolution digital camera (CMOS, Sony, Japan) was used to record the failed interfaces of joints (their fracture surfaces). In addition, an optical microscope (Axio Scope.A1, Zeiss, Germany) was used to observe the defects on the adhesive-adherend interface, i.e., to observe the defects on the surface of adhesive when interfacial failure happened in some joint samples. The microscopic images were analysed by a computer software (Image J) to identify and calculate the area percentage of defects on the interface/surface.

3.8 Summary

In this chapter, the five different types of CFRP studied in this research have been fully described. The types of surface pre-treatments investigated, and the procedures followed to apply these different surface pre-treatments employed prior adhesive bonding have been described. The techniques of tests and characterisations used have also been introduced, including mechanical testing of the CFRPs, diverse interfacial

characterisation to evaluate the surface pre-treatment, and the SLS testing of the adhesive joints. The results of these tests and characterisations will be presented in the next 2 chapters, i.e., Chapter 4 (the results of thermosetting CFRP-1 and CFRP-2) and Chapter 5 (the results for thermoplastic CFRP-3, CFRP-4, CFRP-5).

Chapter 4: Results of the surface property and joint performance for the thermosetting CFRPs

4.1 Introduction

The purpose of this chapter is to present the results of characterisations and tests performed on the thermosetting CFRPs (i.e., CFRP-1 and CFRP-2). The chapter presents a comparison between CFRP-1 and CFRP-2. As described in Chapter 3, the two CFRPs were made with similar fibres and matrix resins but were manufactured via two different methods: CFRP-1 being manufactured via compression moulding and CFRP-2 being manufactured using an autoclave. The different manufacturing routes have been found to affect subsequent surface pre-treatments and ultimately have been found to affect the joint strength.

In this chapter, the mechanical data of the two as-prepared CFRPs are included. Surface topography, surface chemistry, and wettability of them before and after a pre-treatment are compared. SLS test results of homogenous joints (CFRP/CFRP) and hybrid joints to aluminium alloys (CFRP/AA2014) are included.

4.2 Mechanical data of as-prepared CFRPs

As described in Chapter 3, CFRP-1 and CFRP-2 were made of the same carbon fibre and epoxy matrix whose fibre volume fraction were also the same. Table 4-1 presents the mechanical data for the two composites CFRP-1 and CFRP-2. The as-prepared CFRP-1 and CFRP-2 shared a similar density and 0° tensile strength/modulus (e.g., <3%

difference in value). CFRP-2 has a slightly higher 90° tensile strength but slightly lower interlaminar shear strength in comparison to CFRP-1. CFRP-1 and CFRP-2 were thus initially similar in mechanical performance.

Table 4-1. Mechanical performance of CFRP-1 and CFRP-2.

Material Property ^a	CFRP-1	CFRP-2
0° tensile strength (MPa)	2533 ± 60	2589 ± 99
0° tensile modulus (GPa)	136.5 ± 1.6	140.0 ± 1.7
90° tensile strength (MPa)	52.3 ± 2.2	56.3 ± 1.4
90° tensile modulus (GPa)	8.71 ± 0.10	7.24 ± 0.17
0° compressive strength (MPa)	1091 ± 73	1070 ± 29
0° compressive modulus (GPa)	135.2 ± 5.5	142.2 ± 4.6
90° compressive strength (MPa)	190.0 ± 9.3	186.0 ± 6.0
90° compressive modulus (GPa)	10.5 ± 0.6	11.3 ± 0.5
0° bending strength (MPa)	1343 ± 67	1542 ± 74
0° bending modulus (GPa)	109 ± 3.9	143.0 ± 5.1
90° bending strength (MPa)	82.6 ± 5.1	86.4 ± 2.2
90° bending modulus (GPa)	8.00 ± 0.5	7.45 ± 0.11
Interlaminar shear strength (MPa)	102.3 ± 1.5	97.8 ± 2.9
Density (kg/m ³) ^b	1647 ± 40	1676 ± 51

^a 0° means “along fibre direction” and 90° means “perpendicular to fibre direction”.

^b Density=mass/product of dimensions, where the mass is tested using an electronic balance.

4.3 Surface topography and chemistry

4.3.1 Acetone cleaned or plasma treated CFRPs

Figure 4-1 presents a comparative illustration in terms of the surface topography of the compression moulded CFRP-1 and autoclaved CFRP-2 after acetone cleaning or plasma treatment (the plasma treatment used was 100 W for 1 min in this chapter unless otherwise specified). The corresponding results of elementary composition are also shown in Figure 4-1 and are summarised in Table 4-2.

As shown in Figure 4-1a, the CFRP-1 surface after acetone cleaning was relatively smooth under optical microscope observation, and the surface microstructure can be

observed via SEM (i.e., the geometry of the unidirectional fibre). After plasma treatment, the surface topography did not show a significant change. However, the surface chemistry was changed noticeably, as shown in Figure 4-1 b, c.

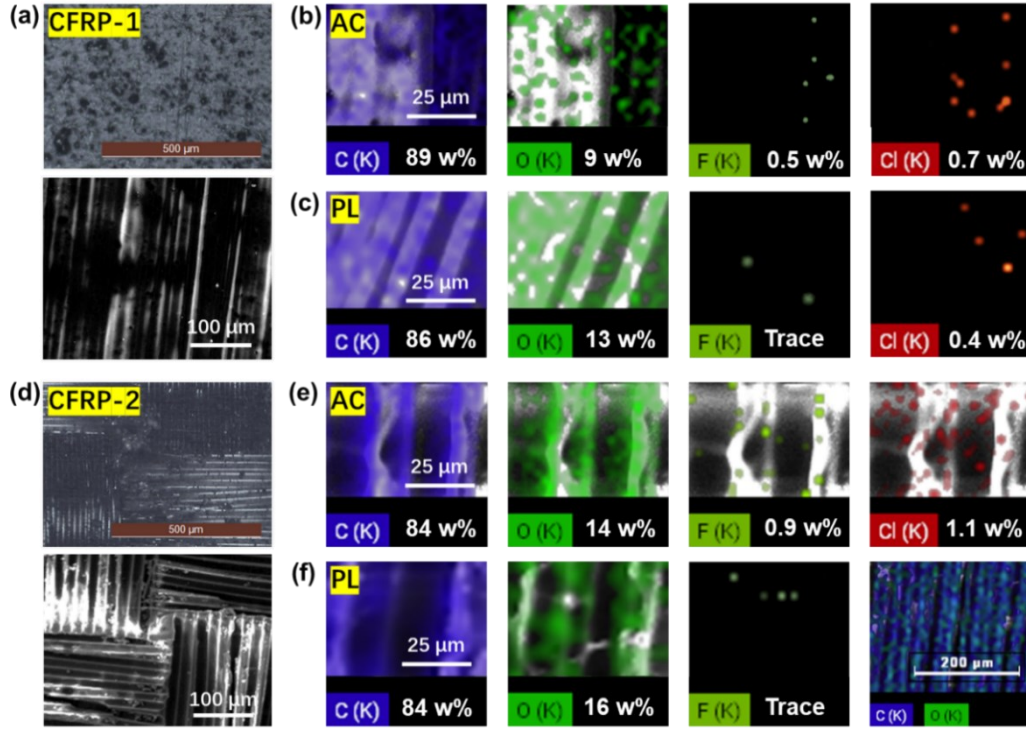


Figure 4-1. Surface topography and chemistry of the thermosetting CFRP samples after acetone cleaning (AC) or plasma treatment (PL). (a) An optical microscopic image and an SEM image of CFRP-1; (b) EDX mapping of CFRP-1 samples after AC; (c) EDX mapping of CFRP-1 samples after PL; (d) an optical microscopic image and an SEM image of CFRP-2; (e) EDX mapping of CFRP-2 samples after AC; (f) EDX mapping of CFRP-2 samples after PL. (One typical mapping image here for each condition, the final results of elementary percentage are displayed in Table 4-2.)

As also displayed in Table 4-2, the percentage of O was increased from 9-10% to 13-14% after the oxygen-plasma treatment. The minor elements (i.e., contaminants or impurities on the surface) were also investigated. For example, the contaminant element F was present from the release agent used during CFRP manufacturing; the contaminant element Cl was present mainly from the impurities with the epoxy matrix; the contaminant element S was present mainly from the impurities in the adhesive curing agent; Si was present due to the use of a silicone oiling agent during carbon fibre production [175]. When acetone cleaning alone was performed: F, Cl, and Si accounted

for 0.3-0.7%, 0.6-0.8%, and a trace amount respectively. After plasma treatment, only trace F and 0.3-0.6% Cl were detected.

Table 4-2. Elementary composition of the thermosetting CFRP samples after acetone cleaning (AC), grit blasting (GB), or plasma treatment (PL) ^a.

Weight %	C	O	F	Cl	S	Si
CFRP-1 (AC)	88-90%	9-10%	0.3-0.7%	0.6-0.8%	<LOD	Trace
CFRP-1 (PL)	86-87%	13-14%	Trace ^d	0.3-0.6%	<LOD	<LOD
CFRP-2 (AC)	83-84%	13-15%	0.8-1.1%	0.9-1.1%	Trace	Trace
CFRP-2 (PL)	84-85%	15-16%	Trace	<LOD	<LOD	<LOD
CFRP (GB-CF) ^b	95-96%	4-5%	<LOD ^e	<LOD	<LOD	<LOD
CFRP (GB-ER) ^c	85-89%	10-14%	0.3-0.6%	Trace	<LOD	<LOD

^a H was excluded as EDX does not detect it

^b GB-CF represents the carbon fibre exposure area (minor) of GB samples of CFRP-1 or CFRP-2

^c GB-ER represents the epoxy matrix remaining area (major) of GB samples of CFRP-1 or CFRP-2

^d Trace means it was sometimes detected using EDX but the result was <0.5% (same hereinafter)

^e <LOD means it was below the limit of detection of EDX (i.e., <0.1-0.2%), the same hereinafter

In contrast to CFRP-1, the CFRP-2 surfaces had patterned structures as shown in Figure 4-1d, which can be attributed to the assistant materials employed in the vacuum-autoclave manufacturing. After plasma treatment, surface topography (at the microscale) did not show significant changes. The percentage of O was slightly raised from 13-15% to 15-16%. As for minor elements, 0.8-1.1% F, 0.9-1.1% Cl, and trace amount of S and Si were detected on acetone cleaned samples as shown in Figure 4-1e. While after plasma treatment, only trace F was detected as shown in Figure 4-1f.

4.3.2 Grit blasted CFRPs

The two acetone cleaned CFRP samples had different surface topographies, but after grit blasting the surfaces were similar (Figure 4-2). As shown in Figure 4-2a, the grit blasted samples of CFRP-1 showed a striped, oriented texture. As shown in Figure 4-2b, CFRP-2 had a similar transforming trend to the CFRP-1. The only difference from CFRP-1 was the fact that the structures were not very uniform. It is suggested that the removal of a small proportion of the surface matrix was not uniform because the surface for grit blasting was patterned (uneven) in the case of CFRP-2. For either CFRP-

1 or CFRP-2, grit blasting would remove some areas of surface resin as shown in Figure 4-2c, while in major areas the resin remained as shown in Figure 4-2d.

In addition, as displayed in Table 4-2, 0.3%-0.6% F and trace Cl remained after grit blasting, showing grit blasting was more effective than acetone cleaning in removing these contaminants. As for CFRP-2, grit blasting was less effective than plasma treatment in removing these contaminants and increasing the O percentage.

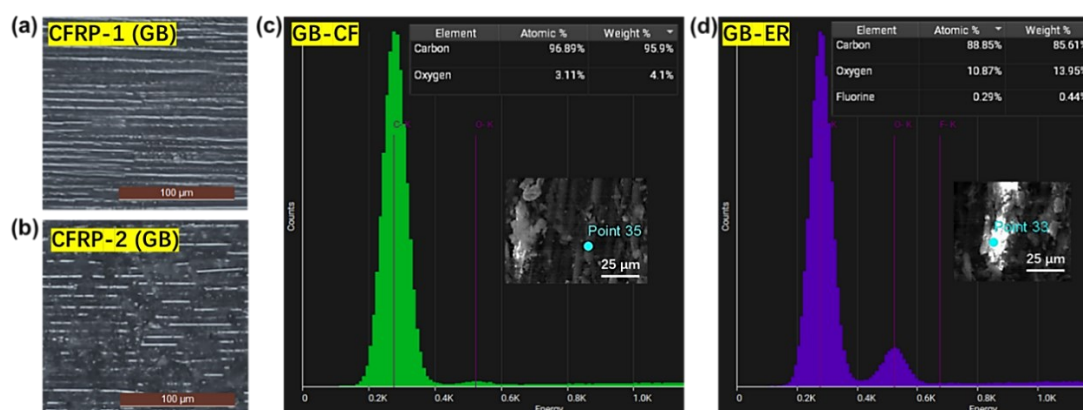


Figure 4-2. Surface topography and chemistry of grit blasted (GB) samples of the thermosetting CFRPs. (a) An optical microscopic image of CFRP-1; (b) An optical microscopic image of CFRP-2; (c) An EDX spectrum with a SEM image of the carbon-fibre exposure area; (d) An EDX spectrum with a SEM image of the epoxy-resin area. (One typical spectrum here for each condition, the final results of composition are displayed in Table 4-2.)

The relative effectiveness of the acetone cleaning, grit blasting or plasma treatments on the CFRP samples for improving wettability is presented in section 4.5. The relative effectiveness of these treatments on the mechanical performance of the joints is presented in section 4.6.

4.4 Aluminium alloys for hybrid joining

The details of how the surface pre-treatments affected the surface topography and chemistry of the aluminium alloy AA2014 are now shown and analysed in Figure 4-3. Table 4-3 shows the change in elementary composition after the surface pre-treatments of acetone cleaning, grit blasting or plasma treatment.

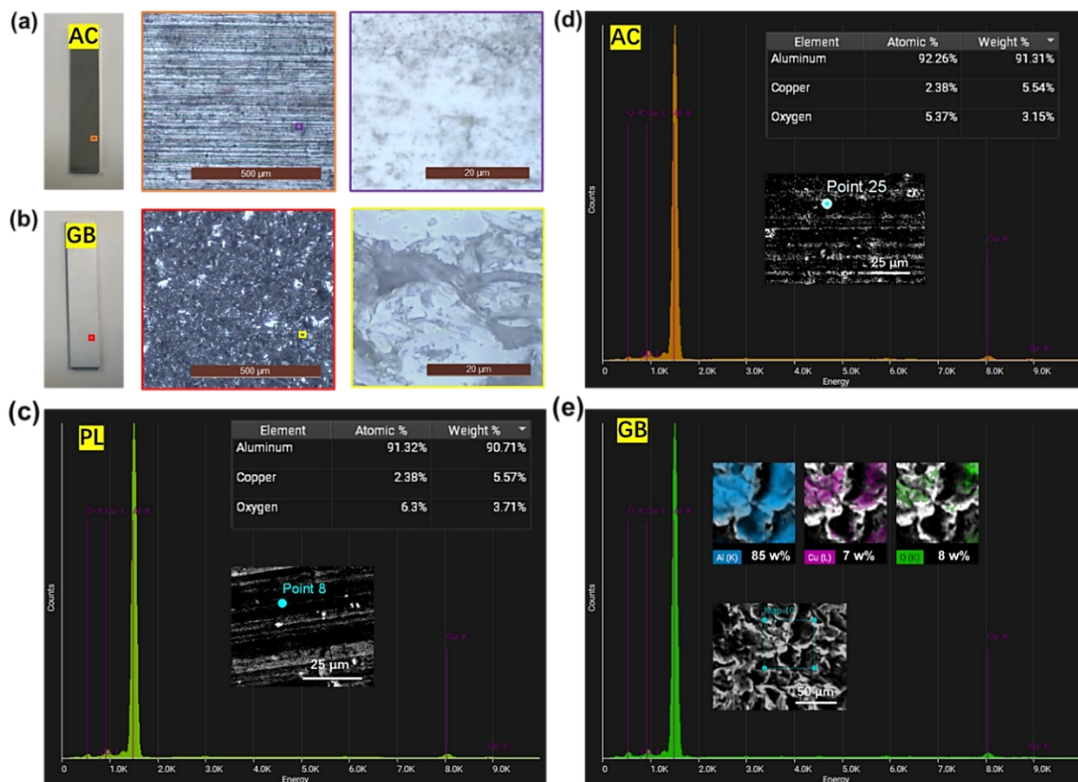


Figure 4-3. Surface topography and chemistry of AA2014 after acetone cleaning (AC), grit blasting (GB) or plasma treatment (PL). (a-b) optical microscopic images of samples after AC or GB; (c-e) EDX spectra with SEM images of samples after AC, GB, PL (one typical spectrum here for each condition, final results of elementary percentage displayed in Table 4-3): (a) shows the surface topography of the AA2014 after AC before GB or PL, which reflected light strongly and were relatively smooth, except for some barely perceptible textures created due to the forming technique; (b) shows the AA2014 after GB, which turned silver in colour and became rough, full of almost-uniformly spread subtle bumps and hollows; (c) and (d) indicates no remarkable change occurred in surface topography after PL in comparison with AC samples; (c) and (e) indicates the percentage of Cu and O was significantly increased after GB in comparison with AC samples; the majority of the O had a similar distribution to the Cu while minor O was distributed across the Al area.

After plasma treatment, the surface topography did not show a significant change and the surface chemistry was also similar, the only notable difference being that the C composition was trace in the acetone cleaned samples but was <LOD after plasma treatment. As for the grit blasted samples, the surfaces became rough, characterised by almost-uniformly distributed subtle bumps and hollows. The percentage of Cu (the

main alloying element in AA2014) and O were greatly increased compared with acetone cleaning treated control samples. The increase in Cu percentage maybe associated with the fact that Cu usually has a higher hardness than Al so grit blasting may remove Al preferentially, leaving a higher proportion of Cu following the treatment. Most of the O had a similar distribution to the Cu while a minority of O was distributed within the Al area, indicating the existing form of O was Cu_xO_y (major) and Al_xO_y (minor).

Table 4-3. Elementary composition of AA2014 samples after acetone cleaning (AC), grit blasting (GB) or plasma treatment (PL) ^a.

Weight %	Al	Cu	O	C
AC samples	90-92%	4-6%	2-4%	Trace
GB samples	83-87%	6-9%	7-10%	Trace
PL samples	90-92%	4-6%	3-4%	<LOD

^a Si, Mg, Mn, Fe, Zn, Ti was in trace amount or <LOD, accounting for <2% in total, which was excluded in analysis

4.5 Wettability after treatments

Surface pre-treatments also influence the surface wettability, which further affect the joint performance. Table 4-4 shows the water contact angles (CA) obtained for CFRP-1, CFRP-2 and AA2014 samples after acetone cleaning, grit blasting, or plasma treatment.

The CA values for the 3 different adherend materials after acetone cleaning was $87.2 \pm 1.1^\circ$, $76.1 \pm 1.3^\circ$ and $63.9 \pm 1.5^\circ$, respectively. After grit blasting, the CA on CFRP-1 showed little change, but the CA on CFRP-2 increased to $90.8 \pm 1.3^\circ$. CFRP-1 and CFRP-2 samples displayed similar CA values after grit blasting because these surfaces were shown to be similar with respect to topography and chemistry. The CA on the AA2014 samples increased to $74.9 \pm 0.9^\circ$ after grit blasting. This might be due to the hydrophobicity of rough micro-structured Al_xO_y and Cu_xO_y [176]. For all plasma treated samples, the measured CA values decreased sharply following treatment to less than 20° , indicating a near super-hydrophilic property.

Table 4-4. Water contact angles measured on the acetone cleaned (AC), grit blasted (GB), or plasma treated (PL; 100 W, 1 min) samples of CFRP-1, CFRP-2, and AA2014 adherend.

Samples	CFRP-1	CFRP-2	AA2014
AC samples	$87.2 \pm 1.1^\circ$	$76.1 \pm 1.3^\circ$	$63.9 \pm 1.5^\circ$
GB samples	$86.9 \pm 0.8^\circ$	$90.8 \pm 1.3^\circ$	$74.9 \pm 0.9^\circ$
PL samples	$14.9 \pm 0.7^\circ$	$11.0 \pm 0.5^\circ$	$13.8 \pm 0.5^\circ$

To further understand the effect of plasma treatment in reducing CA, Figure 4-4 displays the relationship between the CA and the duration or the power of plasma treatment process. As the duration of treatment was increased from 0.5 min to 2 min, and the power of treatment was increased from 100 W to 180 W, the value of CA decreased monotonically on all adherends. The results indicate that the power of the plasma treatment is more significant than the treatment time in respect of its effect on the CA. The results also indicate that plasma treatment was more effective on CFRP-2 (patterned surface) than on CFRP-1 (flat surface) or AA2014 in reducing the CA. This may be because CFRP-2 possesses a higher surface area due to the pattern than CFRP-1 or AA2014. The surface of CFRP-2 became super-hydrophilic ($CA < 5^\circ$) after plasma treatment at a power of 180 W for more than 1 min.

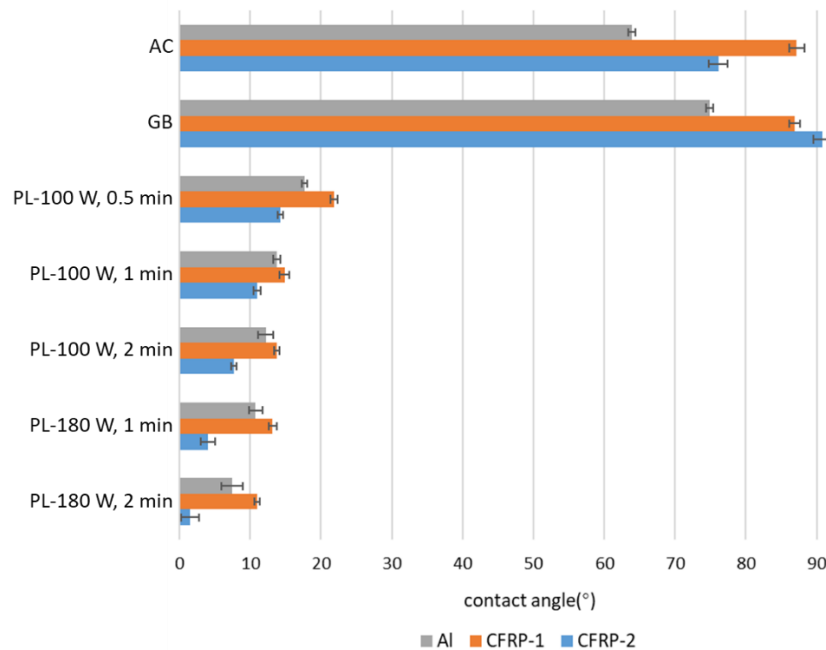


Figure 4-4. The trend of changes in contact angles on CFRP-1, CFRP-2, and AA2014 adherends when the power or duration of the plasma treatment were increased.

4.6 Results of SLS testing

4.6.1 Stress-displacement behaviour

The pre-treated CFRP-1, CFRP-2 and AA2014 adherends were bonded to the same or dissimilar adherends to make SLS joints for mechanical testing as described in Chapter 3. The stress-displacement curves measured from the lap-shear testing of these joints are shown in Figure 4-5.

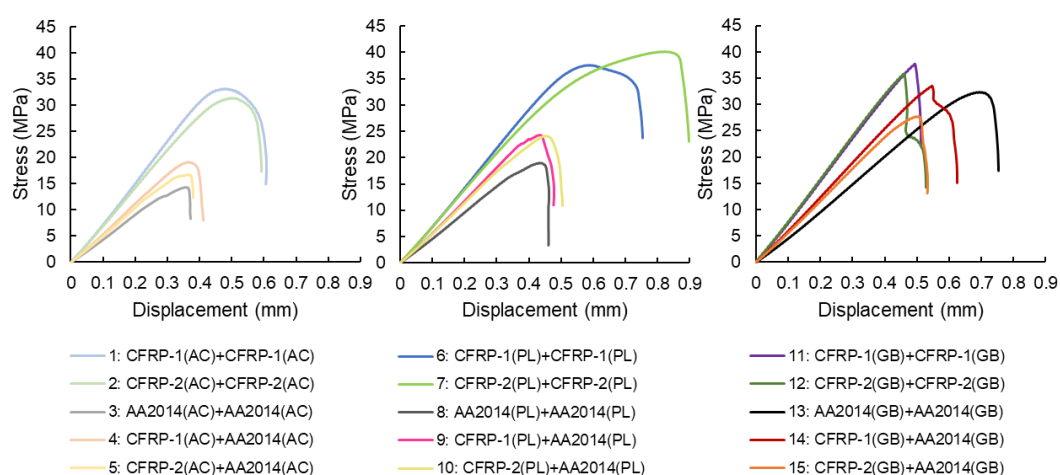


Figure 4-5. Stress-displacement curves measured during the SLS strength tests of CFRP-1/CFRP-1, CFRP-2/CFRP-2, Al/Al, CFRP-1/Al, and CFRP-2/Al joints when the pre-treatment was acetone cleaning (AC), plasma treatment (PL), or grit blasting (GB).

In the first five SLS joint tests (i.e., joint samples No. 1-5, the first column in Figure 4-5), the surface pre-treatment method for the adherends was acetone cleaning. In the second and final five joints, the pre-treatment employed was plasma treatment or grit blasting, respectively. Joint samples No. 1-3, 6-8, and 11-13 (i.e., the first three rows of the legend in Figure 4-5) were formed by the homogenous joining of CFRP-1, CFRP-2, and AA2014, respectively. Joint samples No. 4-5, 9-10, and 14-15 (i.e., the last three rows of the legend in Figure 4-5) were formed by the hybrid joining of CFRP-1 or CFRP-2 to AA2014.

As shown in Figure 4-5, the stress-displacement curves measured for the acetone cleaned and plasma treated samples were relatively smooth. In contrast, noticeable sharp reductions in stress occurred in joint samples No. 11, 12, 14, 15, all of which involved the grit blasted samples of CFRP adherend(s). The sharp points correspond to

the failure mode in the test changing from cohesive in the adhesive, to interlaminar in the composite adherend, which was caused by surface damage to the composite during grit blasting.

4.6.2 SLS strength of joints

The SLS strength (τ), maximum displacement (X_{max}), and failure mode of the 15 joint samples are summarised in Table 4-5.

Table 4-5. SLS strength (τ), maximum displacement (X_{max}), and failure mode of SLS joints of the different CFRP-1/CFRP-1, CFRP-2/CFRP-2, Al/Al, CFRP-1/Al, and CFRP-2/Al.

No. ^a	1	2	3	4	5
Adherend 1	CFRP-1(AC)	CFRP-2(AC)	AA2014(AC)	CFRP-1(AC)	CFRP-2(AC)
Adherend 2	CFRP-1(AC)	CFRP-2(AC)	AA2014(AC)	AA2014(AC)	AA2014(AC)
τ (MPa)	33.0 $\pm$ 1.0	30.9 $\pm$ 0.8	14.4 $\pm$ 0.7	19.1 $\pm$ 0.5	16.7 $\pm$ 1.0
X_{max} (mm)	0.50 $\pm$ 0.02	0.52 $\pm$ 0.03	0.36 $\pm$ 0.01	0.37 $\pm$ 0.03	0.37 $\pm$ 0.03
Failure mode	Interfacial + cohesive(major)	interfacial(major) + cohesive	interfacial, on 2 Al sides	interfacial, on Al side	interfacial, on Al side
No.	6	7	8	9	10
Adherend 1	CFRP-1(PL)	CFRP-2(PL)	AA2014(PL)	CFRP-1(PL)	CFRP-2(PL)
Adherend 2	CFRP-1(PL)	CFRP-2(PL)	AA2014(PL)	AA2014(PL)	AA2014(PL)
τ (MPa)	37.6 $\pm$ 0.8	40.1 $\pm$ 1.1	19.0 $\pm$ 0.8	24.3 $\pm$ 1.1	24.1 $\pm$ 1.0
X_{max} (mm)	0.60 $\pm$ 0.04	0.84 $\pm$ 0.02	0.43 $\pm$ 0.03	0.45 $\pm$ 0.02	0.46 $\pm$ 0.01
Failure mode	cohesive(major) + interlaminar ^c	nearly-fully cohesive ^b	interfacial, on 2 Al sides	interfacial, on Al side	interfacial, on Al side
No.	11	12	13	14	15
Adherend 1	CFRP-1(GB)	CFRP-2(GB)	AA2014(GB)	CFRP-1(GB)	CFRP-2(GB)
Adherend 2	CFRP-1(GB)	CFRP-2(GB)	AA2014(GB)	AA2014(GB)	AA2014(GB)
τ (MPa)	37.6 $\pm$ 0.8	35.7 $\pm$ 0.7	32.3 $\pm$ 0.1	33.6 $\pm$ 1.2	27.8 $\pm$ 0.1
X_{max} (mm)	0.49 $\pm$ 0.02	0.45 $\pm$ 0.01	0.68 $\pm$ 0.02	0.55 $\pm$ 0.02	0.51 $\pm$ 0.01
Failure mode	mostly interlaminar	cohesive + interlaminar	cohesive (major) + interfacial	interfacial(Al) + cohesive + interlaminar	interfacial(Al) + cohesive + interlaminar

^a Samples numbers in this table are the same as those in Figure 4-5

^b Imperceptible CFRP damage was observed

^c Interlaminar means interlaminar fracture of CFRP composites

4.6.2.1 Homogenous joining

The joints made with homogenous bonded and acetone cleaned adherends, i.e., CFRP-2 (joint No. 2) had a lower SLS joint performance in comparison to CFRP-1 (joint No. 1). It is likely that this lower performance of CFRP-2 was caused by the greater level of contamination (F and Cl) which remained on the AC adherends resulting from the patterned surface, as was presented in section 4.3.1.

However, the joints made with the homogenous bonded and plasma treated adherends, i.e., CFRP-2 (joint No. 7) were significantly improved, showing a higher SLS joint performance in comparison to CFRP-1 (joint No. 6). Such an improvement indicates that plasma treatment is more effective on the patterned CFRP-2 adherends than on the flat CFRP-1 adherend. As for the homogenous bonded and grit blasted adherends (joint No. 11, 12), CFRP-2 showed a SLS strength similar to CFRP-1 (or somewhat slightly lower but the difference in value is smaller than that between joints No. 1 and No. 2). This may be due to their similar surface conditions after grit blasting. A comparison of the effectiveness of the different surface pre-treatments and a more detailed discussion of these results is presented in Chapter 6.

4.6.2.2 Hybrid joining

Homogenous joints or hybrid joints involving acetone cleaned or plasma treated aluminium alloys exhibited relatively poor joint performance. It indicates that single acetone cleaning or single plasma treatment are not sufficient for aluminium alloys. Hence, here only the hybrid joints using grit blasted adherends were compared: the SLS strength of CFRP-1/Al (joint No. 14) is 33.6 ± 1.2 MPa, much higher than that of CFRP-2/Al (joint No. 15, 27.8 ± 0.1 MPa).

A detailed discussion of these results, including a discussion of the difference between homogenous joining and hybrid joining, and a discussion of the results of other hybrid joints for comparison (e.g., joints in which two adherends were pre-treated by different methods, and joints involving adherends treated by different levels of plasma treatment for self-comparison or comparison to the thermoplastic CFRPs introduced in Chapter 5) will be included in Chapter 6.

4.6.3 Interface appearance after failure

The failure mode of the SLS joint samples had been described in Table 4-5. Typical images for each failed interface were recorded in Figure 4-6.

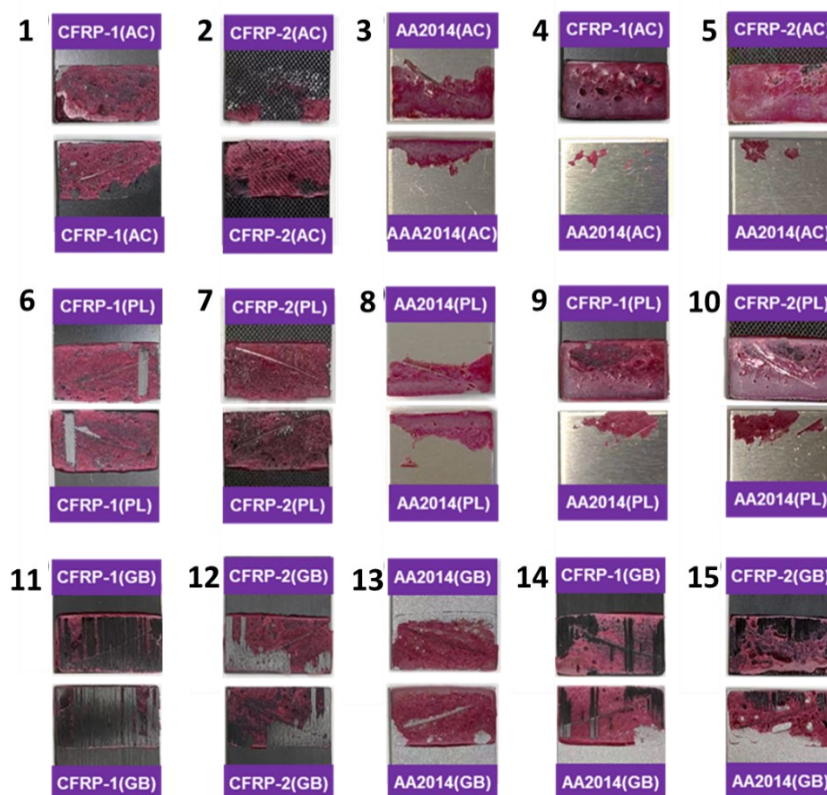


Figure 4-6. Interface appearance of SLS joints after failure.

The interface appearance after failure is in agreement with the results of SLS strength. For example, in acetone cleaned samples, CFRP-2 had a lower SLS strength than CFRP-1 as well as a higher proportion of interfacial failure of the fractured interface (joint No. 2 vs joint No. 1). Joint No. 7 had the highest SLS strength and the highest proportion of cohesive failure (i.e., the failure mode is nearly-fully cohesive as shown in Figure 4-6g). Joints No. 3-5, 8-10 had unsatisfactory joint performance as large area of interfacial failure on Al side was observed as shown in Figure 4-6.

In addition, in joints involving the grit blasted adherends of CFRPs (joints No. 11, 12, 14, 15), interlaminar fracture of the CFRP composites were observed. The damage in these CFRP composites should be the reason for the unsmooth stress-displacement curve of SLS testing near failure as mentioned in section 4.5.1. For the joint No. 14 or

joint No. 15, a very complicated sequence of failures took place in a single joint sample, which has rarely been reported in previous papers. The failure mode includes the interfacial failure on aluminium side, the cohesive failure of the adhesive, and the interlaminar fracture of the CFRP composites. A detailed discussion of these complicated failure modes is presented in Chapter 6.

4.7 Summary

In this chapter, the performance of SLS joints made using the thermosetting CFRP adherends manufactured via the two different processes of compression moulding and autoclaving have been investigated following the application of three different surface pre-treatments to the adherends before adhesive bonding: acetone cleaning, oxygen plasma treatment, and grit blasting. Results show that acetone cleaning alone could not fully remove some contaminations and gave the lowest joint strength. Plasma treatment or grit blasting further removes the contaminations, changes some surface properties, and results in a better joint performance. Plasma treatment remarkably improve the wettability with minor changes in surface topography, while grit blasting remarkably changes the surface topography.

More importantly, results also show that although the two thermosetting CFRPs are initially mechanically similar, they had very different surface topographies (i.e., compression moulded CFRPs had a relatively flat surface and autoclaved CFRP had a patterned surface) which influenced the effectiveness of the surface pre-treatments. For example, homogenous SLS joints made using plasma treated autoclaved CFRPs showed the highest SLS joint strength. As for the hybrid joining to aluminium alloys, compression moulded CFRPs usually had a higher joint strength than the autoclaved patterned CFRPs no matter what surface pre-treatments had been applied. Detailed explanation and discussion of these results will be included in Chapter 6, after the next chapter that displayed the results for thermoplastic CFRPs.

Chapter 5: Results of the surface property and joint performance for the thermoplastic CFRPs

5.1 Introduction

This chapter presents the results of the tests and characterisations performed on the thermoplastic CFRPs (i.e., CFRP-3, CFRP-4, and CFRP-5) and their joints. As described in Chapter 3, these composites were manufactured using the same technology (i.e., compression moulding) but were made using different prepregs. The prepregs of CFRP-3 and CFRP-4 both contain the PEEK matrix but with different specifications as they were manufactured by different companies, and the prepregs of CFRP-5 contain the PAEK matrix.

In this chapter, firstly the mechanical performance of the three as-prepared CFRPs are compared. Secondly, the surface properties (wettability, surface topography, surface chemistry) of the three composites are investigated in their as-received condition and after various surface treatments. Finally, the mechanical performance of their bonded joints is evaluated using SLS tests and the results of homogenous joints (CFRP/CFRP) and hybrid joints (CFRP/AA2014) are studied.

5.2 Mechanical data of as-prepared CFRPs

Table 5-1 shows the mechanical data of the thermoplastic CFRP-3, CFRP-4, and CFRP-5. In terms of the CFRP-3 and CFRP-4, which was made of two different T700 grade carbon fibre prepregs, the 0° tensile strength was around 2000 MPa. As for the

CFRP-5 made of T800S grade carbon fibre preregs, the 0° tensile strength reached near 3000 MPa (when appropriate carbon fibre surface treatment and optimised moulding pressure are used in manufacturing CFRP-5 as shown in Appendix A.1).

Table 5-1. Mechanical performance of as-prepared CFRP-3, CFRP-4, and CFRP-5.

Material Property	CFRP-3	CFRP-4	CFRP-5
0° tensile strength (MPa)	2192 ± 66	1843 ± 96	2932 ± 53
0° tensile modulus (GPa)	160 ± 2	126 ± 5	147 ± 3
90° tensile strength (MPa)	85 ± 3	47 ± 4	68 ± 2
90° tensile modulus (GPa)	9.0 ± 0.2	9.2 ± 0.4	8 ± 1
0° compressive strength (MPa)	1184 ± 53	1084 ± 35	1250 ± 43
0° compressive modulus (GPa)	144 ± 4	116 ± 8	134 ± 2
0° bending strength (MPa)	2052 ± 53	1762 ± 48	1319 ± 58
0° bending modulus (GPa)	122 ± 4	87 ± 6	135 ± 4
Interlaminar shear strength (MPa)	112 ± 3	97 ± 1	81 ± 1

Comparing the two composites with a PEEK matrix (i.e., CFRP-3 and CFRP-4) CFRP-3 possessed the higher strength in all directions/modes (tensile, transverse, compressive, bending and interlaminar shear). Also, CFRP-3 was of higher modulus than CFRP-4 in all directions except transverse (90° tensile modulus). Comparing next the PEEK matrix composites (CFRP-3 and CFRP-4) with the PAEK matrix composite (CFRP-5) then CFRP-5 possessed the greatest 0° tensile and compressive strengths but the lowest bending and interlaminar shear strengths.

These data would suggest that CFRP-3 possessed generally the best fibre-matrix interfacial performance (based upon the values of the 90° tensile and interlaminar shear strengths). CFRP-3 may therefore be least likely to delaminate when bonded as an adherend in a SLS joint. On the same basis, CFRP-4 may be the most likely to delaminate based upon the lowest 90° tensile strength.

5.3 Wettability after treatment

The water contact angles (CA) were measured on these composites both prior to

any surface pre-treatment and after the various pre-treatments. Figure 5-1 shows the images of the water droplets on the surfaces of CFRP-3, CFRP-4, and CFRP-5 after the different treatments. The image shows one droplet from the set of repeat droplets made for each surface condition, and the result of CA testing (i.e., the mean value with the deviation) was summarised in Table 5-2 and Figure 5-2.

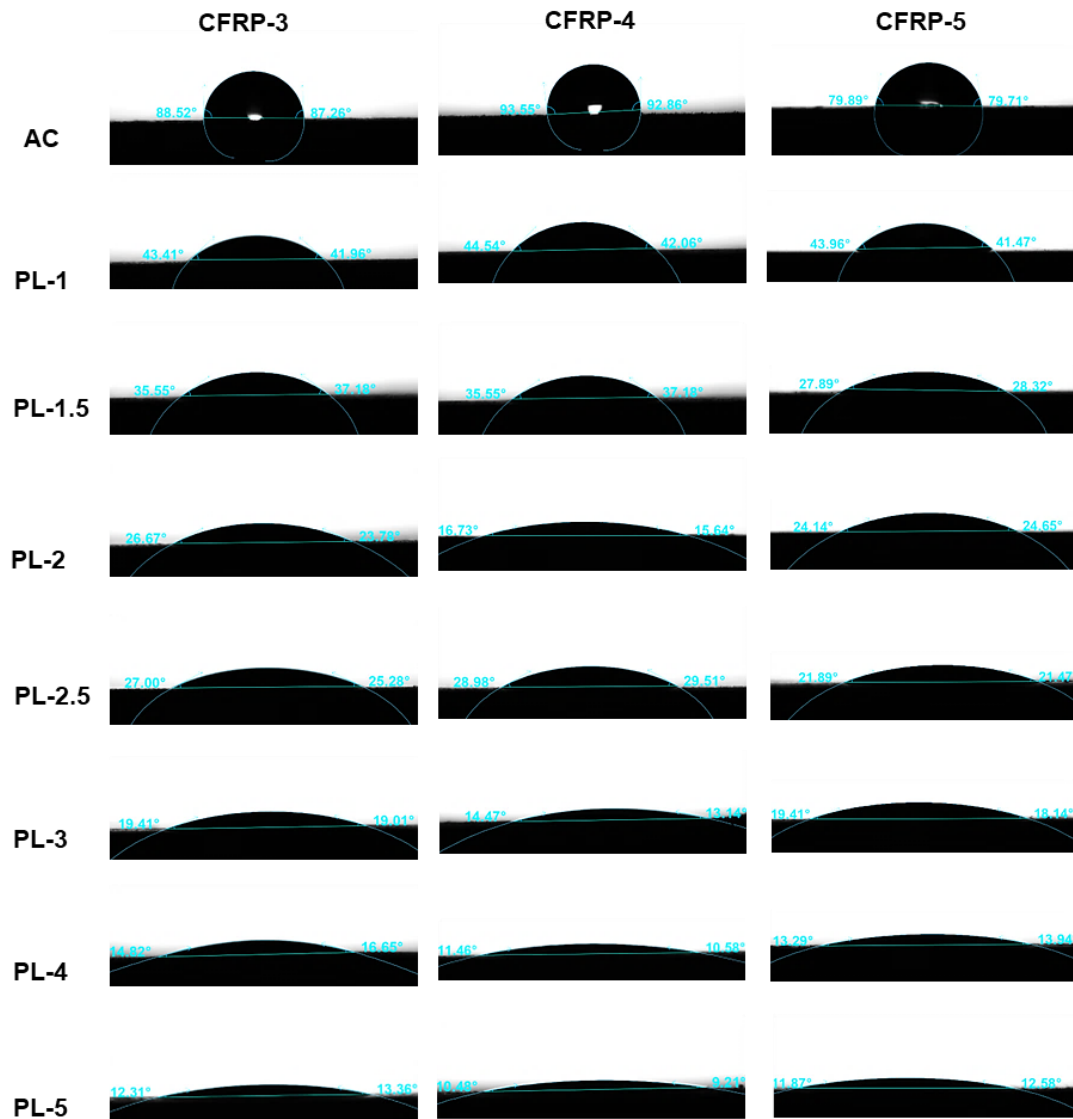


Figure 5-1. Images of water contact angle on CFRP-3, CFRP-4, and CFRP-5 adherends before and after plasma treatment of different power or duration was carried out. (AC: acetone cleaned with no further plasma treatment; PL-1: with 100 W, 0.5 min plasma treatment; PL-1.5: 100 W, 1 min; PL-2: 100 W, 2 min; PL-2.5: 180 W, 1 min; PL-3: 180 W, 2 min; PL-4: 180 W, 5 min; PL-5: 180 W, 8 min.) An image here shows one droplet from the set of repeat droplets made for each surface. The results (mean values and standard deviations) are summarised in Table 5-2.

Table 5-2. Water contact angle values on CFRP-3, CFRP-4, and CFRP-5 adherends before and after plasma treatment of different power or duration was carried out.

Treatment	Details	CFRP-3	CFRP-4	CFRP-5
AC	No plasma treatment	87.4 ± 1.9	93.2 ± 1.2	79.8 ± 0.8
PL-1	AC + 100 W, 0.5 min PL	43.1 ± 2.5	43.6 ± 1.1	42.3 ± 3.2
PL-1.5	AC + 100 W, 1 min PL	37.1 ± 2.8	35.8 ± 2.0	28.2 ± 1.3
PL-2	AC + 100 W, 2 min PL	25.2 ± 1.8	16.6 ± 0.9	24.2 ± 2.4
PL-2.5	AC + 180 W, 1 min PL	27.4 ± 1.6	29.3 ± 2.9	21.7 ± 1.1
PL-3	AC + 180 W, 2 min PL	19.2 ± 0.4	14.0 ± 1.0	18.6 ± 0.9
PL-4	AC + 180 W, 5 min PL	15.5 ± 1.8	10.8 ± 2.2	13.3 ± 0.7
PL-5	AC + 180 W, 8 min PL	13.0 ± 1.6	10.2 ± 0.9	12.0 ± 0.7

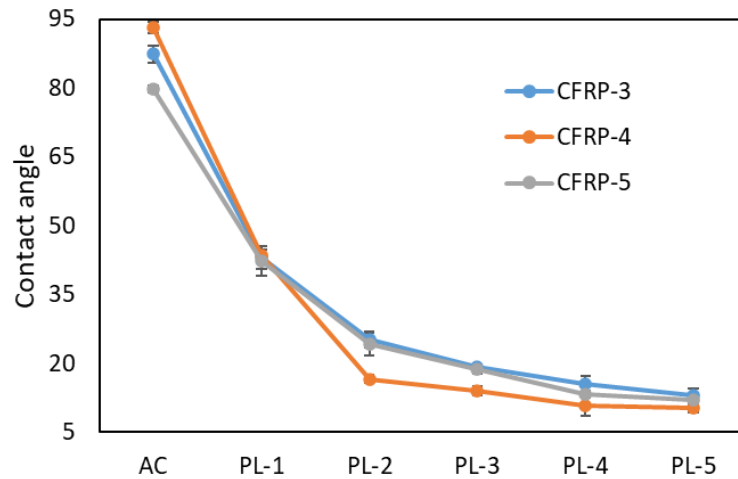


Figure 5-2. The trend of water contact angle on CFRP-3, CFRP-4, and CFRP-5 adherends before and after plasma treatment of different power or duration was carried out (the numerical data is shown in Table 5-2)

In terms of the two PEEK matrix composites (i.e., CFRP-3 and CFRP-4), the acetone cleaned samples were nearly hydrophobic. The CA on CFRP-3 ($87.4 \pm 1.9^\circ$) is lower than the CA on CFRP-4 ($93.2 \pm 1.2^\circ$), which is associated with the better interfacial performance as mentioned in section 5.1. After 100 W plasma treatment for 0.5 min (PL-1), the CA on both composites dropped sharply to around 43° . In comparison to CFRP-3, CFRP-4 was more sensitive to plasma treatment (as shown in Figure 5-2). For example, after a plasma treatment of 100 W for 2 min (PL-2), the CA on CFRP-3 was $25.2 \pm 1.8^\circ$ (reduced by 62.2° in comparison to acetone cleaned samples), which was

much higher than that on CFRP-4 (i.e., $16.6 \pm 0.9^\circ$, reduced by 76.6°). Increasing the power or duration of plasma treatment could further reduce the CA. However, the effect on CA reduction became much slower. For example, when the duration of 180 W plasma treatment was increased from 2 min (PL-3) to 5 min (PL-4), the CA decreased from $19.2 \pm 0.4^\circ$ to $15.5 \pm 1.8^\circ$ on CFRP-3 and from $14.0 \pm 1.0^\circ$ to $10.8 \pm 2.2^\circ$ on CFRP-4. When the duration of 180 W plasma treatment was further increased to 8 min (PL-5), the CA on CFRP-3 only slightly decreased to $13.0 \pm 1.6^\circ$ and the CA on CFRP-4 almost unchanged in comparison to the PL-4 samples.

In terms of the CFRP-5 consisting of T800S carbon fibre/PAEK matrix, the CA of the acetone cleaned samples were 79.8 ± 0.8 , lower than the two T700 carbon fibre/PEEK samples. However, plasma treatment showed a similar effect in reducing the CA on these thermoplastic CFRPs. After PL-1 was applied to the surface, the CA of CFRP-5 decreased sharply to $42.3 \pm 2.5^\circ$. After the application of PL-2 or PL-3, the CA further noticeably decreased to $24.2 \pm 2.5^\circ$ and $18.6 \pm 2.5^\circ$, respectively. After the application of PL-4 or PL-5 in which the plasma treatment was 180 W for 5 min or 8 min, the CA measured were $13.3 \pm 0.7^\circ$ and $12.0 \pm 0.7^\circ$, respectively.

The plasma treatment was effective in improving the wettability (i.e., reducing the CA) on these thermoplastic CFRP samples. The improvement in wettability may result from the removal of hydrophobic mould releasing agents as well as the introduction of hydrophilic oxygen-containing functional groups, which will be demonstrated in the following sections.

5.4 Surface topography, surface chemistry, and CFRP/CFRP joints of CFRP-3

5.4.1 Surface topography

The surface topography of the CFRP samples after acetone cleaning or plasma treatment usually did not show any remarkable change at the macroscopic scale (Figure 5-3a), but changes to the surface micro/nano-structures of some plasma treated samples were observed as shown in Figure 5-3b,c.

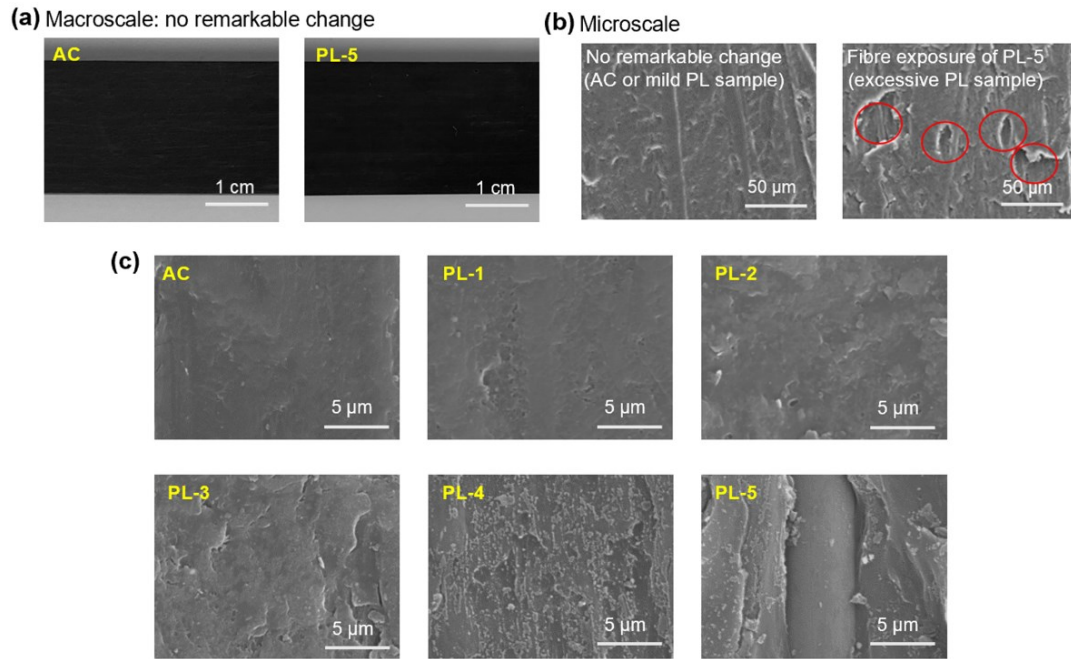


Figure 5-3. Photos and SEM images of CFRP-3 surfaces after different surface pre-treatments. (a) At the macroscopic scale: no visually significant change; **(b)** At the microscale when the scale bar is 50 μm: the surfaces did not show remarkable change after a mild plasma treatment, while fibre exposure was observed on samples where the plasma treatment was excessive; **(c)** At the microscale when the scale bar is 5 μm: relatively flat surfaces of acetone cleaned samples (AC) without plasma treatment (PL), no remarkable changes in topography after 100 W, 0.5 min PL (PL-1), roughness appearing after 100 W, 2 min PL (PL-2), rough micro-structure becoming obvious after 180 W, 2 min PL (PL-3), remarkable rough micro/nano-structures after 180 W, 5 min PL (PL-4), noticeable fibre exposure after 180 W, 8 min PL (PL-5).

The acetone cleaned samples of CFRP-3 had a relatively flat surface. This is because the compression moulding created flat surfaces on the CFRP plates and the acetone cleaning did not affect the surface topography. The surface topography at the microscale also did not show any remarkable changes after a plasma treatment of 100 W for 0.5 min. However, when the duration of the 100 W plasma treatment was increased to 2 min, roughness appeared on the CFRP surfaces, due to a noticeable amount of resin removal. When the power was increased to 180 W but the duration was unchanged (2 min), the rough structure was more distinct (PL-3). When the plasma treatment was 180 W for 5 min (PL-4), not only the microstructure was remarkable but also a nanostructure appeared, i.e., some grooves at the nanoscale were observed

under SEM. It is suggested that this is because the long-time high-power vacuum plasma creates a nano-etching effect. Such observations have also been reported in plasma research for other applications [177,178]. When the plasma treatment applied was 180 W for 8 min (PL-5), fibre exposure was frequently observed, which was caused by the excessive removal of surface resin after this intense level of treatment.

5.4.2 Surface chemistry

Carbon and oxygen are the main elements of CFRPs. The XPS software is able to deconvolute the carbon peaks into the different carbon bonds present as the binding energy of the individual bonds are known. Figure 5-4 shows the XPS spectra of C-C, C-O-C, O-C=O bond on CFRP-3 surface.

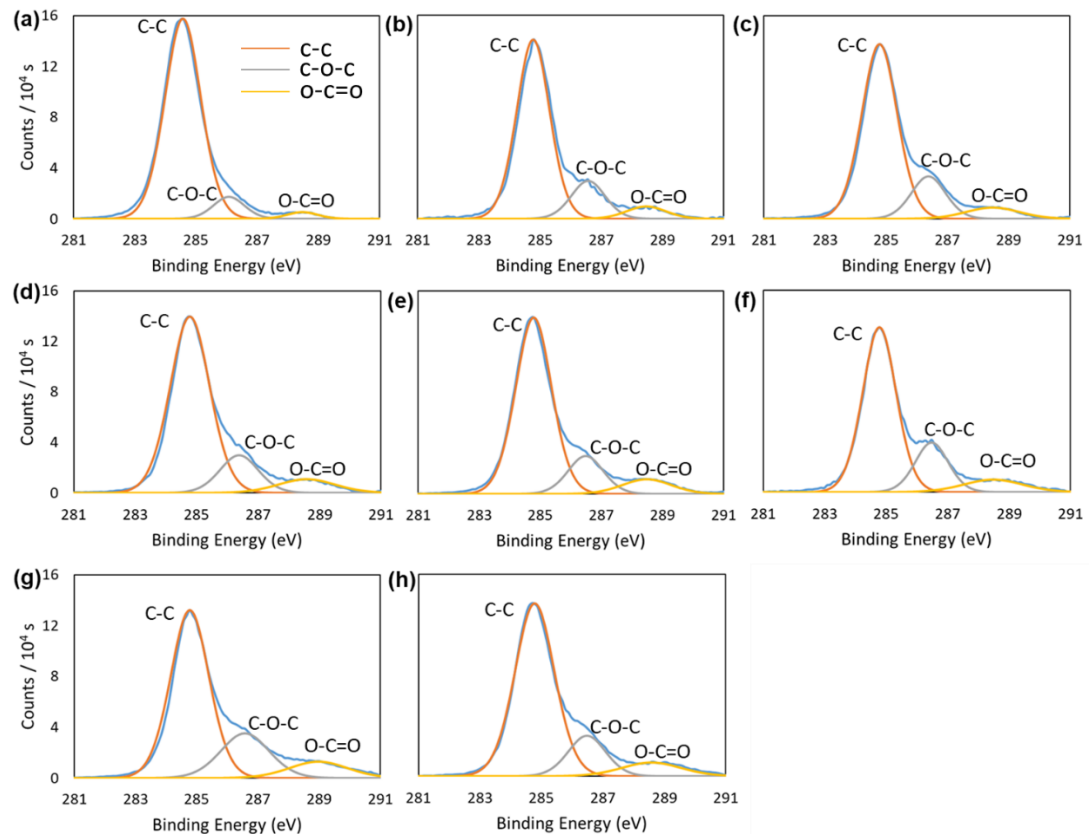


Figure 5-4. XPS spectra of CFRP-3 after different surface pre-treatments. (a) acetone cleaned samples (AC) with no plasma treatment (PL); (b) 100 W, 0.5 min PL (PL-1); (c) 100 W, 1 min (PL-1.5); (d) 100 W, 2 min (PL-2); (e) 180 W, 1 min PL (PL-2.5); (f) 180 W, 2 min PL (PL-3); (g) 180 W, 5 min PL (PL-4); (h) 180 W, 8 min PL (PL-5).

Table 5-3. Chemical composition of CFRP-3 after different surface pre-treatments.

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Samples ^a	O/C ratio	C-C ^b	C-O-C ^b	O-C=O ^b	Si	Cl
AC	0.22	88.9%	8.5%	2.6%	Trace ^c	Trace
PL-1	0.30	76.9%	16.7%	6.4%	Trace	<LOD
PL-1.5	0.33	74.7%	17.7%	7.6%	Trace	<LOD
PL-2	0.39	75.8%	15.7%	8.5%	<LOD	<LOD
PL-2.5	0.42	75.4%	16.2%	8.4%	Trace	<LOD
PL-3	0.45	69.7%	20.8%	9.5%	<LOD	<LOD
PL-4	0.45	67.4%	22.7%	9.9%	<LOD	<LOD
PL-5	0.43	74.3%	16.6%	9.1%	Trace	<LOD

^a The samples labels in this table are the same as those in Table 5-2.

^b The total of C-C, C-O-C and O-C=O percentage was set to be 100% (the same hereinafter).

^c LOD was around 0.5-1% (atomic); Trace means in some repeats it was slightly >LOD.

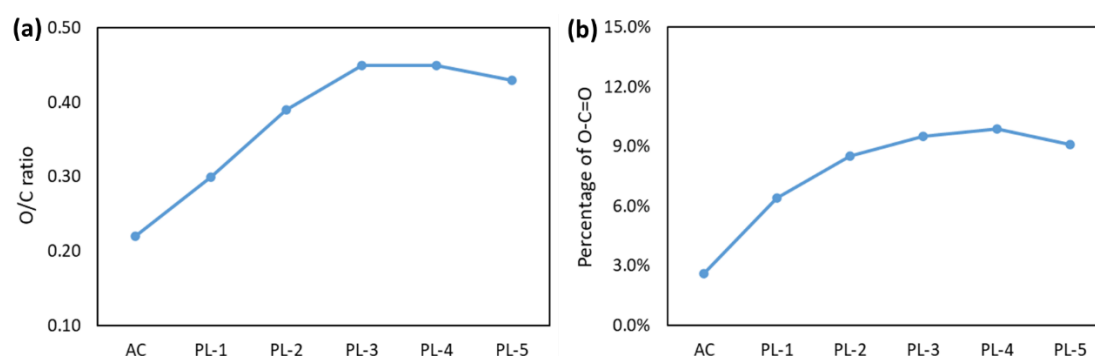


Figure 5-5. The trend of O/C ratio and percentage of O-C=O of CFRP-3 after different surface pre-treatments (the numerical data is shown in Table 5-3)

The XPS software is also able to calculate the percentage of the different bonds using the spectra. Table 5-3 shows the statistical results of surface chemistry of CFRP-3 after the different levels of plasma treatment, whose trend is displaced in Figure 5-5. It is evident that plasma treatment can considerably increase the presence of oxygen on the CFRP surfaces, especially in the form of the carbon-oxygen double bond.

Considering the acetone cleaned samples of CFRP-3, the O/C ratio was only 0.22. The atomic percentage of the C-C, C-O-C, and O-C=O bonds were 88.9%, 8.5%, and 2.6%, respectively. When the power and duration of the plasma treatment was increased from 100 W, 0.5 min to 180 W, 5 min, the O/C ratio showed a monotonic increase from 0.30 to 0.45. Meanwhile, the percentage of C-C bond decreased from 76.9% to 67.4% while the percentage of O-C=O bond increased from 6.4% to 9.9%. In

comparison to the acetone cleaned samples, the percentage of the carbon-oxygen double bond in the PL-4 (180 W, 5 min) samples nearly quadrupled.

The maximum value of the O/C ratio and percentage of O-C=O, together with the minimum percentage of C-C, occurred after a plasma treatment of 180 W, 5 min (PL-4). Considering the PL-5 samples where the duration of the 180 W plasma treatment was raised to 8 min, the O/C ratio and the percentage of O-C=O showed small decrease. The percentage of C-C increased to 74.3% and the percentage of C-O-C decreased remarkably from 22.7% (of PL-4 samples) to 16.6%. The adverse trend of PL-5 samples may be associated the fibre exposure as mentioned in section 5.4.1.

Plasma treatment was also effective in removing surface contamination that may affect the subsequent adhesive bonding. For example, the elements of Cl and Si were the main impurities found on the CFRP-3 surface. The Cl contamination came from the storage or transport of the prepregs or from the mould used in the CFRP manufacturing. As shown in Table 5-3, the Cl was not removed by acetone cleaning, but following all plasma treatments the percentage of Cl was reduced to being below the minimum amount which the apparatus could detect. The Si contamination (which comes from the Si-based mould releasing agent) remained on the surfaces of the PL-1, PL-1.5, and PL-2.5 samples. For the plasma treatments of PL-2, PL-3, or PL-4 i.e., 100 W-180 W for 2 min or 180 W for 2-5 min, Si could not be detected. For the PL-5 samples (180 W for 8 min), Si was detected again. Since the fibre exposure was observed in the PL-5 samples, it is suggested that the Si here might be the minor composition or impurities of the carbon fibres.

5.4.3 SLS tests of CFRP/CFRP joints

5.4.3.1 Stress-displacement behaviour

The mechanical performance of the homogenous joints (CFRP/CFRP) was studied to show the effectiveness of plasma treatment as an effective surface pre-treatment prior to adhesive bonding of these thermoplastic matrix CFRPs. Two CFRP adherends after the same surface treatment were bonded together. The naming convention for the joints corresponds to the naming convention for the surface pre-treatments

applied. Figure 5-6a shows the stress-displacement curves obtained for the CFRP-3 joints in the six different surface treatment conditions investigated. The initial slopes of the stress-displacement curves for the joints AC and PL-1,2,3,4 were similar prior to the failure points. The PL-5 samples showed a somewhat different slope, especially when approaching failure, which may be related to the fibre exposure caused by excessive plasma treatment.

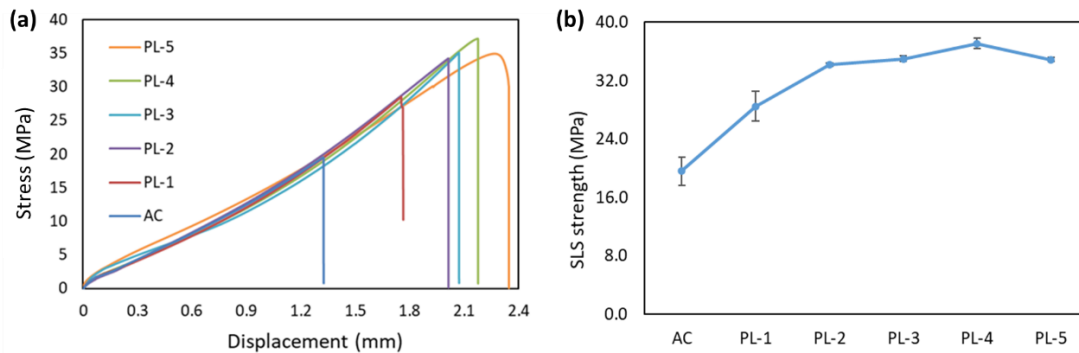


Figure 5-6. SLS strength tests of CFRP-3/CFRP-3 joints when the pre-treatment was acetone cleaning or plasma treatment of different power or duration (AC: acetone cleaned, PL-1: 100 W, 0.5 min plasma pre-treated, PL-2: 100 W, 2 min plasma pre-treated, PL-3: 180 W, 2 min plasma pre-treated, PL-4: 180 W, 5 min plasma pre-treated, PL-5: 180 W, 8 min plasma pre-treated). (a) Strength-displacement curves; (b) The trend of SLS strength after the different treatment.

5.4.3.2 SLS strength & interfacial appearance after failure

The SLS strength (Figure 5-6b) and failure mode of these CFRP-3/CFRP-3 joints (Figure 5-7) are summarised in Table 5-4. The SLS strength of the acetone cleaned samples was 19.6 ± 1.9 MPa and the fracture surface was visually assessed to be nearly-fully interfacial. The SLS strength of the joint samples PL-1 to PL-3 increased from 28.5 ± 2.0 MPa to 35.0 ± 0.4 MPa. The fracture surfaces of these joints were visually assessed to be a mixture of both interfacial and cohesive failure. The proportion of cohesive failure increased considerably when the duration or power of the plasma treatment was increased. The maximum SLS strength (37.1 ± 0.7 MPa) was recorded following the plasma treatment PL-4 (180 W, 5 min plasma), where the failure was almost fully cohesive.

Table 5-4. SLS strength and failure mode of CFRP-3/CFRP-3 joints when the pre-treatment was acetone cleaning (AC) or plasma treatment (PL) of different power or duration. (The

photographs of the failed interfaces are shown in Figure 5-5.)

Sample	Pre-treatment details	X_{max} (mm)	τ (MPa)	Failure mode
AC	No plasma treatment	1.32 ± 0.08	19.6 ± 1.9	interfacial
PL-1	AC + 100 W, 0.5 min PL	1.74 ± 0.03	28.5 ± 2.0	interfacial (major) + cohesive
PL-2	AC + 100 W, 2 min PL	2.01 ± 0.02	34.2 ± 0.2	interfacial + cohesive
PL-3	AC + 180 W, 2 min PL	2.07 ± 0.05	35.0 ± 0.4	cohesive (major) + interfacial
PL-4	AC + 180 W, 5 min PL	2.17 ± 0.02	37.1 ± 0.7	cohesive
PL-5	AC + 180 W, 8 min PL	2.25 ± 0.05	34.9 ± 0.3	1) cohesive (major) + interfacial 2) interlaminar

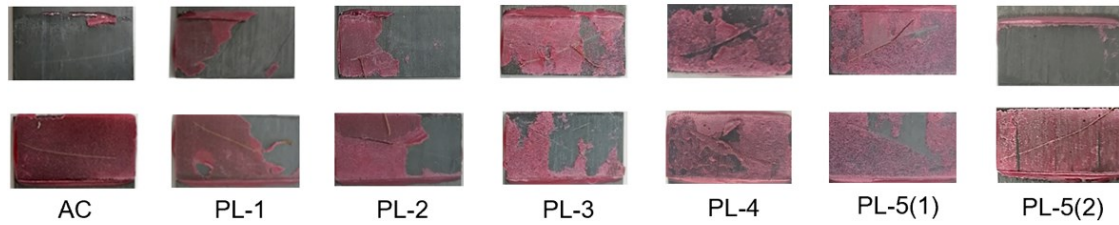


Figure 5-7. Photographs of the failed interface of the SLS joints of CFRP-3/CFRP-3 when the surface pre-treatment was acetone cleaning or plasma treatment of different power or duration. (AC: acetone cleaned, PL-1: 100 W, 0.5 min plasma pre-treated, PL-2: 100 W, 2 min plasma pre-treated, PL-3: 180 W, 2 min plasma pre-treated, PL-4: 180 W, 5 min plasma pre-treated, PL-5: 180 W, 8 min plasma pre-treated).

The best SLS joint performance was obtained following the plasma treatment of 180 W for 5 min (PL-4). This can be attributed to the attainment of the best surface conditions after the pre-treatment (as introduced in section 5.3 and 5.4), i.e., the surfaces were in possession of not only microscale roughness but also they possessed a nanostructure, the highest value of the O/C ratio and the highest percentage of O-C=O bonds, and a low CA. For example, the activated surface chemistry led to an improved chemical bond. At the same time, the micro/nano-structure on the surface was beneficial in creating mechanical interlocking. The nano-grooves caused by the nano-etching effect of the plasma treatment may play a significant role in enhancing the adhesion. This is discussed in more detail in Chapter 6.

Considering the joints PL-5 (180 W for 8 min), the SLS strength reduced to 34.9 ± 0.3 MPa. Two different failure modes were usually observed from different specimens

used in the repeated tests, as shown in the specimen PL-5(1) and PL-5(2) in Figure 5-5. In the specimen PL-5(1), most of the area of the fracture surface was associated with cohesive failure but some of the area indicated interfacial failure had occurred. The presence of interfacial failure in this specimen may derive from the fibre exposure area of CFRP adherend caused by the 8-min plasma treatment. The exposed carbon fibre resulted in poor adhesion locally to adhesives. In the joint PL-5(2), adherend damage was the main failure mode. The fibre exposure after the plasma treatment, namely the excessive removal of matrix resin, developed into interlamination fracture of the CFRP during mechanical testing. In a word, pre-treating the CFRPs till fibre exposure or even breakage should be regarded as overtreating herein, which has side effects on adhesive bonding.

5.5 Surface topography, surface chemistry, and CFRP/CFRP joints of CFRP-4

5.5.1 Surface topography

Figure 5-8 shows the surface topography of CFRP-4 after acetone cleaning or plasma treatment of different processing parameters. The acetone cleaned samples and the samples treated with a relatively mild plasma had a relatively flat surface, as shown in Figure 5-8a. In Figure 5-8b when the AC, PL-1, PL-2 samples were compared, the roughness of CFRP-4 surface showed a slightly decrease. The roughness was decreasing slightly in the 100 W for ≤ 2 min plasma treatment because in such a mild process the plasma was just removing surface contaminations and the partial matrix resin which was relatively non-uniformly spread initially. When the power of the 2-minute plasma treatment was increased to 180 W (PL-3), remarkable roughness was created on the surface. When the duration 180 W plasma treatment was increased to 5 min (PL-4), remarkable micro/nano-structures were observed. When the plasma treatment was 180 W for 8 min (PL-5), remarkable fibre exposure can be observed.

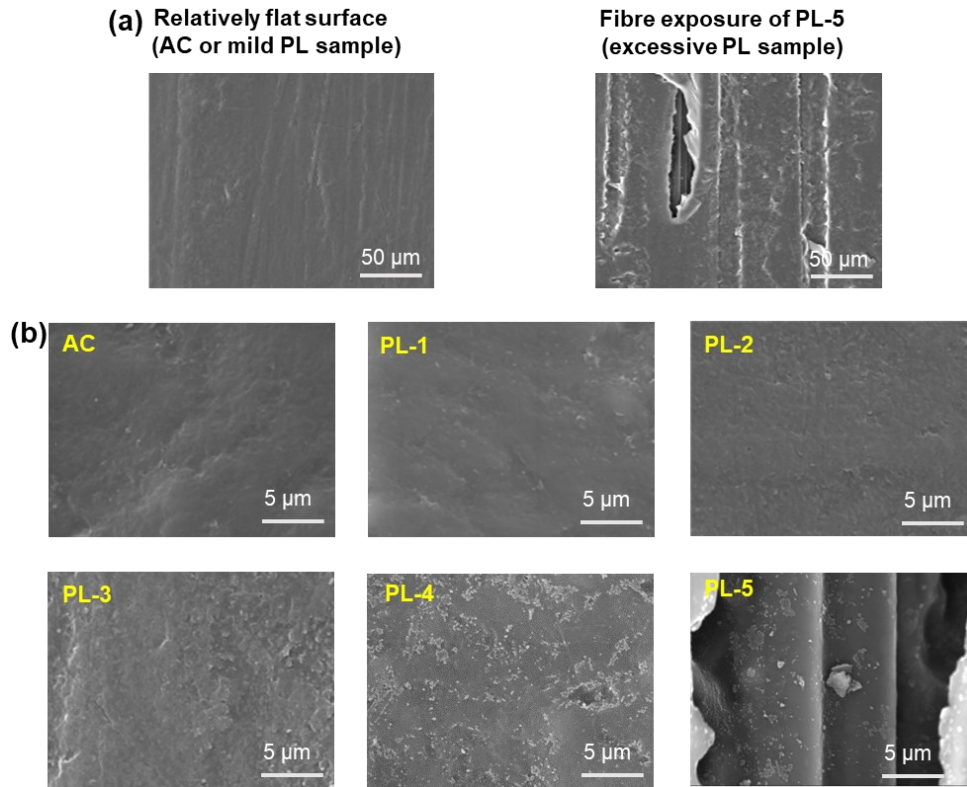


Figure 5-8. SEM images of CFRP-4 surfaces after different surface pre-treatments. (a) When the scale bar is 50 µm, the surface remained relatively flat after acetone cleaning or mild plasma treatment while fibre exposure took place in PL-5 samples on which the plasma treatment was excessive; (b) When the scale bar is 5 µm: relatively flat surface of acetone cleaned (AC) samples without plasma treatment (PL), the roughness slightly decrease after 100 W plasma treatment for 0.5 min (PL-1) or 2 min (PL-2), remarkable roughness created after 180 W, 2 min PL (PL-3), remarkable micro/nano-structures after 180 W, 5 min PL (PL-4), noticeable local fibre exposure after 180 W, 8 min PL (PL-5).

5.5.2 Surface chemistry

Surface chemistry was characterised using XPS via peak deconvolution. Figure 5-9 shows the XPS spectra of C-C, C-O-C, O-C=O bond on CFRP-4 surface after different treatments. Table 5-5 shows the corresponding statistical results of CFRP-4. Figure 5-10 shows the trend of elementary changes of CFRP-4 when the power or duration of plasma treatment were increased.

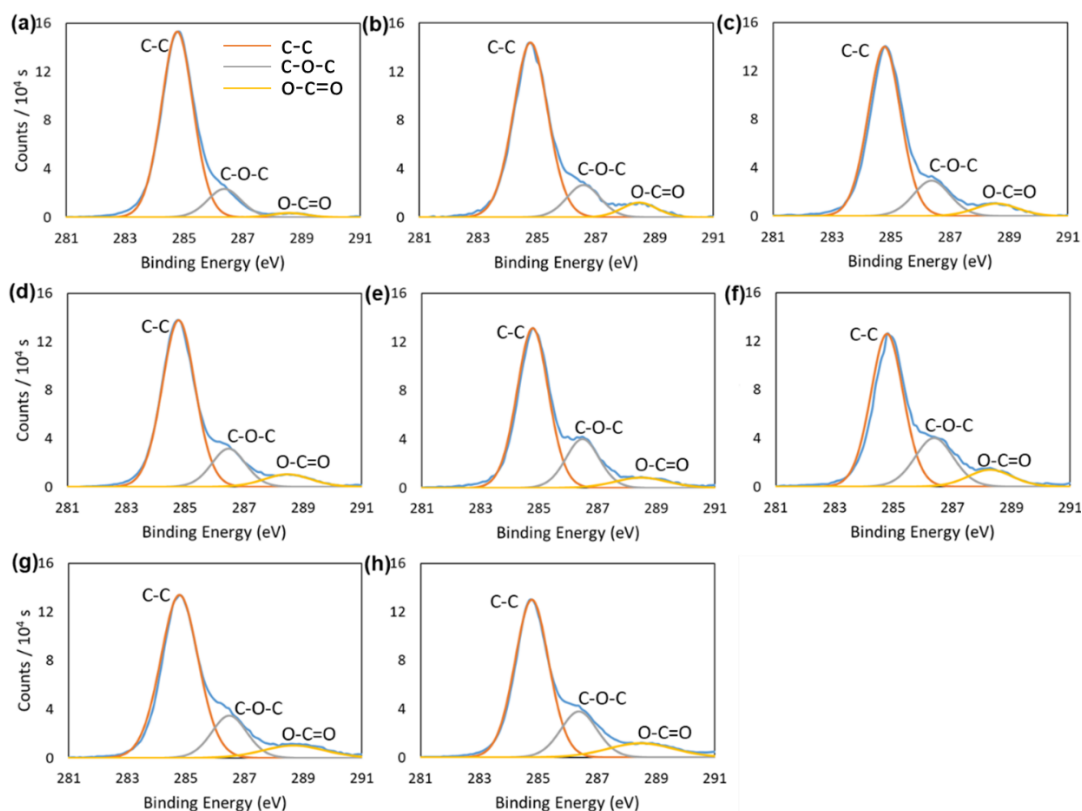


Figure 5-9. XPS spectra of CFRP-4 after different surface pre-treatments. (a) acetone cleaned samples (AC) with no plasma treatment (PL); (b) 100 W, 0.5 min PL (PL-1); (c) 100 W, 1 min (PL-1.5); (d) 100 W, 2 min (PL-2); (e) 180 W, 1 min PL (PL-2.5); (f) 180 W, 2 min PL (PL-3); (g) 180 W, 5 min PL (PL-4); (h) 180 W, 8 min PL (PL-5). (The statistical results characterised using XPS is summarised in Table 5-5 in the next page.)

Table 5-5. Chemical composition of CFRP-4 after different surface pre-treatments.

Samples ^a	O/C ratio	C-C ^b	C-O-C ^b	O-C=O	Si	S
AC	0.18	84.1%	13.7%	2.2%	Trace ^b	Trace
PL-1	0.42	79.0%	14.3%	6.7%	Trace	<LOD
PL-1.5	0.43	75.0%	17.6%	7.4%	Trace	<LOD
PL-2	0.40	74.1%	17.7%	8.2%	Trace	<LOD
PL-2.5	0.43	69.7%	22.6%	7.7%	Trace	<LOD
PL-3	0.44	65.6%	24.6%	9.8%	<LOD	<LOD
PL-4	0.49	72.2%	17.6%	10.2%	<LOD	<LOD
PL-5	0.35	67.1%	21.0%	11.9%	Trace	Trace

^a The samples labels in this table are the same as those in Table 5-2, Figure 5-1, and Figure 5-7.

^b LOD was around 0.5-1% (atomic); Trace means in some repeats it was slightly >LOD.

Considering the acetone cleaned samples of CFRP-4, the O/C ratio was only 0.18 and the atomic percentage of O-C=O bond was only 2.2%. After plasma treatment, the O/C ratio and O-C=O bond could be respectively increased to 2-3 times and 3-5 times. The percentage of O-C=O bond showed a monotonic increase (Figure 5-10a) as the duration or power of plasma increased, reaching 10.2% on PL-4 samples and peaking at 11.9 on PL-5 samples.

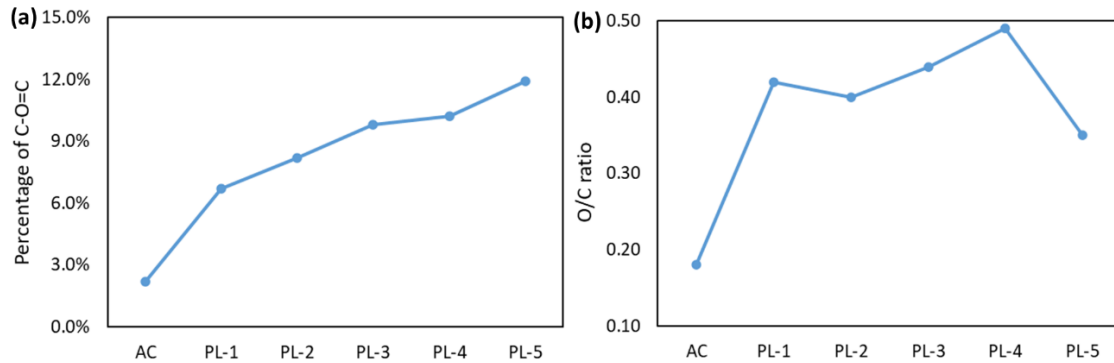


Figure 5-10. The trend of percentage of O-C=O and O/C ratio of CFRP-4 after different surface pre-treatments (the numerical data is shown in Table 5-5)

From the PL-1 to PL-1.5 and PL-2 samples on which the duration of 100 W plasma treatment was increased from 0.5 min to 1 min and 2 min, the O/C ratio fluctuated (as shown in Figure 5-10b). This is because surface contamination which contains oxygen was removed during the plasma treatment but meanwhile the oxygen-plasma brought groups containing oxygen. The same reason is also associated with the change in surface roughness as explained in section 5.5.1. From the PL-2.5 to PL-3 and PL-4 samples on which the duration of 180 W PL treating was increased from 1 min to 2 min and 5 min, the O/C ratio showed a monotonic increased (Figure 5-10b). The maximum value of the O/C ratio (0.49) occurred on PL-4 samples. For the PL-5 samples where the duration of the 180 W PL was raised to 8 min, the O/C ratio decreased to 0.35. This may be associated with the fibre exposure as mentioned in section 5.5.1.

Plasma treatment was effective in removing surface contamination. On the acetone cleaned CFRP-4 samples, the elements of S and Si were detected. The Si contamination comes from the mould release agent during CFRP manufacturing. The S contamination comes from the storage or transport of the prepregs/the CFRPs. The S

element was removed as long as 100 W, 0.5 min plasma treatment (PL-1) was applied, but the Si element was not removed until 180 W, 2 min plasma treatment was employed (PL-3). On the PL-4 samples, Si and S could not be detected. However, on the PL-5 samples which involve fibre exposure, Si and S were detected again. Si and S might be the minor composition or impurities of the carbon fibres.

5.5.3 SLS tests of CFRP/CFRP joints

5.5.3.1 Stress-displacement behaviour

The stress-displacement curves obtained for CFRP-4 joints in the six different surface treatment conditions investigated were shown in Figure 5-11a. The initial slopes of the stress-displacement curves for the joints AC and PL-1,2,3,4 were similar prior to the failure points. The PL-5 samples showed a somewhat different slope, especially when approaching failure, which may be related to the fibre exposure caused by excessive plasmas treatment.

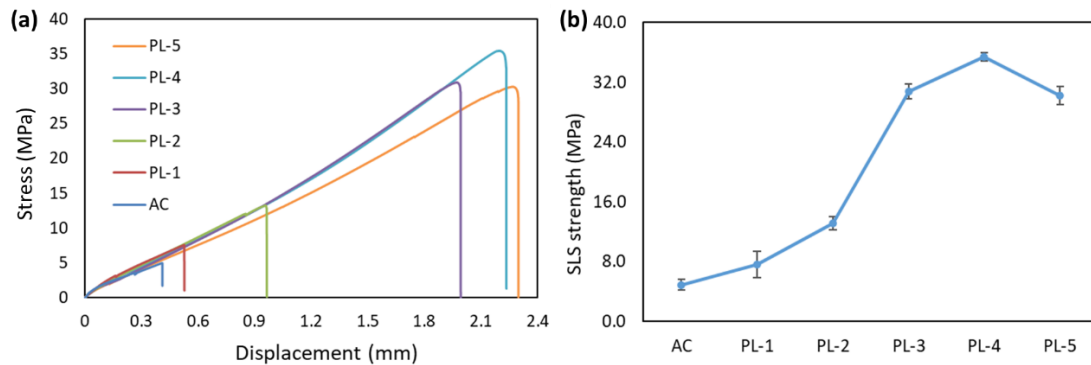


Figure 5-11. SLS strength tests of CFRP-4/CFRP-4 joints when the pre-treatment was acetone cleaning or plasma treatment of different power or duration (AC: acetone cleaned, PL-1: 100 W, 0.5 min plasma pre-treated, PL-2: 100 W, 2 min plasma pre-treated, PL-3: 180 W, 2 min plasma pre-treated, PL-4: 180 W, 5 min plasma pre-treated, PL-5: 180 W, 8 min plasma pre-treated). (a) Strength-displacement curves; (b) The trend of SLS strength after the different treatment.

5.5.3.2 SLS strength & interfacial appearance after failure

The SLS strength (Figure 5-11b) and failure mode of these CFRP-4/CFRP-4 joints (Figure 5-12) were recorded in Table 5-6. The SLS strength of the acetone cleaned samples was only 4.9 ± 0.7 MPa and the fracture surface was visually assessed to be

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interfacial. For the PL-1 and PL-2 joint samples, the SLS strength was also very low (i.e., 7.6 ± 1.8 MPa and 13.1 ± 0.9 MPa, respectively) and the fracture surfaces of these joints were also visually assessed to be interfacial. For the PL-3 samples, the SLS strength increased remarkably to 30.8 ± 1.0 MPa. The corresponding fracture surfaces were visually assessed to be a mixture of both interfacial and cohesive failure.

The maximum strength was recorded (35.4 ± 0.6 MPa) following the plasma treatment PL-4 (180W, 2 min), where the failure was almost fully cohesive. For the PL-5 samples which involves fibre exposure, the SLS strength was decreased to 30.2 ± 1.2 MPa in comparison to the PL-4 samples. Also, larger area of interfacial failure can be observed on the PL-5 samples.

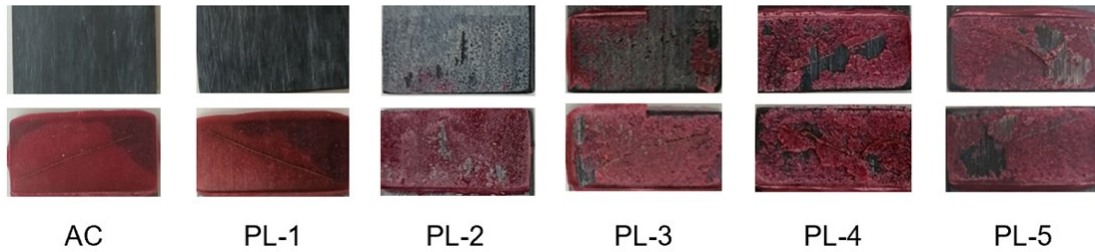


Figure 5-12. Photographs of the failed interface of the SLS joints of CFRP-4/CFRP-4 when the pre-treatment was acetone cleaning or plasma treatment of different power or duration. (AC: acetone cleaned, PL-1: 100 W, 0.5 min plasma pre-treated, PL-2: 100 W, 2 min plasma pre-treated, PL-4: 180 W, 2 min plasma pre-treated, PL-5: 180 W, 5 min plasma pre-treated, PL-5: 180 W, 8 min plasma pre-treated).

Table 5-6. SLS strength and failure mode of CFRP-4/CFRP-4 joints when the pre-treatment was acetone cleaning (AC) or plasma treatment (PL) of different power or duration. (The photographs of the failed interfaces are shown in Figure 5-9).

Sample	Pre-treatment details	X_{max} (mm)	τ (MPa)	Failure mode
AC	No plasma treatment	0.40 ± 0.02	4.9 ± 0.7	interfacial
PL-1	AC + 100 W, 0.5 min PL	0.54 ± 0.09	7.6 ± 1.8	interfacial
PL-2	AC + 100 W, 2 min PL	0.96 ± 0.09	13.1 ± 0.9	mostly interfacial
PL-3	AC + 180 W, 2 min PL	1.97 ± 0.07	30.8 ± 1.0	interfacial + cohesive
PL-4	AC + 180 W, 5 min PL	2.19 ± 0.05	35.4 ± 0.6	mostly cohesive
PL-5	AC + 180 W, 8 min PL	2.29 ± 0.08	30.2 ± 1.2	cohesive (major) + interfacial

The trend of SLS strength of the CFRP-4 joint samples is similar to the trend of the

CFRP-3 samples as analysed in section 5.3.3. However, in comparison to CFRP-3, which has a better initial mechanical performance as mentioned in section 5.1 as well as a lower contact angle as mentioned in section 5.2, CFRP-4 generally had a lower SLS strength. The similarities and the differences between the results for CFRP-3 and CFRP-4 are discussed in more detail in Chapter 6.

5.6 Surface topography, surface chemistry, and CFRP/CFRP joints of CFRP-5

5.6.1 Surface topography

The surface topography of CFRP-5 after acetone cleaning or plasma treatment of different processing parameters are shown in Figure 5-13. When the scale bar was 50 μm as shown in Figure 5-13a, no significant differences can be identified between the acetone cleaned samples and the PL-5 samples, except the outline of the carbon fibre becoming distinct on the PL-5 samples.

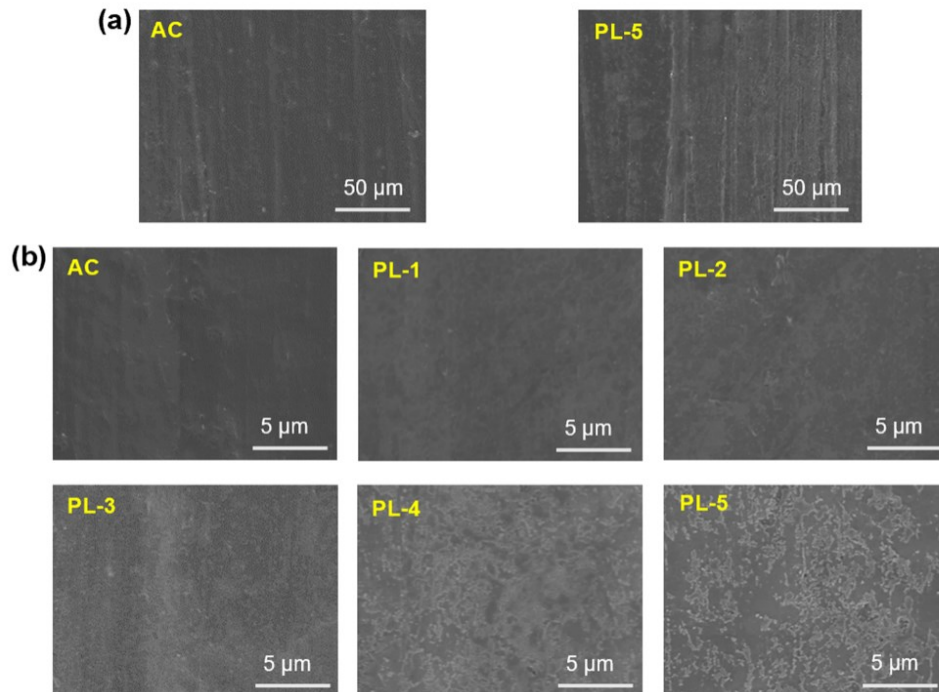


Figure 5-13. SEM images of CFRP-5 surfaces after different surface pre-treatments. (a) When the scale bar is 50 μm , no significant change except the outline of the carbon fibre becoming distinct on PL-5 samples; (b) When the scale bar is 5 μm : relatively flat

surface of acetone cleaned samples (AC) without plasma treatment, no noticeable change when the plasma treatment is 100 W for 0.5 min (PL-1) or 2 min (PL-2), roughness appearing when the plasma treatment is 180 W for 2 min (PL-3), roughness becoming remarkable when the plasma treatment is 180 W, 5 min (PL-4), remarkable micro/nano-structure when the plasma treatment is 180 W, 8 min (PL-5).

When the scale bar was 5 μm as shown in Figure 5-13b, the surfaces of the AC, PL-1, and PL-2 samples were visually flat. When it comes to the PL-3 samples, some rough structure appeared. The rough structure became remarkable when the plasma treatment was 180 W, 5 min (PL-4). When the plasma treatment was 180 W, 8 min (PL-5), the micro/nano-structures became more distinct on the surface.

5.6.2 Surface chemistry

Surface chemistry was characterised using XPS via peak deconvolution. Table 5-7 shows the statistical results of XPS of CFRP-5 after different treatments. Figure 5-14 shows the XPS spectra of C-C, C-O-C, O-C=O bond on CFRP-5 surface. Figure 5-15 shows the trend of elementary changes of CFRP-5 when the power or duration of plasma treatment were increased.

Table 5-7. Chemical composition of CFRP-5 after different surface pre-treatments.

Samples ^a	O/C ratio	C-C ^b	C-O-C ^b	O-C=O	Si	S
AC	0.20	74.5%	21.9%	3.6%	Trace ^b	Trace
PL-1	0.33	72.1%	18.9%	8.8%	Trace	Trace
PL-1.5	0.34	71.1%	20.0%	8.9%	Trace	<LOD
PL-2	0.34	70.7%	20.1%	9.2%	<LOD	<LOD
PL-2.5	0.35	68.8%	22.3%	8.9%	Trace	<LOD
PL-3	0.36	70.7%	19.9%	9.4%	<LOD	<LOD
PL-4	0.43	69.3%	20.5%	10.2%	<LOD	<LOD
PL-5	0.43	69.8%	19.8%	10.4%	<LOD	<LOD

^a The samples labels in this table are the same as those in Table 5-2, Figure 5-1, and Figure 5-11.

^b LOD was around 0.5-1% (atomic); Trace means in some repeats it was slightly >LOD.

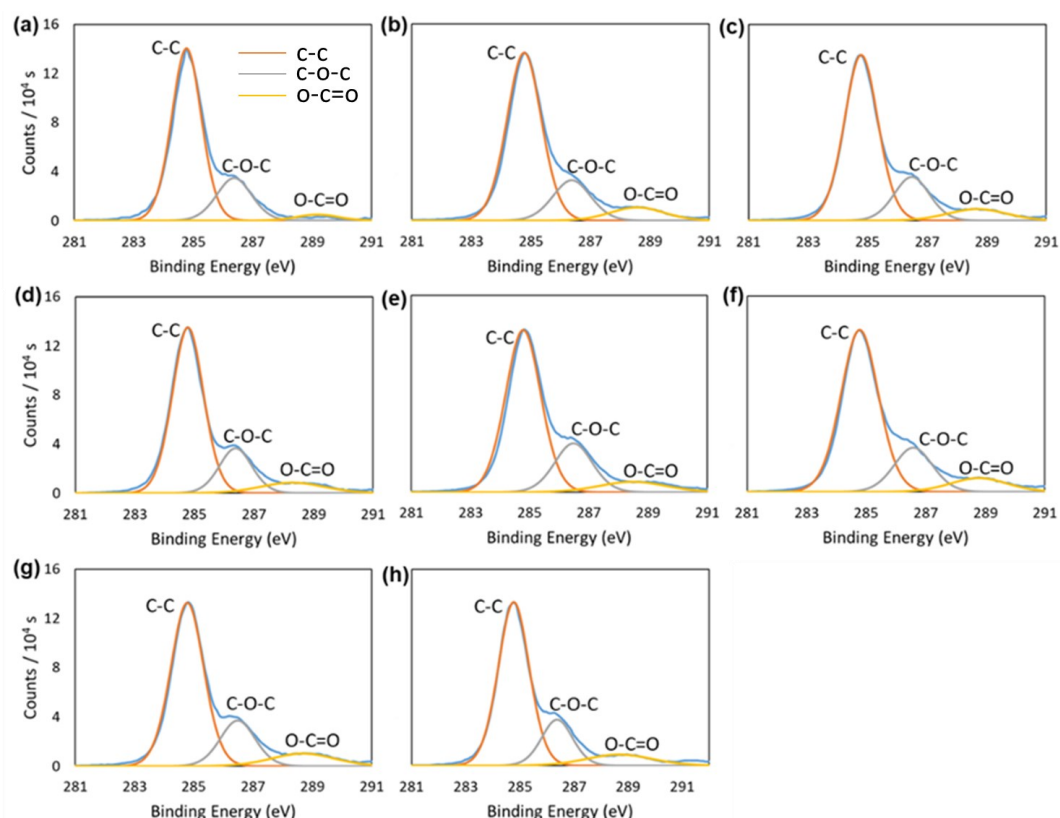


Figure 5-14. XPS spectra of CFRP-5 after different surface pre-treatments. (a) acetone cleaned samples (AC) with no plasma treatment (PL); (b) 100 W, 0.5 min PL (PL-1); (c) 100 W, 1 min (PL-1.5); (d) 100 W, 2 min (PL-2); (e) 180 W, 1 min PL (PL-2.5); (f) 180 W, 2 min PL (PL-3); (g) 180 W, 5 min PL (PL-4); (h) 180 W, 8 min PL (PL-5). (The statistical results characterised using XPS is summarised in Table 5-7)

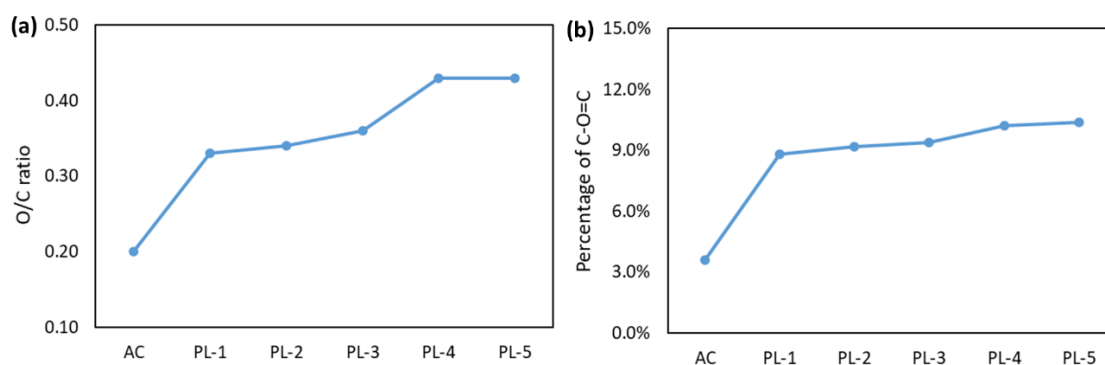


Figure 5-15. The trend of O/C ratio and percentage of O-C=O of CFRP-5 after different surface pre-treatments (the numerical data is shown in Table 5-7)

Considering the acetone cleaned samples of CFRP-5, the O/C ratio was only 0.20 and the atomic percentage of O-C=O bond was 3.6%. After plasma treatment, the O/C ratio and O-C=O bond could be increased to 2-3 times. The percentage of O/C ratio

showed an increasing trend (Figure 5-15a) as the duration or power of plasma increased, peaking at 0.43 on PL-4 and PL-5 samples.

Increasing the duration or time of plasma treatment can contribute to a decrease in the percentage of C-C bond or/and an increase in the percentage of O-C=O bond. For example, when duration of the 100 W plasma treatment was increased from 0.5 min (PL-1) to 2 min (PL-2), the percentage of C-C bond decreased monotonically from 72.1% to 70.7%, and the percentage of O-C=O bond increased monotonically from 8.8% to 9.2% (Figure 5-15b). When the power of 2-min plasma treatment was increased from 100 W (PL-2) to 180 W (PL-3), the percentage of O-C=O bond increased to 9.4%. When the duration of the 180 W plasma treatment was increased from 2 min (PL-3) to 8 min (PL-5), the percentage of O-C=O bond showed a monotonic increase, peaking at 10.4%.

It is evident that plasma treatment was effective on CFRP-5 in removing surface contamination. On the acetone cleaned CFRP-5 samples, the elements of S and Si were detected. The Si contamination comes from mould releasing agent in CFRP manufacturing. The S contamination comes from the storage or transport of the prepregs/the CFRPs. S was only detected on the 100 W, 0.5 min plasma treated (PL-1) samples. On the other plasma treated samples when the power or duration of plasma treatment was increased (i.e., the PL-1.5, PL-2, PL-2.5, PL-3, PL-4, and PL-5 samples), S was reduced to being below the minimum amount which the apparatus could detect. In terms of the Si element, it could not be detected when the plasma treatment was 100 W or 180 W for ≥ 2 min (i.e., the PL-2, PL-3, PL-4, and PL-5 samples).

5.6.3 SLS tests of CFRP/CFRP joints

5.6.3.1 Stress-displacement behaviour

The stress-displacement curves obtained for CFRP-5 joints in the six different surface treatment conditions investigated were shown in Figure 5-16a. No matter what the surface pre-treatment methods and the processing parameters were used, the initial slopes of the stress-displacement curves for these joints were similar prior to the failure points.

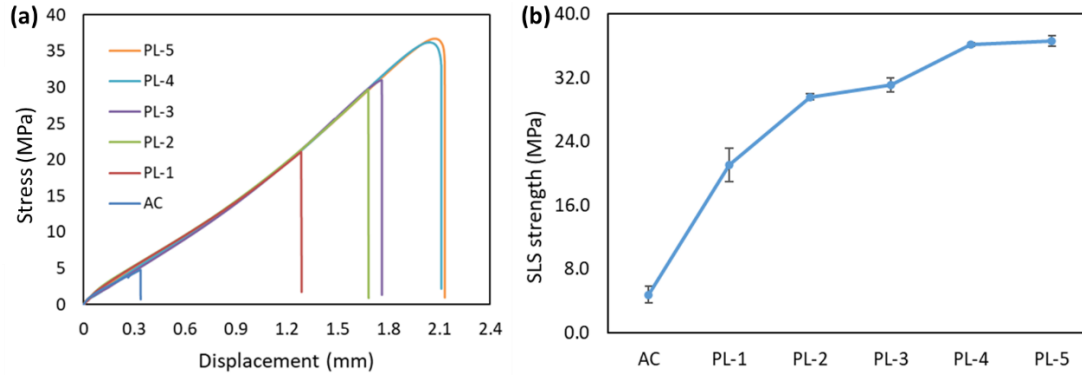


Figure 5-16. SLS strength tests of CFRP-5/CFRP-5 joints when the pre-treatment was acetone cleaning or plasma treatment of different power or duration (AC: acetone cleaned, PL-1: 100 W, 0.5 min plasma pre-treated, PL-2: 100 W, 2 min plasma pre-treated, PL-3: 180 W, 2 min plasma pre-treated, PL-4: 180 W, 5 min plasma pre-treated, PL-5: 180 W, 8 min plasma pre-treated). (a) Strength-displacement curves; (b) The trend of SLS strength after the different treatment.

5.6.3.2 SLS strength & interfacial appearance after failure

The SLS strength (Figure 5-16b) and failure mode of these CFRP-5/CFRP-5 joints (Figure 5-17) are shown in Table 5-8. The SLS strength of the acetone cleaned samples was only 4.8 ± 1.0 MPa and the fracture surface was visually assessed to be fully interfacial. The SLS strength of the joint samples PL-1 to PL-2 increased from 21.1 ± 2.1 MPa to 29.6 ± 0.4 MPa. The fracture surfaces of these joints were visually assessed to be mostly interfacial. The SLS strength of the joint sample PL-3 increased to 31.1 ± 0.9 MPa. Interfacial failure was still the major failure mode, but in some areas the cohesive failure in-between the adhesive layers were observed.

Table 5-8. SLS strength and failure mode of CFRP-5/CFRP-5 joints when the pre-treatment was acetone cleaning (AC) or plasma treatment (PL) of different power or duration. (The photographs of the failed interfaces are shown in Figure 5-13.)

Sample	Pre-treatment details	X_{max} (mm)	τ (MPa)	Failure mode
AC	No plasma treatment	0.34 ± 0.06	4.8 ± 1.0	interfacial
PL-1	AC + 100 W, 0.5 min PL	1.29 ± 0.10	21.1 ± 2.1	mostly interfacial
PL-2	AC + 100 W, 2 min PL	1.69 ± 0.03	29.6 ± 0.4	mostly interfacial
PL-3	AC + 180 W, 2 min PL	1.78 ± 0.04	31.1 ± 0.9	interfacial (major) + cohesive
PL-4	AC + 180 W, 5 min PL	2.04 ± 0.01	36.2 ± 0.2	cohesive
PL-5	AC + 180 W, 8 min PL	2.11 ± 0.05	36.6 ± 0.7	cohesive

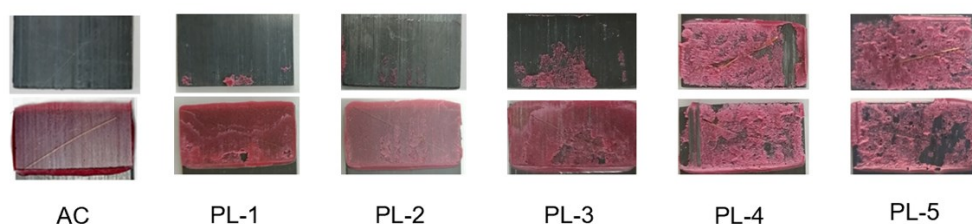


Figure 5-17. Photographs of the failed interface of the SLS joints of CFRP-5/CFRP-5 when the pre-treatment was acetone cleaning or plasma treatment of different power or duration. (AC: acetone cleaned, PL-1: 100 W, 0.5 min plasma pre-treated, PL-2: 100 W, 2 min plasma pre-treated, PL-4: 180 W, 2 min plasma pre-treated, PL-5: 180 W, 5 min plasma pre-treated, PL-5: 180 W, 8 min plasma pre-treated).

The SLS strength of PL-4 or PL-5 (180 W, 5-8 min plasma) was 36-37 MPa, and the fracture surfaces were visually assessed to be almost fully cohesive, which indicates a strong adhesion. The SLS strength of the PL-5 joint samples of CFRP-5/CFRP-5 did not reduce like the CFRP-3/CFRP-3 or CFRP-4/CFRP-4 joints. This is because plasma induced fibre exposure did not take place on the CFRP-5 adherends, which will be discussed in detail in Chapter 6.

5.7 CFRP/Al hybrid joining

5.7.1 Stress-displacement behaviour

Figure 5-18 shows the stress-displacement curves for the thermoplastic CFRP/Al joints and Al/Al homogenous joints. The surface pre-treatment applied to the thermoplastic CFRP adherends was acetone cleaning (AC) or plasma treatment. The plasma treatment applied to the thermoplastic CFRPs prior to the hybrid joining was 180 W for 5 min (PL-4) since this level of treatment was considered optimum (resulting in good adhesion with no fibre exposure occurring). The surface pre-treatment method applied to the aluminium alloy adherends AA2014 was acetone cleaning (AC) or silane agent treatment (SA). The effect of the two treatment methods on the surface topography, chemistry, and wettability of AA2014 is detailed in Appendix A2.

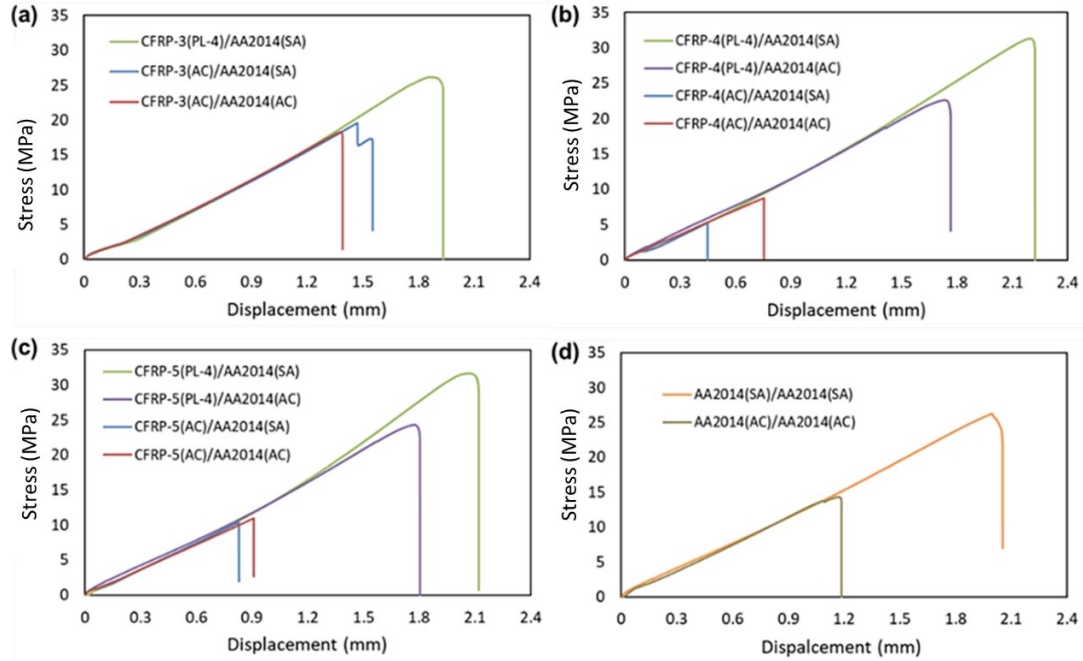


Figure 5-18. Stress-displacement curves of the SLS strength tests of thermoplastic CFRP/Al joints and Al/Al joints, when the pre-treatment for CFRP was AC or PL-4 and the pre-treatment for AA2014 was AC or SA (AC: acetone cleaned, PL-4: 180 W, 5 min plasma treated, SA: silane agent treated).(a) CFRP-3/AA2014 joints; (b) CFRP-4/AA2014 joints; (c) CFRP-5/AA2014 joints; (d) AA2014/AA2014 joints¹.

As shown in Figure 5-18a, considering the results for the CFRP-3/AA2014 SLS joint samples, no matter what surface pre-treatment method was used for each adherend, the graphs of stress-displacement showed a similar slope before failure. Similar observations can be made considering the results for the CFRP-4/AA2014 joint samples (Figure 5-18b), for the CFRP-5/AA2014 joint samples (Figure 5-18c), and for the AA2014/AA2014 joint samples (Figure 5-18d).

5.7.2 SLS strength & fracture behaviour

The SLS strength and fracture behaviour (failure location) of the thermoplastic CFRP/Al joints are presented in Table 5-9. The corresponding fracture surfaces are shown in Figure 5-19.

¹ In Chapter 4, AA2014(AC)/AA2014(AC) joints were also tested. In comparison to the results here, they showed almost the same SLS strength but different X_{max} . This is because two different testing instruments (different model/manufacture) were used as explained in Chapter 3 due to the COVID-19 lockdown. Using the different instruments will not affect the testing results of SLS strength but the X_{max} can be different. Hence, the SLS strength is herein highlighted while the data of X_{max} for CFRP or AA2014 joints in different chapters (using different testing instruments) are not used for comparison.

Table 5-9. SLS strength and failure location of SLS joints of the different CFRP-3/AA2014, CFRP-4/AA2014, and CFRP-5/AA2014.

No.	1	2	3	
Adherend 1	CFRP-3(AC)	CFRP-3(AC)	CFRP-3(PL-4)	
Adherend 2	AA2014(AC)	AA2014(SA)	AA2014(SA)	
τ (MPa)	18.2 ± 0.6	19.6 ± 0.6	26.3 ± 0.2	
X_{max} (mm)	1.38 ± 0.03	1.48 ± 0.06	1.86 ± 0.01	
Failure mode	interfacial on Al (major) and CFRP	interfacial on Al (major) + cohesive	cohesive (major) + interfacial on both	
No.	4	5	6	7
Adherend 1	CFRP-4(AC)	CFRP-4(AC)	CFRP-4(PL-4)	CFRP-4(PL-4)
Adherend 2	AA2014(AC)	AA2014(SA)	AA2014(AC)	AA2014(SA)
τ (MPa)	8.8 ± 1.7	5.3 ± 0.5	22.6 ± 0.2	31.4 ± 1.0
X_{max} (mm)	0.76 ± 0.10	0.45 ± 0.02	1.74 ± 0.03	2.17 ± 0.10
Failure mode	interfacial on CFRP	interfacial on CFRP	mostly cohesive	mostly cohesive
No.	8	9	10	11
Adherend 1	CFRP-5(AC)	CFRP-5(AC)	CFRP-5(PL-4)	CFRP-5(PL-4)
Adherend 2	AA2014(AC)	AA2014(SA)	AA2014(AC)	AA2014(SA)
τ (MPa)	11.0 ± 1.2	10.3 ± 0.4	25.0 ± 1.0	32.0 ± 0.8
X_{max} (mm)	0.90 ± 0.10	0.83 ± 0.04	1.79 ± 0.07	2.04 ± 0.13
Failure mode	interfacial on CFRP	interfacial on CFRP	cohesive (major) + interfacial	cohesive

When the surface pre-treatment applied to the CFRP or AA2014 adherends was only acetone cleaning, the hybrid CFRP-3/AA2014 joints failed at a SLS strength (18.2 ± 0.6 MPa) which was much greater than the SLS strength measured for either the CFRP-4/AA2014 joints (8.8 ± 1.7 MPa) or the CFRP-5/AA2014 (11.0 ± 1.2 MPa) joints. This is because the as-prepared CFRP-3 adherends and the acetone cleaned CFRP-3 adherends had a superior interfacial performance to the CFRP-4 and the CFRP-5 as introduced in section 5.1 and 5.2. For example, the failure mode of CFRP-4/AA2014 or CFRP-5/AA2014 joints was the interfacial failure only on the CFRP surface, while the failure mode of CFRP-3/AA2014 joints was composed of interfacial failure on not only the AA2014 but also the CFRP surface (together with subliminal cohesive failure).

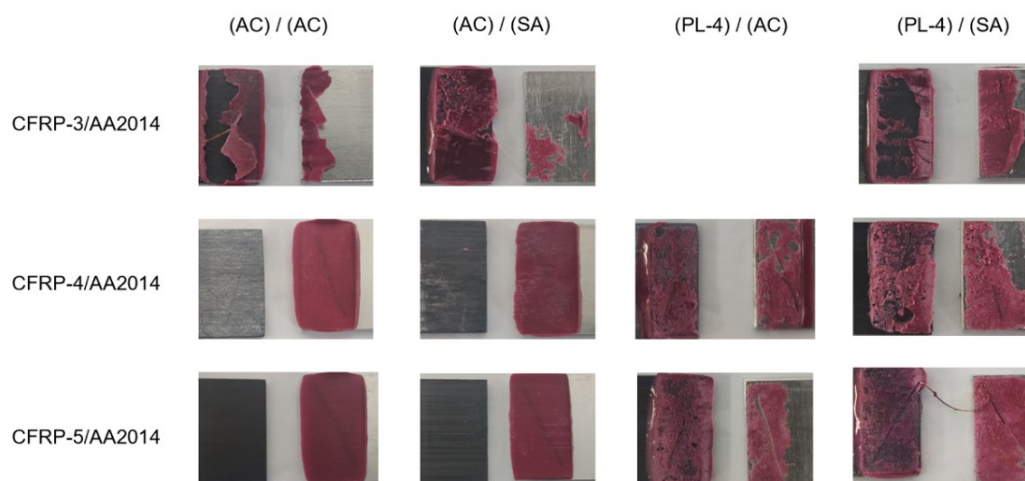


Figure 5-19. Photographs of the failed interface of the SLS joints of the thermoplastic CFRP/Al joints, when the pre-treatment for CFRP was AC or PL-4 and the pre-treatment for AA2014 was AC or SA. (AC: acetone cleaned, PL-4: 180 W, 5 min plasma treated, SA: silane agent treated).

When the surface pre-treatment was applied on the AA2014 adherend of CFRP-3/AA2014 joints, on the CFRP-4 adherend of CFRP-4/AA2014 joints, or on the CFRP-5 adherend of CFRP-5/AA2014 joints), the SLS strength showed noticeable increase. This is because the interfacial failure on these adherends would be reduced a lot if the surface pre-treatment was applied. For example, the SLS strength of CFRP-4(PL-4)/AA2014(AC) joints was 22.6 ± 0.2 MPa, over 2.5 times of the SLS strength of CFRP-4(AC)/AA2014(AC) joints. The failure mode transformed into mostly cohesive.

When the CFRP adherend was pre-treated via 180 W plasma for 5 min (PL-4) and the AA2014 adherend was pre-treated using the silane agent, CFRP-5 showed the highest SLS strength (i.e., 32.0 ± 0.8 MPa) of all the hybrid thermoplastic CFRP/Al joints. The failure mode of the CFRP-5(PL-4)/AA2014(SA) was observed to be fully cohesive. The corresponding SLS strength for CFRP-3 and CFRP-4 was 26.3 ± 0.2 MPa and 31.4 ± 1.0 MPa, respectively. In comparison to the hybrid joints formed using the CFRP-3 and CFRP-4 adherends, the higher strength of hybrid joints measured when CFRP-5 adherends were employed may relate to the flatter surface topography of CFRP-5 (see Figure 5-3, 5-8, 5-13 to compare). A flatter surface usually is more compatible with the flat surface of the aluminium alloy adherend when joining. The compatibility of the surfaces in hybrid joints is discussed in more detail in Chapter 6.

5.8 Summary

In this chapter, the effects of processing parameters of plasma treatment on the surface properties and joint performance of the thermoplastic CFRPs were studied. Firstly, it was clearly shown that plasma treatment is effective in improving the wettability of, and removing surface contaminations from, the different thermoplastic matrix composite adherends. It was proposed that a plasma treatment of 180 W for over 2 min created microstructures on the surface which were favourable for adhesive bonding. The thermoplastic CFRP adherends after a plasma treatment of 180 W for 5 min usually had developed the most appropriate surface topography, chemistry and wettability for adhesive bonding, and showed the highest SLS strength of all joints with CFRP/CFRP homogenous joining.

Secondly, for the plasma treated thermoplastic matrix adherends, as the power was increased from 100 W to 180 W or the duration was increased to 5 min, the percentage of carbon-oxygen double bonds showed an increasing trend. As a result, the SLS joint strength also showed an increasing trend. However, for the carbon fibre reinforced PEEK composites (CFRP-3 and CFRP-4), a plasma treatment of 180 W for ≥ 8 min resulted in exposure of fibres on the CFRP surface. Such a fibre exposure was shown to be harmful to adhesive bonding, leading to locally poor adhesion to the adhesive or leading to interlaminar failure of the CFRP adherends in the SLS joint tests. Either of these result in a lower CFRP/CFRP joint strength in comparison to the joints where the adherends had received a 180 W plasma treatment for 5 min. Fibre exposure was not observed on the carbon fibre reinforced PAEK composite (CFRP-5) following the same plasma treatment.

By comparing the results of SLS joint strength for the three thermoplastic CFRPs studied, it is evident that CFRP-3 (following 180 W plasma for 5 min) possessed the highest joint strength in terms of CFRP-CFRP homogeneous joining. Considering hybrid joining to AA2014, the carbon fibre reinforced PAEK composite (CFRP-5) showed the highest joint strength (when AA2014 samples were treated with silane agent and the CFRP samples were treated with 180 W plasma for 5 min).

Chapter 5: Results of the surface property and joint performance for the thermoplastic CFRPs

A further discussion and evaluation of the results presented in this chapter, including detailed comparisons between the three different thermoplastic CFRP samples in this chapter and the thermosetting CFRPs presented in Chapter 4, and also a comparison between the results for hybrid joining and homogenous joining, will be presented in Chapter 6.

Chapter 6: Discussion of results

6.1 Introduction

The results concerning the effect of the different surface pre-treatments were presented in Chapter 4 (for the thermosetting composite adherends) and in Chapter 5 (for the thermoplastic composite adherends). The effectiveness of the various surface pre-treatments was shown to depend upon various factors including the polymeric matrix used to form the composite, and the method used to manufacture the composite.

In this chapter, these effects are discussed in detail including the effect of CFRP manufacturing on subsequent surface pre-treatment and the final adhesive bonding, the effectiveness of the different surface treatments on the different CFRP adherends, and the difference between the thermoplastic CFRPs and the thermosetting CFRPs in terms of the surface pre-treatment and adhesive bonding. In addition, the effect of surface pre-treatments on aluminium alloy is summarised. The hybrid joints of CFRP/AA2014 are compared with the homogeneous joints CFRP/CFRP to develop a better understanding of the important mechanisms active in hybrid joining.

6.2 Effect of CFRP manufacturing

6.2.1 Effect of manufacturing methods

To evaluate the effects of the manufacturing methods on the subsequent adhesive bonding, the results for compression moulded CFRP-1 and the autoclaved CFRP-2 were compared. As was presented in Chapter 4, the two composites were made using the same carbon fibres and epoxy resin, and the as-prepared plates possessed very similar mechanical performance. Their significant difference, however, was in their surface topographies which resulted from the different manufacturing methods

employed. The compression moulded CFRP-1 had a relatively flat surface topography while CFRP-2 had a patterned surface topography due to the assistant materials used in the vacuum autoclave processing. These contrasting surface topographies can not only influence the curing of the adhesive, but they can also affect any subsequent surface pre-treatments that are performed. Both factors ultimately affect joint performance. Figure 6-1 compares the elementary composition, contact angle CA, and the homogenous SLS joint strength of CFRP-1 and CFRP-2 after acetone cleaning or plasma treatment.

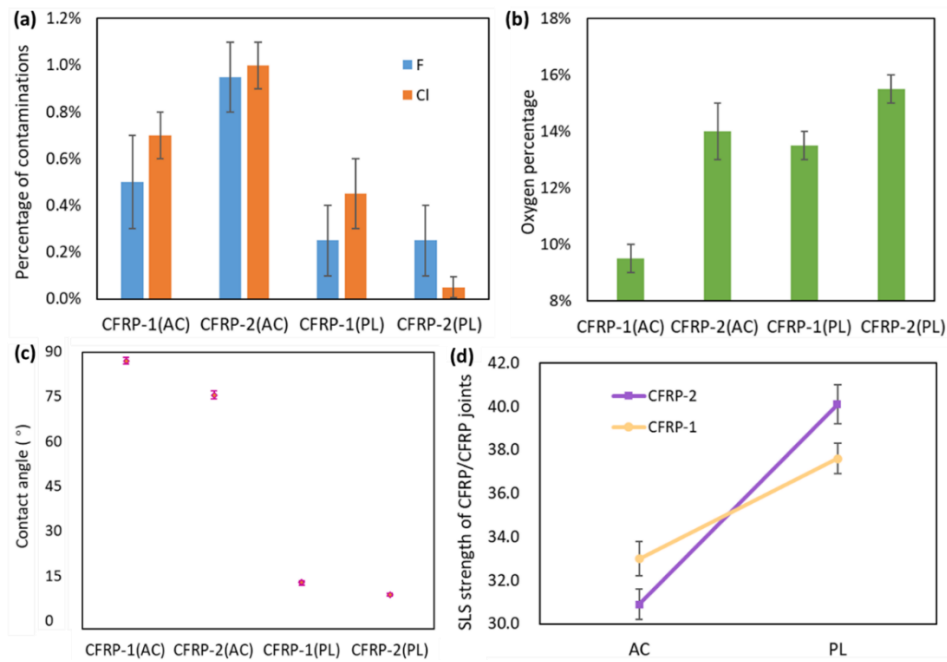


Figure 6-1. Comparison between CFRP-1 and CFRP-2 in terms of surface chemistry, CA, and corresponding CFRP/CFRP SLS joint strength after acetone cleaning (AC) or plasma treatment (PL). (a) Percentage of F contaminations or Cl on the pre-treated samples; (b) Percentage of oxygen on the pre-treated samples; (c) Contact angle on the pre-treated samples; (d) SLS strength of the homogenous joints.

Figure 6-1a shows the percentage of F and Cl contamination on the surfaces of the composites after either acetone cleaning or plasma treatment. The contamination (especially the F and Cl) are detrimental to adhesive bonding as they can introduce weak boundary layers reducing the stability of the interface [27,43]. As shown in Figure 6-1 b-d, in terms of the acetone cleaned samples, CFRP-2 had a lower CA but surprisingly a lower SLS joint strength in comparison to CFRP-1. The lower CA of CFRP-2 than CFRP-1 after acetone cleaning was mainly due to the greater concentration of O

on the surface as measured by the XPS analysis (Figure 6-1b,c) which is hydrophilic and the patterned surface which can improve the wettability. The lower lap shear performance of CFRP-2 joints compared to CFRP-1 joints, as shown in Figure 6-1d following acetone cleaning, resulted from the greater level of F and Cl contaminations (Figure 6-1a).

However, after the plasma treatment (i.e., 100 W, 1 min for CFRP-1 or CFRP-2), the performance of CFRP-2 joints was significantly improved, showing a higher SLS joint strength in comparison to CFRP-1 (Figure 6-1d). The superiority of the plasma treated samples of CFRP-2 resulted from i) the lower CA, ii) less F or Cl contamination and iii) the surface topography with increased surfaced area with more opportunity for mechanical interlocking effects to occur.

It is suggested that the diverse performance of CFRP-1 and CFRP-2 joints after acetone cleaning or plasma treatment may be because the manual cleaning operation or the high-energy plasma treatment had a different influence on the flat and patterned surfaces (Figure 6-2). In terms of acetone cleaning, more contamination remained on CFRP-2 surfaces as the manual operations of acetone wiping and washing were not as effective on a patterned surface compared to a smooth surface. When a surface is wiped using an acetone-infused cloth by hand, a flat surface is often easier to clean than an uneven one (Figure 6-2a). In other words, it is difficult to remove the contamination in the grooves of the patterned surface. During acetone washing, with a low kinetic energy, the contamination still remains in the grooves. Therefore, acetone cleaning is less effective on CFRP-2 than on CFRP-1. However, when plasma treatment was employed, the high-energy of the activated gas molecules interacting with the surface is powerful and effective in removing contaminations from all parts of the surface. The higher surface area of the patterned CFRP-2 becomes advantageous when plasma treated. During plasma treatment, a higher surface area enhances the exposure to the activated gas (O_2 plasma), which may not only accelerate the removal of contamination but also benefits the activation of the surface (Figure 6-2b).

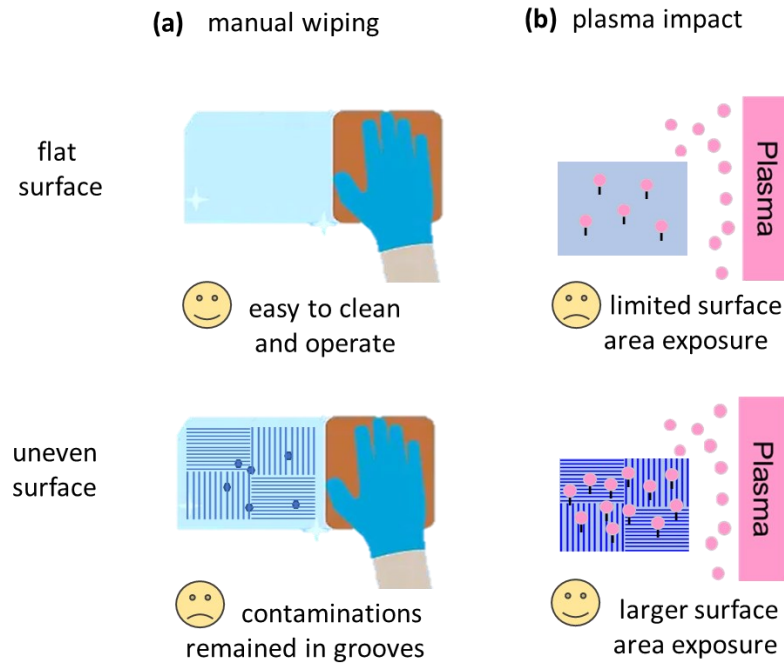


Figure 6-2. Sketch diagram of comparison between the flat surface (CFRP-1) and the patterned uneven surface (CFRP-2) in terms of the effect of acetone cleaning or plasma treatment. (a) Acetone cleaning: on a flat surface it is easy to operate the manual wiping and easy to clean the surface, while on an uneven surface contamination may remain in grooves after manual wiping; (b) Plasma treatment: the uneven surface has a larger specific surface area exposed to the plasma environment in comparison with the flat surface.

Considering next the grit blasted CFRP adherends, as was presented in Chapter 4, the joints consisting of CFRP-1 adherends perform better than the joints consisting of CFRP-2 adherends. One explanation may lie in their slightly different CA. Another explanation might relate to the relatively continuous occurrence of micro-groove and bumps on the surface. As shown schematically in Figure 6-3, the microstructures on CFRP-2 surface are not continuous, but on CFRP-1 surface the microstructures are relatively continuous. The discontinuous microstructures on CFRP-2 surface resulted from the bidirectional pattern under the impact of grit blasting (as was shown in Figure 4-1d and 4-2). The lower CA with continuous microstructures on the CFRP-1 adherend can realise a greater contact area with the adhesive and also realise less air retention in a bonded joint in comparison to the CFRP-2 adherend under a same pressure during curing process.

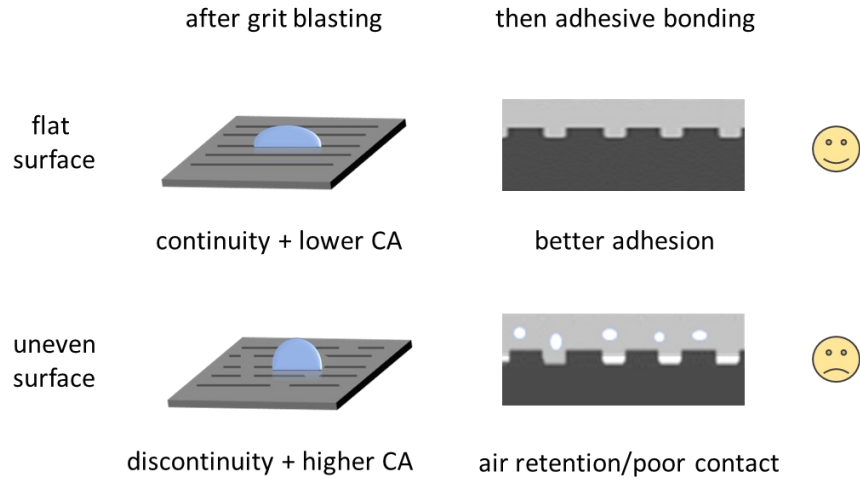


Figure 6-3. Schematic diagram of comparison between the flat surface (CFRP-1) and the patterned uneven surface (CFRP-2) after grit blasting.

6.2.2 Effect of fibre-matrix adhesion in the prepreg

The effect of the fibre-matrix adhesion in the prepreg was not considered when the comparison was made between CFRP-1 and CFRP-2 because they shared the same carbon fibres, epoxy resin, and a similar mechanical performance. In this subsection, the effect of the prepreg is considered via making comparison between CFRP-3 and CFRP-4. Their matrix resin was PEEK and their carbon fibres were of the same grade (T700 grade). They were made using the same technology (i.e., compression moulding, to have a flat surface. However, the difference between the prepreps of CFRP-3 and CFRP-4 lies in their fibre-matrix adhesion. This adhesion can be characterised by considering their values of 90° tensile strength and interlaminar shear strength. As shown in Figure 6-4a, as-prepared CFRP-3 has superior fibre-matrix adhesion in this respect to as-prepared CFRP-4.

After the surface treatment and adhesive bonding of homogenous SLS joints, all CFRP-3/CFRP-3 joint samples showed a higher SLS strength than CFRP-4/CFRP-4 joint samples regardless of which surface pre-treatment was performed (Figure 6-4b). The higher SLS strength of CFRP-3/CFRP-3 joints in comparison to CFRP-4/CFRP-4 joints are relevant to the superior fibre-matrix of the CFRP-3 prepreg in comparison to the CFRP-4 prepreg. The high 90° tensile strength and interlaminar shear strength of CFRP-3 demonstrate the strong adhesion between the carbon fibres and matrix resin in a CFRP.

These higher strengths indicate that the composite adherend is less likely to delaminate. When the surface pre-treatment is sufficient and not excessive, the fracture surface is more likely to be fully cohesive.

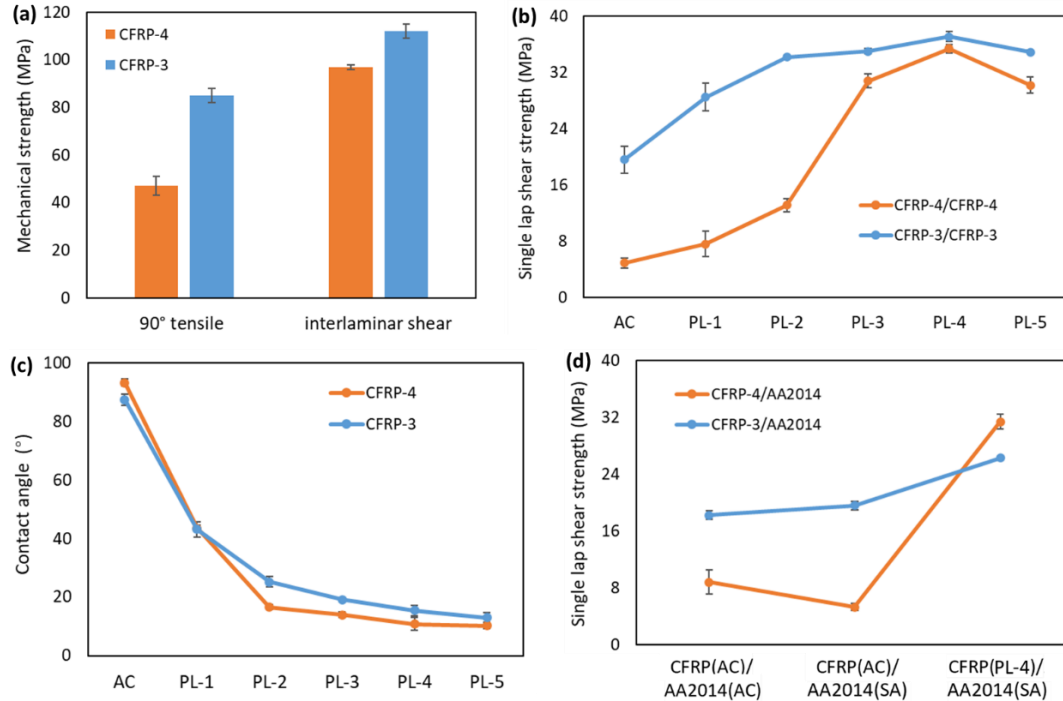


Figure 6-4. Comparison between CFRP-3 and CFRP-4 (a) 90° tensile strength and interlaminar shear strength of as-prepared CFRP; (b) SLS strength of CFRP/CFRP joining following different surface pre-treatments on CFRP adherends; (c) contact angle on CFRPs after a treatment; (d) SLS strength of CFRP/AA2014 joining following different surface pre-treatments on CFRP or AA2014 adherends. (AC: acetone cleaned, PL-1: 100 W, 0.5 min plasma pre-treated, PL-2: 100 W, 2 min plasma pre-treated, PL-4: 180 W, 2 min plasma pre-treated, PL-5: 180 W, 5 min plasma pre-treated, PL-5: 180 W, 8 min plasma pre-treated, SA: silane agent pre-treated.)

In the research concerning the adhesive-joint performance of homogenous joints CFRP/CFRP, the interfacial adhesion between the fibre and matrix was found to be significant. On the one hand, if the failure mode of the joints following mechanical testing included the interlaminar fracture of the CFRP adherend, the joint strength is controlled by the characteristics of the composite, including the interfacial adhesion between the carbon fibres and matrix resin in the CFRPs. On the other hand, if the failure mode of the joints included interfacial failure between the surface of the CFRP adherends and the adhesive, then the joint strengths were controlled by the CFRP-

adhesive adhesion. As shown in Figure 6-4a,b, CFRP-3, which had a 90° tensile strength and an interlaminar shear strength higher than CFRP-4, also showed higher SLS strengths.

However, considering next the hybrid joining of CFRP/AA2014, some other factors also influence the comparison of the joint strengths. As shown in Figure 6-4c, the acetone cleaned CFRP-4 showed a slightly higher CA than the acetone cleaned CFRP-3, while following plasma treatment ≥ 100 W for ≥ 2 min, CFRP-4 showed a slightly lower CA than the CFRP-3. Although this change did not noticeably affect the comparison in terms of homogenous joining (Figure 6-4b), the hybrid joining was affected. As shown in Figure 6-4d, in terms of the CFRP/AA2014 joints involving acetone cleaned CFRP, the CFRP-3 adherends gave rise to a much higher SLS strength than the CFRP-4 adherends. However, as for the CFRP/AA2014 joints involving plasma treated CFRP, the CFRP-4 adherends showed a remarkably superior performance in comparison to the CFRP-3 adherends. As delamination were not observed, the reason for a higher joint strength is due to the change in wettability, which relates to the spreading/fluidity of adhesive at the interface, playing a significant role in hybrid joining since the two adherends were asymmetrical. A further discussion focusing on the difference in adhesive bonding mechanism between the homogenous joining and the hybrid joining is presented in section 6.7.

6.2.3 Effect of processing parameters

An additional study concerning the manufacturing of CFRP-5 carried out by the author and collaborators is detailed in Appendix A1. This study investigated how the processing parameters of the surface treatment applied to the carbon fibres prior to forming the prepreg, and how the compression moulding pressure applied when consolidating the prepregs into CFRP panels, affected the mechanical performance of the manufactured CFRP (CFRP 5). From this research, it was clear that optimising the two processing parameters remarkably improved the mechanical performance (e.g., the tensile/compression/bending/interlaminar-shear strength) because the fibre-matrix interfacial performance of the prepreg were significantly improved. For

example, after an appropriate surface treatment to the carbon fibres, the impurities on the fibre surfaces were reduced and the resin wettability on fibres was improved. Also, increasing the compression moulding pressure (e.g., from 2 MPa to 4 MPa) effectively improved the fluidity of the thermoplastic resin, which can reduce the air retention during the CFRP manufacturing. Then the relationship between the fibre-matrix interfacial performance and the effect of surface pre-treatment prior to adhesive bonding as well as the final joint strength can be referred to the example as explained in section 6.2.2.

6.3 Effectiveness of pre-treatments on CFRPs

As was reviewed in Chapter 2, an appropriate surface pre-treatment for adhesive bonding should be neither insufficient nor excessive. Figure 6-5 illustrates schematically the requirements for an appropriate surface pre-treatment on CFRPs. The pre-treatment should be sufficient to achieve: a high degree of wettability (i.e., lower CA), it should encourage mechanical interlocking and/or physical or chemical interactions between the adhesive and adherend surfaces, and it should remove surface contamination (e.g., moisture, dust, grease, etc). Surface treatment should also not be excessive i.e., it is important to avoid secondary contamination (see the following subsection 6.3.2.1) and it should avoid causing damage to the adherend (e.g., exposure or breakage of fibres, cracking, or delamination; see the following subsections 6.3.1 and 6.3.2.2). Based on the above observations, in this section the effectiveness of the different surface pre-treatments as applied to the CFRPs investigated are evaluated.

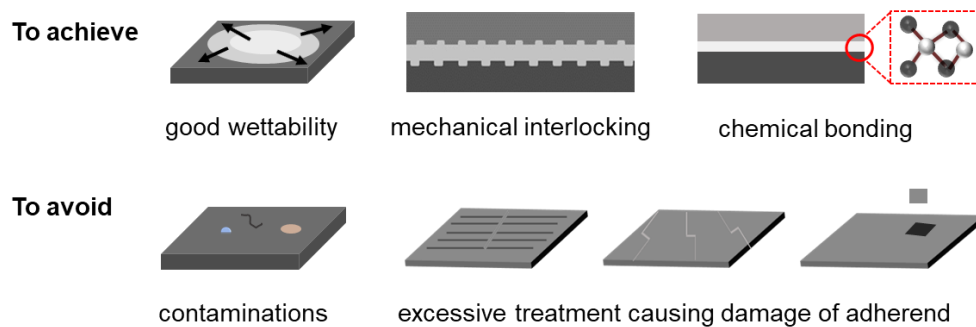


Figure 6-5. The summary of an appropriate surface pre-treatment for evaluation.

6.3.1 Grit blasting

Grit blasting was performed on the thermosetting composites CFRP-1 and CFRP-2. The results indicated that grit blasting can effectively enhance the SLS strength of the CFRP joints by improving mechanical interlocking. However, such improvement was realised by sacrificing the integrity of the CFRP adherends. Grit blasting tended to damage the surface region of the CFRP by exposing or even fracturing the fibres which then led to an interlaminar failure mode (i.e., failure within the CFRP) in the joint. In addition, grit blasting had the effect of reducing the value of X_{max} in the SLS tests, indicating that these SLS joints were less ductile.

6.3.2 Plasma treatments of different power/duration

6.3.2.1 Thermosetting CFRPs

The effectiveness of plasma treatment on thermosetting CFRP adherends was discussed in section 6.2. A plasma treatment of 100 W for 1 min can be regarded as a mild process, after which the adherends usually gave satisfactory results for surface properties (appropriate surface topography, surface chemistry and wettability) and subsequently of joint strength. Increasing the duration or power of the plasma treatment was shown to further reduce the CA (see Figure 4-4) but to only contribute to a similar or lower joint strength as shown in Table 6-1.

Table 6-1. SLS strength of CFRP-1/CFRP-1 and CFRP-2/CFRP-2 joints when plasma treatment of different time or duration was employed.

Joints	CFRP-1/CFRP-1	CFRP-1/CFRP-1	CFRP-1/CFRP-1	CFRP-2/CFRP-2	CFRP-2/CFRP-2
Plasma ^a	2 min, 100 W	1 min, 180 W	5 min, 180 W	2 min, 100 W	1 min, 180 W
SLS strength	37.9 ± 0.6 MPa	37.7 ± 0.6 MPa	31.6 ± 1.6 MPa	38.9 ± 0.5 MPa	39.2 ± 0.8 MPa

^a The typical plasma pre-treating for the thermosetting CFRP-1 and CFRP-2 was 100 W, 1 min. The corresponding SLS strength values for the CFRP-1(PL)/CFRP-1(PL) joints and CFRP-2(PL)/CFRP-2(PL) joints were 37.6±0.8 MPa and 40.1±1.1 MPa as mentioned in Chapter 4, respectively. This table show the results of an additional experiment for discussing the effectiveness of increasing the duration or power of the plasma pre-treating.

A lower CA should be beneficial for wettability but a surface with too low a CA can quickly attract moisture from the atmosphere which is harmful to the adhesion and

can lead to greater porosity in the cured bond-line, reducing the joint strength [179,180]. In addition, when the plasma was 180 W for >2 min, local fibre exposure was observed, which is detrimental (e.g., when the duration was 5 min: the SLS strength was reduced to 31.6 MPa, i.e., even lower than when using acetone cleaned adherends only).

6.3.2.2 Thermoplastic CFRPs

In terms of the adherends manufactured using thermoplastic CFRP, a more intense plasma treatment (i.e., using a much higher power or/and extended duration) was found to be required in comparison to treating the adherends manufactured thermosetting CFRP adherends. Taking CFRP-3 as an example, Figure 6-6 summarises how the plasma treatment affects the surface of the CFRP as the power or duration increase.

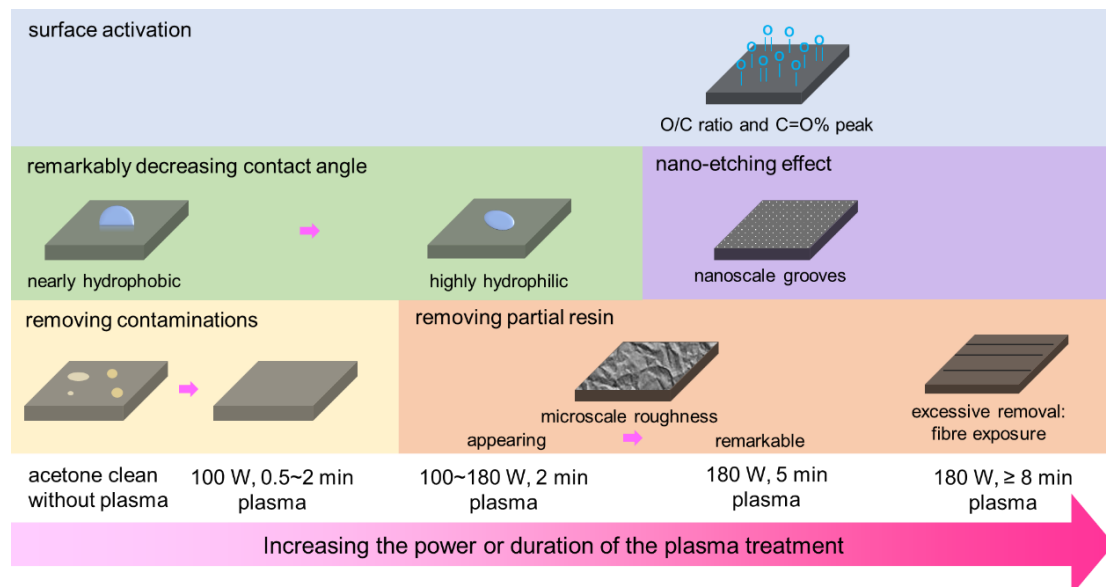


Figure 6-6. Influence of increasing power or/and duration of plasma treating on the surface of thermoplastic CFRP (taking CFRP-3 as an example).

Firstly, a 100 W or 180 W plasma treatment for up to 2 min can be regarded as a relatively mild treatment for thermoplastic adherends. During this treatment, the main modification to the CFRP surface was the removal of contamination together with a sharp decrease in CA. When the duration of the 180 W plasma was further increased (> 2 min), the CA only showed a small further decrease. However, a microscale roughness became noticeable on the surface as the plasma had removed some resin.

When the duration was increased further to 8 min, fibre exposure caused by excessive removal of resin was observed. The removal of contamination and the partial removal of surface resin are mainly physical changes to the surface as shown in Figure 6-7a.

Chemical reactions (Figure 6-7b) also took place during plasma treatment, but these usually require a much higher energy than for the physical changes. Hence, only when a relatively intense plasma treatment (e.g., 180 W, 5 min) was carried out, the effect of chemical reactions became remarkable. Also, although surface activation took place throughout the plasma treatment, the maximum value of the O/C ratio and the percentage of carbon-oxygen double bond occurred after the 180 W, 5 min plasma treatment. At the same time, the nano-etching effect of plasma became noticeable: nanoscale grooves appeared.

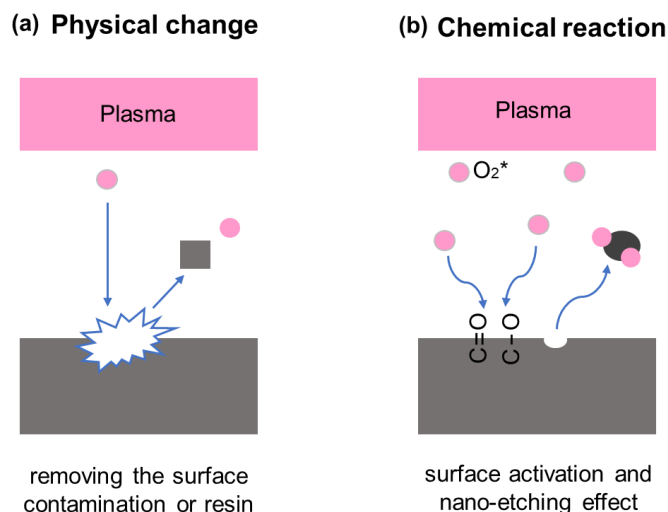


Figure 6-7. Changes in CFRP surface caused by plasma treatment. (a) Physical change: the removal of surface contamination or partial resin; (b) Chemical reaction: the surface activation by oxygen plasma and a nano-etching effect on surface topography.

As CFRP-3 has a chemical composition similar to CFRP-4 (i.e., carbon fibre/PEEK), the effect of increasing the plasma power or/and duration on CFRP-4 was somewhat similar to the effect on CFRP-3. CFRP-5 also showed a similar response to these plasma treatments except that the fibre exposure was not observed in this study because CFRP-5 was manufactured using a different grade carbon fibre and a new PAEK resin with higher toughness in comparison to CFRP-3 or CFRP-4. The higher toughness PAEK resin was more resistance to erosion by the plasma treatment.

6.4 Effectiveness of pre-treatments on Al

6.4.1 Plasma treatment

The trace levels of carbon on the acetone cleaned AA2014 surfaces originate from oil/grease contamination and perhaps some residual acetone. Plasma treatment was shown to be more effective in removing these contaminations in comparison to acetone cleaning. However, neither acetone cleaning nor plasma treatment were sufficient when applied to the AA2014 surfaces as the SLS strength values of these joint samples were very low and a large area of interfacial failure was observed during their SLS joint tests.

6.4.2 Grit blasting

In comparison to plasma treatment, grit blasting was much more effective when applied to the aluminium alloy adherend surfaces for reducing the degree of interfacial failure and improving the SLS strength. However, for the joints made with grit blasted AA2014 samples, the failures remained partially interfacial even when the resulting SLS strength exceeded 27 MPa. Figure 6-8 proposes the failure mechanism for homogenous and hybrid SLS joints comprising grit blasted AA2014 adherend(s), which is consistent with the interfacial appearance after failure (e.g., in Figure 4-6m-o).

Within the central area of the SLS joint overlap, the loading is mainly by shear and failure is mostly of the sliding mode (mode II) fracture. The grit blasted surfaces led to improved mechanical interlocking which was effective in increasing the resistance to mode II fracture. This is consistent with the experimental observations, where the central part of the overlapped region usually failed cohesively. However, at the ends of the overlap, loading is mainly by tensile peel and failure is mostly of the opening mode (mode I) fracture type. The surface topography after grit blasting may be insufficient to create mechanical interlocking when the loading is mode I, and therefore the interfacial failure remains at the ends of the overlap.

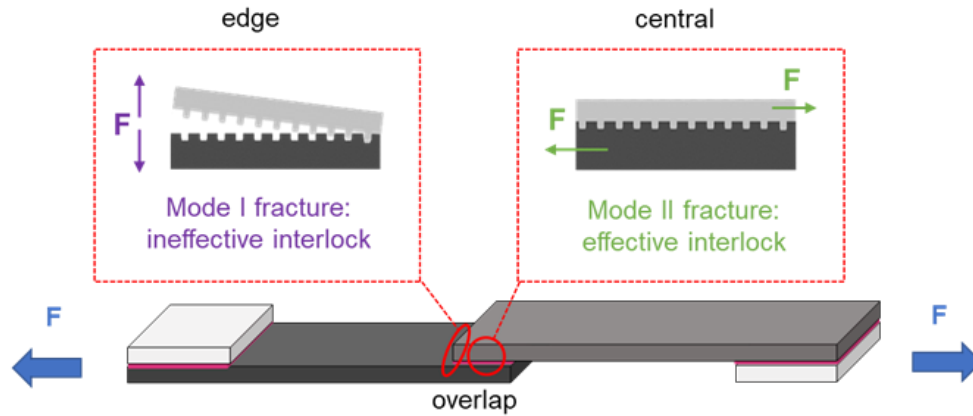


Figure 6-8. Mechanism of mechanical interlocking in SLS joints: effective for mode II fracture in the central area of overlap but ineffective for mode I fracture at the edge of overlap.

6.4.3 Silane agent treatment

As a surface pre-treatment method for AA2014, the silane agent treatment in this study was inferior to grit blasting in improving SLS strength of AA2014/AA2014 homogenous joints. It is suggested that in this study, mechanical interlocking may play a more significant role than the chemical bonding. However, silane agent treatment was satisfactory and effective in bonding AA2014 to the CFRPs. A detailed discussion in section 6.7 concerning the difference between homogenous joining and hybrid joining offers an explanation of this observation.

6.5 A comparison of results for thermosetting and thermoplastic matrix composites

To illustrate the difference between the thermosetting and the thermoplastic CFRPs in their surface pre-treatment and adhesive bonding, thermosetting CFRP-1 was compared to the thermoplastics CFRP-3, CFRP-4, and CFRP-5, all of which were manufactured via the same technology (i.e., compression moulding). Table 6-2 summarises the advantages and disadvantages of using the thermosetting or the thermoplastic matrix resin in the composite manufacturing process when the composites further require surface treatment and are used as adherends in CFRP/CFRP adhesive bonding.

Table 6-2. The advantages and disadvantages of the thermosetting or the thermoplastic matrix when the composite is used in surface treatment for CFRP/CFRP adhesive bonding.

	Thermosetting (epoxy)	Thermoplastic (PEEK or PAEK)
After cleaning with no further surface activation	A relatively high joint strength when the adhesive is epoxy	A very low joint strength with fully interfacial failure
Cleaning effect of plasma	Effective; very fast	Effective; fast but slower than the thermosetting
Fibre exposure (detrimental)	Can occur using relatively mild plasma, e.g., 180 W, 2 min	Taking place when the power is high or the duration is long, e.g., 180 W for over 8 min
Plasma nano-etching effect	Not remarkable as fibre exposure come first	Can be observed; beneficial to adhesive bonding
General reaction to plasma treatment	Sensitive to plasma: a more sharply reducing CA, resulting in a high joint strength after a mild plasma treating process, e.g., 100 W, 1 min	High matrix toughness resists erosion: enables long durations for surface activation with minimised damage, room for optimising the parameters
Advantage for an industrial process	Saving time and energy during a plasma treatment	High fault tolerance (not sensitive to small changes in plasma processing parameters)

6.5.1 Differences in SLS strength

Figure 6-9 compares the thermosetting CFRP-1 and the thermoplastic CFRP-3, CFRP-4, and CFRP-5 adherends in terms of the SLS strength of their homogenous joints with and without plasma surface pre-treatment. As for the acetone cleaned adherends with no further surface activation, the thermosetting epoxy-based composite (CFRP-1) showed a much higher SLS strength than the thermoplastic CFRPs. The higher strength results from the surface chemical composition of the thermosetting CFRP, i.e., the epoxy-based matrix which enabled higher adhesion to the epoxy-based adhesive. The thermoplastic CFRP-3, which had a noticeably better interfacial performance than the thermoplastic CFRP-4 and CFRP-5 (as explained in section 6.2.2), showed a SLS strength

higher than measured for the CFRP-4 and CFRP-5 joints. However, it was still much lower than that measured for the thermosetting epoxy-based CFRP-1. Hence, if the matrix resin of the composite is not compatible with the adhesive used for bonding, the pre-treatment which activates the adherend surface for the thermoplastic composites is necessary.

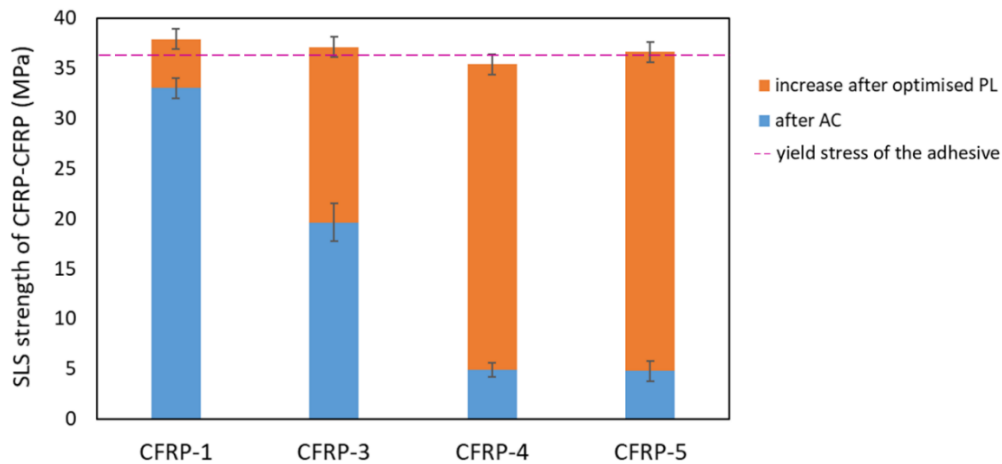


Figure 6-9. Comparison between thermosetting CFRP-1 and thermoplastic CFRP-3, CFRP-4, and CFRP-5 in terms of the SLS strength of homogenous joining with and without plasma surface pre-treatment.

After a plasma treatment when the processing parameters were optimised for each CFRP adherend respectively, the values of SLS strength of the homogeneously bonded thermoplastic CFRPs increased dramatically (e.g., CFRP-5: increased by 660%). The various values of SLS strength attained a value near the value for thermosetting epoxy-based CFRP-1. In addition, all optimised plasma treated CFRPs in this PhD study show a SLS strength near or higher than the yield stress of the adhesive employed in the experiment. It is confirmed that plasma treatment is valuable and effective when applied to common CFRPs, either the thermosetting or the thermoplastic adherends.

6.5.2 Different responses to the processing parameters of plasma treatment

When applied to the different types of CFRP, although the plasma treatment can be similarly effective in obtaining a high joint strength, the plasma treatment changes the surface conditions in different ways. Figure 6-10 compares the thermosetting CFRP-

1 and thermoplastic CFRP-4 in terms of the effect of plasma treatment in reducing the CA and eroding the resin which leads to fibre exposure. Here the comparison is made between the two CFRPs because not only were they manufactured via the same technology, but also they were made using the same grade carbon fibre from the same company: comparing CFRP-1 to CFRP-4 therefore demonstrates how the different types of matrix resin can affect the response of the composite to plasma treatment.

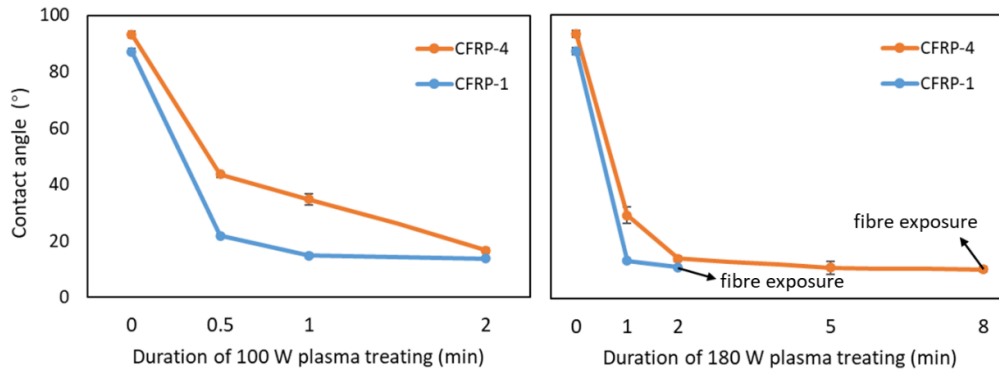


Figure 6-10. Comparison between thermosetting CFRP-1 and thermoplastic CFRP-4 in terms of the effect of plasma treatment employing different processing parameters in CA reduction and fibre exposure.

As shown in Figure 6-10, the CA on the thermosetting CFRP-1 was reduced much more sharply than the CA on the thermoplastic CFRP-4 when the duration of 100 W or 180 W plasma treatment was <2 min. The thermoplastic CFRP-4 was less sensitive to plasma treatment than the thermosetting CFRP-1 because: i) the thermoplastic PEEK has lower initial surface energy than the thermosetting epoxy resin, ii) the thermoplastic PEEK has a higher toughness to resist erosion by the plasma in comparison to the thermosetting epoxy (where the matrix is rapidly eroded).

The higher erosion resistance slowed down the removal of the matrix, reducing fibre exposure. For example, in 180 W plasma treatment, fibre exposure takes place on CFRP-1 after 2 min while on CFRP-4 the duration should be ≥ 8 min. This means the tough thermoplastic PEEK matrix can sustain a long treatment duration for surface activation or plasma nano-etching, while for the thermosetting epoxy matrix, the nano-etching effect failed to develop as the rate of matrix erosion was too great, so that fibre exposure (or even fibre breakage, or other types of damage of CFRP) usually occurred instead. Hence, thermoplastic CFRPs have great potential for use in industry, having

the potential for optimising the parameters of the treatment to improve the joint strength. Additionally, a similar conclusion can be drawn if the CFRP-1 adherends are compared with those of CFRP-3 or CFRP-5.

To further explain how increasing the duration or/and power of plasma treatment influences the SLS strength of CFRP/CFRP, here two concepts are introduced, i.e., the efficiency in SLS strength and the energy cost of plasma treatment. The efficiency is the proportion of the SLS strength attained after a surface treatment compared to the maximum value attained after the optimum treatment. The energy cost of a plasma treatment is determined by multiplying the power of the treatment by its duration.

Figure 6-11 establishes comparisons between the treatment of thermosetting and thermoplastic composite adherends in terms of their efficiency-energy cost curves. The thermosetting CFRPs maintain a high efficiency (>90%) in a mild plasma treatment process (e.g., the energy cost is less than 20-30 kJ). The thermoplastic CFRPs require a much higher energy cost (e.g., 54 kJ for CFRP-3 or CFRP-4) to achieve the 100% efficiency but the range of energy costs to maintain relatively high efficiency is very wide, which should be beneficial in practical industrial production. For example, as shown in Figure 6-11a, the efficiency for thermosetting CFRP-1 fell to 83% when the plasma energy cost was 54 kJ; however, when range of the plasma energy cost was 22-86 kJ, the efficiency for thermoplastic CFRP-4 remained over 85%.

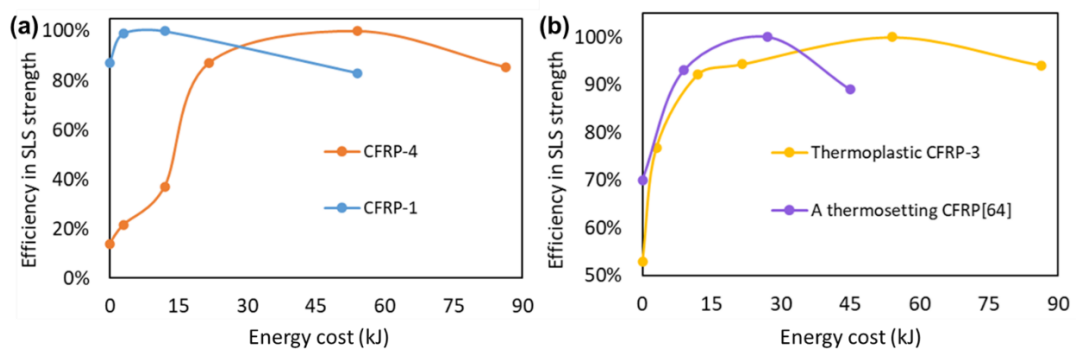


Figure 6-11. Comparisons in terms of the efficiency-energy cost curve of plasma treatment. (a) Between thermosetting CFRP-1 and thermoplastic CFRP-4. (b) Between a thermosetting CFRP in a previous paper [64] and thermoplastic CFRP-3.

To illustrate further, thermoplastic CFRP-3 has been compared with a

thermosetting CFRP reported in the literature [64]. This comparison can be made to draw more comprehensive conclusions because the carbon fibre prepreg employed in [64] had a very similar interfacial performance, i.e., the factors related to interfacial performance of the prepreg can be discounted in this discussion. As shown in Figure 6-11b, the thermoplastic CFRP requires a higher-energy plasma treatment to achieve the 100% efficiency than for the thermosetting matrix CFRP. However, for the thermoplastic CFRP, plasma treatments in the range of 12-86 kJ can provide over 92% efficiency. Although fibre exposure occurred in the 86 kJ treatment, the efficiency in SLS strength still reached 94%. To summarise for industry, employing the epoxy-based thermosetting composites can save time and energy costs, while the thermoplastic PEEK or PEAK based composites show a high tolerance to variation (faults) in surface pre-treatment.

6.6 Comparison to materials in other studies

To understand how the composite adherends and plasma treatments employed in the present study compare with those reported previously in the literature, a comparison with some previously published work is now presented. Figure 6-12 compares the maximum SLS strength values (i.e., when the optimised plasma treatment is employed) of CFRP/CFRP joints bonded using a same adhesive film as used in the present study (i.e., the AF163-2 series from 3M, USA).

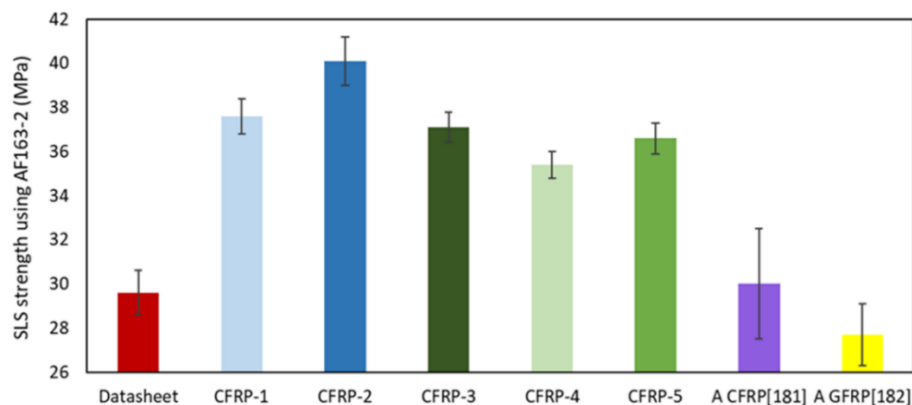


Figure 6-12. The CFRP adherends studied in the present work in comparison to previous studies [181,182] in which the adhesive is AF163-2.

The five different composite adherends employed in this PhD study are compared with i) degreased and abraded CFRP recorded in the datasheet of AF163-2, ii) a carbon fibre reinforced epoxy resin after peel-ply treatment [181], and iii) a glass fibre reinforced epoxy resin after peel-ply treatment [182].

Kadioglu et al [181] reported that the SLS strength for a peel-ply treated thermosetting CFRP was approximately 30 MPa. Demiral and Ferhat [182] reported that the value for a peel-ply treated GFRP was approximately 27.7 MPa. The datasheet of the adhesive AF163-2 from 3M company shows that the company had degreased and abraded some CFRPs for homogenous joining and the SLS strength was around 29.6 MPa. However, it is also shown in the datasheet that the ultimate strength and yield stress of the adhesive was up to 47.9 MPa and 36.2 MPa, respectively. The two values indicate that there was potential for enhancing the SLS strength either by employing CFRPs with superior interfacial/mechanical performance or by employing alternative surface treatments. In the present study, the SLS strength values of the homogenous bonded thermosetting CFRPs (i.e., CFRP-1 and CFRP-2) were around 38-40 MPa and for the thermoplastic CFRPs (i.e., CFRP-3, CFRP-4, and CFRP-5) the values were in the range 35-37 MPa.

6.7 The mechanisms of hybrid joining

The performance of a homogenous joint (one possessing two identical adherends) depends to a significant extent upon the surface properties and condition of the adherends. Considering hybrid joints (joints possessing dissimilar adherends), it was found in this study that the dissimilarity (e.g., in the surface topography or the surface chemistry) between the two adherends in a joint is a significant factor which can negatively affect the joint strength. Inferred from previous papers [183,184], the difference in the coefficient of thermal conductivity or thermal expansion may affect the adhesive curing process, e.g. by allowing residual stresses to develop in the joint. Also, defects resulting from adhesive curing [185-187] or a highly asymmetric structure may contribute to stress concentrations, reducing the joint performance.

In this study, the dissimilarity in the surfaces of the two adherends are highlighted. The mechanisms proposed for hybrid joining are summarised as follows: in the case of hybrid joining, the pressure exerted on the adhesive was not uniformly distributed. In a non-vacuum environment, this non-uniformity may increase the possibility that voids will form as well as increase the susceptibility to trapped air or moisture during the heating and cooling imposed during joint manufacture. When an adhesive with low fluidity (e.g., a highly viscous adhesive, or an adhesive film i.e., what is used in the present study) is employed, such an effect may be significant, finally affecting the performance of hybrid joints.

Hence, in hybrid joining, not only are the surface topography, surface chemistry, and wettability of each adherend important but also important is the dissimilarity between the surface properties of two adherends. This finding offers an important new proposal for the industry: that the effect of dissimilarity of the two adherends should be considered especially when film adhesives or highly-viscous adhesives are used.

In the next sections, a detailed analysis is presented of some examples in this study, which compare the homogenous joining and hybrid joining to exemplify the above “dissimilarity” mechanism.

6.7.1 Examples in the thermosetting CFRPs

When the pre-treatment applied to the CFRP adherends was acetone cleaning or plasma treatment, the value of SLS strength of CFRP-AA2014 hybrid joints was usually an intermediate value between the strength of the homogeneous joints CFRP/CFRP and or AA2014-AA2014. Also, the value of the strength of the hybrid joints was much closer to the lower value, i.e., the strength of AA2014-AA2014 joints. For example, (as was presented in Table 4-5) the SLS strength of CFRP-1(PL)/AA2014(PL) (24.3 ± 1.1 MPa) is between the corresponding strengths of CFRP-1(PL)/CFRP-1(PL) (37.6 ± 0.8 MPa) and AA2014(PL)/AA2014(PL) (19.0 ± 0.8 MPa), and the values are much closer to AA2014(PL)/AA2014(PL). These samples showed such a trend because interfacial failure on AA2014 was the main failure mode. The joint performance was limited by its weakest link- here the weaker interface. This result is understandable according to

current weak boundary layer theory: aluminium alloys will have a naturally grown oxide layer which may be weak and highly variable in thickness.

However, in the joints where the pre-treatment for adherends was grit blasting, the values of SLS strength did not always show the above trend. For example, CFRP-1 showed the above trend while CFRP-2 did not. In terms of CFRP-1, the strength of the hybrid joints was 33.6 ± 1.2 MPa, which is between 37.6 ± 0.8 MPa (for CFRP-1 homogenous joints) and 32.3 ± 0.1 MPa (for AA2014 homogeneous joints). However, considering the results for the second type of CFRP adherends, CFRP-2, the SLS strength of the hybrid joints is $27.8 \text{ MPa} \pm 0.1 \text{ MPa}$, lower than either 35.7 ± 0.7 MPa (for CFRP-2 homogenous joints) or 32.3 ± 0.1 MPa (for AA2014 homogeneous joints). A complex failure mode was observed in the hybrid joints following grit blasting, which was not observed in other joints investigated here and has seldom been reported in the literature previously. The failure mode involved a combination of interfacial failure on the AA2014 adherend, cohesive failure in the adhesive, and interlaminar failure in the CFRP adherend. (The reasons for these types of failure were analysed in Chapter 4 or in this chapter). It is suggested that these types of failure affect the SLS strength in different ways. Therefore, the SLS strength of a hybrid joint can be in-between or lower than either homogenous joint.

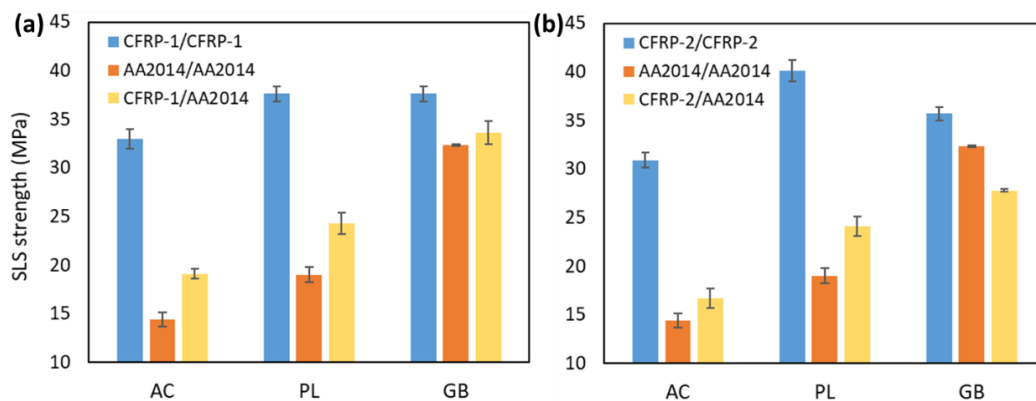


Figure 6-13. SLS strength of hybrid joints (CFRP/AA2014) in comparison to homogenous joints (CFRP/CFRP, AA2014/AA2014). (a) CFRP-1; (b) CFRP-2.

Figure 6-14 helps to explain the superiority of CFRP-1 over CFRP-2 in hybrid joining by showing the fracture surfaces of the joints where interfacial failure occurred. The fracture surfaces (as shown in Chapter 4) were further observed via an optical

microscope, and the images were analysed using Image J to capture the defects and to calculate their area %, as was described in section 3.7.

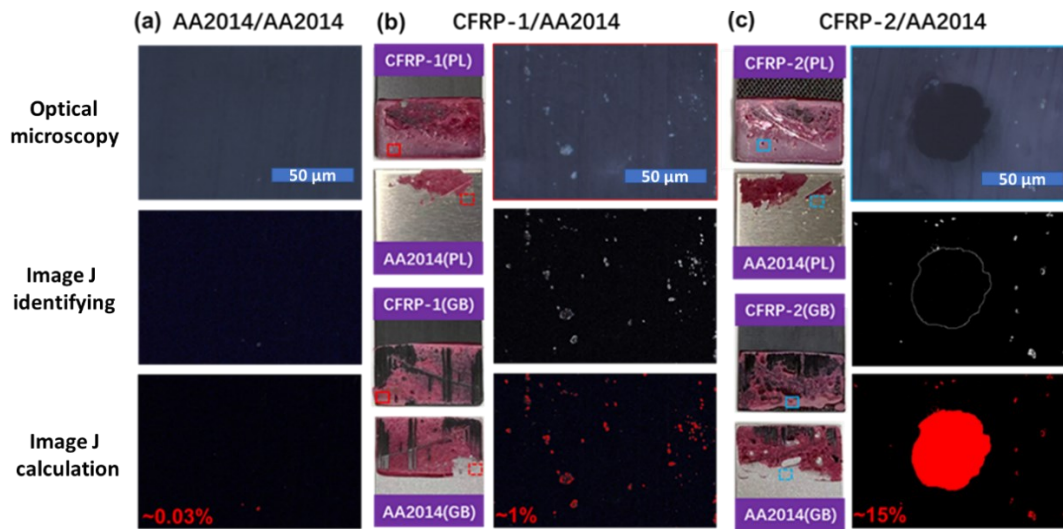


Figure 6-14. Defects on the adhesive layer where interfacial failure took place on AA2014 side. (a) homogenous bonding of AA2014, almost no defects present; (b) CFRP-1/AA2014 joining, some minor defects no matter what surface pre-treatment was employed; (c) CFRP-2/AA2014 joining, large defects observed regardless of the surface pre-treatment was employed.

Considering the CFRP-1(GB)/AA2014(GB) joints as shown in Figure 6-14b, minor defects (in the range of 3-8 μm in diameter) can be observed on the surface of adhesive layer, accounting for about 1% of the total surface area. Considering next the CFRP-2(GB)/AA2014(GB) joints as shown in Figure 6-14c, much larger defects (around 50 μm in diameter) were sometimes (2 out of 6 repeats) observed which account for approximately 15% of the total surface area. The joints with the fewer surface defects (i.e., (b) in CFRP-1/AA2014 joints) exhibited superior interfacial contact with the adherend, which resulted in the higher joint strength.

The joints formed with the adherends CFRP-1 exhibited higher joint strength than joints formed with CFRP-2 in their hybrid joints when bonded to AA2014, even when CFRP-2 exhibited higher strength in their homogenous joints. In comparison to CFRP-2, the surface topographies of CFRP-1 after a pre-treatment (i.e., relatively flat surface without uneven pattern) were more similar to the surface topographies of AA2014. As illustrated in Figure 6-15, the similarity in surface topography can reduce trapped air

or bubbles to minimise the defects. Also, the similarity with fewer defects present improves the joint performance.

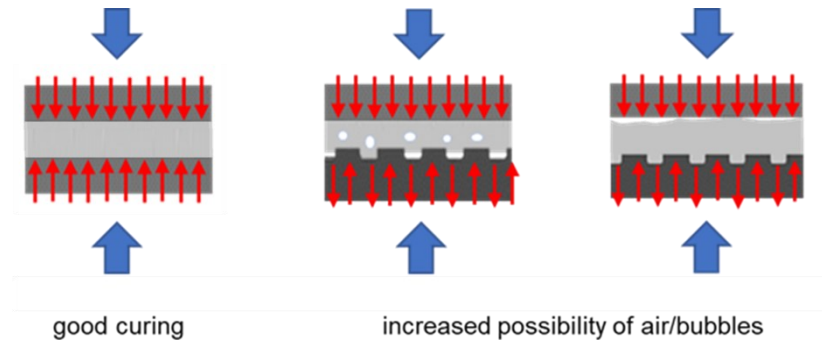


Figure 6-15. The effect of dissimilarity in surface property during the curing process of adhesive: the dissimilarity in surface property (e.g., the asymmetrical surface topographies of the two adherends as illustrated in this figure) can increase the possibility of trapped air or bubbles during the curing process of adhesive bonding, causing defects or/and poor interfacial adhesion.

To further show the significance of such an effect, CFRP-2(PL) and AA2014(GB), which showed the highest SLS strength in their respective homogenous joints, were bonded together. As shown in Figure 6-16, the SLS strength measured was only 30.3 ± 1.1 MPa, lower than joint samples CFRP-1(GB)/AA2014(GB) and even lower than joint samples AA2014(GB)/AA2014(GB).

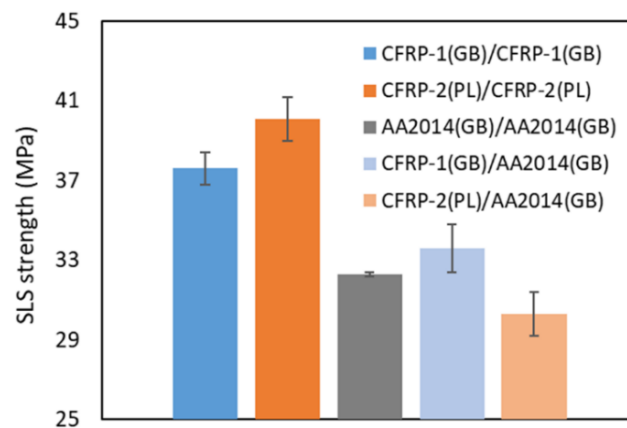


Figure 6-16. SLS strength of homogenous joints of grit blasted CFRP-1, plasma treated CFRP-2, and grit blasted AA2014 in comparison to hybrid joints of CFRP-1(GB)/AA2014(GB) and CFRP-2(PL)/AA2014: plasma treated CFRP-2 show the highest SLS strength in homogenous joining but show a lower SLS strength in the hybrid joining to aluminium alloys.

In this case, the superiority of one adherend which can realise stronger interaction

with the adhesive could not compensate for the influence of increasing the dissimilarity between the two adherends.

6.7.2 Examples in the thermoplastic CFRPs

In hybrid joining, the two adherends have different levels of adhesion to the adhesive. Therefore, on one adhesive/adherend interface there was relatively weak interfacial bonding while on the second adhesive/adherend interface there was relatively strong interfacial bonding. The results presented in Chapter 5 indicate that the SLS strength can be improved by strengthening the initially relatively-weak interface through surface pre-treatments, while strengthening the initially relatively-strong interface usually does not improve joint performance.

For example, in CFRP-4 or CFRP-5 hybrid joining to AA2014, when the surface pre-treatment was acetone cleaning with no further treatment, the weaker interface was on the CFRP-4 or CFRP-5 side as the fully interfacial failure of the joint was observed on this side. Applying appropriate surface pre-treatment to the CFRP-4 or CFRP-5 side could remarkably increase SLS strength of the hybrid joint (Figure 6-17). However, only applying pre-treatment to the AA2014 side, which was initially stronger than the CFRP-4 or CFRP-5 side, resulted in a reduction in the SLS strength (Figure 6-17) since the dissimilarity between the two adherends was increased.

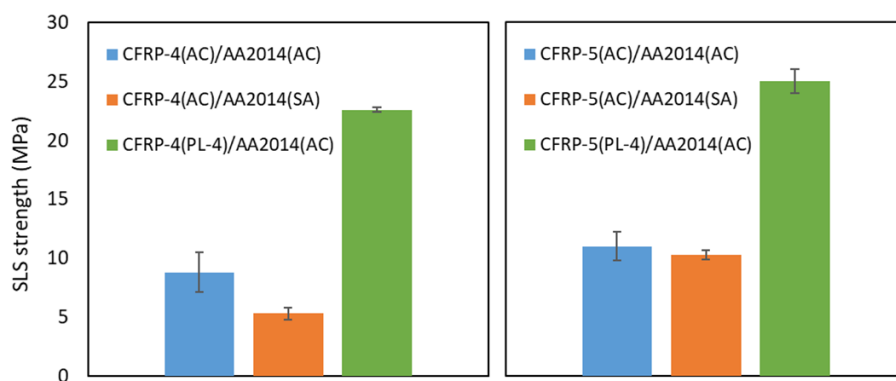


Figure 6-17. SLS strength of hybrid joints of CFRP-4/AA2014 and CFRP-5/AA2014 after different surface pre-treatment: only adding pre-treatment on the AA2014 side reduces the SLS strength while only adding pre-treatment on the CFRP side increases the SLS strength.

In terms of the surface pre-treatments on the aluminium alloy, the silane agent treatment was inferior to grit blasting in the homogenous joints of AA2014/AA2014 but was competitive to grit blasting in the hybrid joints of CFRP/AA2014, as shown in Figure 6-18. Silane agent treatment applied to AA2014 adherends was satisfactory when considering the hybrid joints of CFRP/AA2014, as the treatment coated the carbon and oxygen composition (i.e., organic functional groups) onto the surface (see Appendix A2). This enable the aluminium adherend to possess a surface chemistry compatible with the epoxy adhesive and the CFRP adherends, i.e., reducing the difference between the two adherends in respect of surface chemistry.

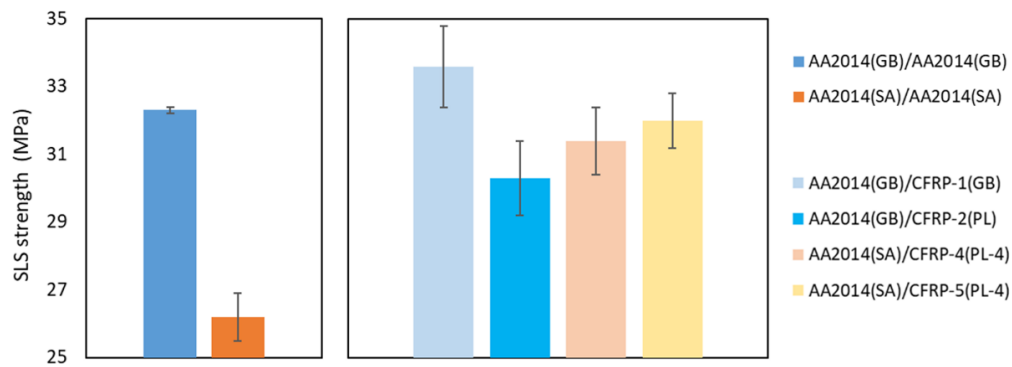


Figure 6-18. SLS strength of AA2014/AA2014 and CFRP/AA2014 joints after different surface pre-treatment: in terms of the surface pre-treatment on AA2014, silane agent treatment (SA) was inferior to grit blasting (GB) in the homogenous joining but was competitive in the hybrid joining.

6.8 Summary

In this chapter, the results from the testing of SLS joints formed using adherends manufactured from different CFRPs following a diverse range of surface pre-treatment were discussed. Firstly, the factors related to manufacture of the CFRP adherend materials (e.g., manufacturing methods, processing parameters, the types of carbon fibre/matrix, and the interfacial properties of the prepreg) which strongly influence the mechanical performance and surface properties of manufactured CFRPs, was discussed. It was found that these factors can affect the effectiveness of a surface pre-treatment and therefore affect the joint performance (see detailed conclusions in Chapter 7).

Secondly, the effects of the plasma treatment parameters employed were discussed. It was concluded that plasma treatment is usually an effective surface treatment method for the CFRPs. When the plasma treatment parameters were optimised, plasma treatment was effective in removing surface contamination, improving the wettability, activating the surface chemistry, and creating surface micro/nano-structures. It was also notable that thermosetting CFRPs and thermoplastic CFRPs showed very different responses to the plasma treatment parameters. The pre-treatment of thermoplastic CFRPs, in comparison to the thermosetting CFRPs, required a much longer duration of plasma treatment.

Thirdly, by comparing the joint strengths in the present study with some published results in the literature and the datasheet from the adhesive manufacturer, the optimised surface pre-treatment for the CFRP adherends in this study are sufficient and effective.

Finally, the differences between hybrid joining and homogenous joining were discussed with respect to their various surface pre-treatments. It was concluded that in homogenous joining, surface pre-treatment to optimise the surface chemistry, surface topography, and wettability is an essential step towards achieving high joint strength. However, considering hybrid joining, it was concluded that not only are the surface properties of each adherend important, but also an important factor affecting the joint performance is the dissimilarity between the two adherends. This dissimilarity can increase the likelihood of defects or stress concentrations being present, reducing the hybrid joint performance.

The conclusions of this research are presented in Chapter 7, together with recommendations for future work.

Chapter 7: Conclusions and re-commendations for future work

7.1 Conclusions

In this study, a diverse range of aerospace-grade CFRP adherends were prepared, pre-treated, and adhesively bonded to manufacture CFRP/CFRP homogenous joints or CFRP/Al hybrid joints using an aerospace epoxy-film adhesive. The effectiveness of a wide range of surface pre-treatments applied to either the CFRP adherends or to aluminium alloy adherends were investigated. The manner in which the pre-treatments were applied to the various adherends affected the surface topography, surface chemistry, wettability, and the final joint performance in single lap shear joint testing was investigated in detail. The effects of the manufacturing route used to form the composite adherends (i.e., compression moulding versus vacuum autoclaving) on the subsequent joint strength was studied. The effects of the treatments on the various adherend materials were also studied, and in particular, the effects of applying different levels of oxygen plasma treatment to the surfaces of thermosetting and thermoplastic CFRPs and also to aluminium alloy adherends were investigated. A comparative study between homogenous joining and hybrid joining was presented. Based on the above work, the following conclusions can be drawn.

7.1.1 The thermosetting CFRPs

The surface pre-treatment and adhesive bonding of fibre composites based upon thermosetting matrices was investigated first. Two epoxy-based carbon-fibre composites were studied, CFRP-1, which had been manufactured using compression moulding, resulting in an initially smooth surface and CFRP-2, which had been

manufactured using an autoclave where the release fabric assistant materials used had imparted a patterned surface to the composite. The two composites were otherwise very similar, possessing almost identical mechanical properties.

The surface pre-treatments of acetone cleaning, oxygen plasma treatment and grit blasting were applied to the composite adherends such that the control surface was acetone cleaned, and then this was followed by either plasma treatment or grit blasting. Treated surfaces were analysed using SEM, EDX, and CA measurement. Adhesive joints were prepared by bonding adherends with a structural epoxy-film adhesive (AF163-2) to form single lap shear joints, which were tested according to the standards GB/T 33334 and ISO 4587.

In comparison to acetone cleaning, the plasma treatment or grit blasting on either CFRP-1 or CFRP-2 can further remove surface contamination and results in a superior joint performance. They can change some surface properties, e.g., plasma treatment remarkably improves the wettability with minor changes in surface topography, while grit blasting remarkably changes the surface topography.

Considering CFRP-1 (flat surface) plasma treatment or grit blasting were equally effective in preparing the surfaces for adhesive bonding with both techniques increasing the lap shear strength by 13.9% relative to the control condition. Considering CFRP-2 (patterned surface) plasma treatment was more effective in preparing the surfaces for adhesive bonding than grit blasting, with plasma treatment increasing the lap shear strength by 29.8% and grit blasting increasing it by 15.5%, relative to the control condition. These are important conclusions as grit blasting is a slow and manual process which is difficult to apply to large surface areas in a consistent manner. Plasma treatment was equally effective as a surface pre-treatment on the flat surfaces but was more effective on the patterned surfaces than grit blasting. Thus, plasma treatment can be considered as an effective replacement for grit blasting on CFRP adherends manufactured using an epoxy matrix, regardless of whether the manufactured surface condition was flat or patterned.

Considering the joints formed using aluminium alloy adherends (Al/Al) then it was clear that plasma treatment was insufficient to avoid interfacial failure and grit blasting

significantly outperformed plasma treatment in the lap shear joint tests. Whilst plasma treatment increased the lap shear strength by 31.9%, grit blasting increased the strength by 124.3%, relative to the control. Importantly, the plasma treated joints failed in an interfacial manner, whilst the grit blasted joints exhibited predominantly cohesive failures in the adhesive layer.

The hybrid joints (dissimilar adherends) formed by either CFRP-1 (flat) or CFRP-2 (patterned) bonded to the aluminium alloy adherends tended to exhibit joint strengths limited by the weaker interface. Whilst plasma treatment gave modest improvements in joint strength compared to the control condition, as grit blasting was the more effective pre-treatment on aluminium alloy, then this followed through to the hybrid joints with the strength of the CFRP-1/Al joints increasing by 75.9% relative to the control condition.

It was noteworthy that grit blasting was less effective as a surface pre-treatment on CFRP-2/Al hybrid joints than on the CFRP-1/Al hybrid joints. In addition to being more difficult to effectively grit blast a patterned surface, it is proposed that the greater dissimilarity between the patterned surfaces of CFRP-2 and aluminium alloy are at least partly responsible for this observation.

7.1.2 The thermoplastic CFRPs

The surface pre-treatment and adhesive bonding of fibre composites based upon high performance thermoplastic matrices was also investigated. Three thermoplastic CFRPs were studied, i.e., CFRP-3 (T700 grade carbon fibre/PEEK), CFRP-4 (T700 grade carbon fibre/PEEK but showing lower mechanical strengths in comparison to CFRP-3), and CFRP-5 (T800S grade carbon fibre/PAEK).

The surface pre-treatments of acetone cleaning and plasma treatment (with different levels of treatment powers/durations) were applied to the CFRP adherends such that the control surface was acetone cleaned only, and then this was followed by a plasma treatment. Treated surfaces were analysed using SEM, CA measurement, and XPS. Adhesive joints were prepared by bonding adherends with a structural epoxy-film adhesive (AF163-2) to form single lap shear joints, which were tested according to the

standards GB/T 33334 and ISO 4587.

On these thermoplastic matrix CFRPs, plasma treatment was shown to be an effective technique to improve the wettability of the surfaces and to remove surface contamination. Following a plasma treatment of 100-180W for over 2 min, the surface contamination was typically reduced to only a trace amount or to even below the limit of detection. Also, a microstructure developed on the surface due to plasma erosion. The thermoplastic CFRP adherends, following a plasma treatment of 180 W for 5 min, had usually developed a highly appropriate combination of surface topography, chemistry and wettability for adhesive bonding, showing the highest single lap shear joint strength.

When the duration of the 180 W plasma treatment was increased to 8 min, fibre exposure was observed on the surfaces of the CFRP-3 and CFRP-4 (T700 grade carbon fibre/PEEK) joints but no fibre exposure was observed on the surfaces of the CFRP-5 (T800S grade carbon fibre/PAEK) joints. It was noteworthy that in this study where a high-performance epoxy-film adhesive was used and all adherends were also of a high-performance aerospace grade, then a plasma treatment which exposes the fibres of the CFRP can be considered as excessive. Fibre exposure reduces single lap shear strength of the joints either by introducing interlaminar failure in the composite adherends or by causing interfacial failure due to the poor adhesion between the exposed fibres and the adhesive.

Considering the single lap shear strength of the CFRP-CFRP homogenous joints, CFRP-3 (following a plasma treatment of 180 W for 5 min), which initially showed the highest 90° tensile strength and interlaminar shear strength, possessed the highest joint strength of these thermoplastic CFRPs. Considering the hybrid joining to aluminium alloy, CFRP-5 (carbon fibre/PAEK) showed the highest joint strength (when aluminium alloy samples were treated with a silane agent and the CFRP samples were plasma treated for 180 W for 5 min).

7.1.3 Factors related to the CFRP adherend materials

In this study, five different types of CFRP were investigated, including i) two

thermosetting CFRPs made using similar prepregs but formed into the composite material using different manufacturing techniques of compression moulding and autoclave moulding, and ii) three thermoplastic CFRPs, in which the carbon fibre was either T700 grade or T800S grade and the matrix resin was either PEEK or PAEK. Through comparative investigation, the following conclusions are drawn.

- (1) The manufacturing of the CFRP adherends via autoclave processing imparted a patterned surface to the composite which was different to the relatively flat surface imparted via compression moulding. This patterned surface was shown to be: i) beneficial to adhesion if a plasma treatment was to be applied to the adherend due to the higher specific surface area of a patterned surface exposed to plasma, compared to a flat surface, ii) beneficial to the joint strength in homogenous joints due to an increase in mechanical interlocking when the joint is loaded at least partly in shear, as in the single lap shear joint.
- (2) The interfacial properties of the carbon fibres (within a CFRP) or the cured prepregs not only affect the quality of the manufactured CFRPs but also they may affect the secondary adhesive bonding (when the cured CFRP is subsequently adhesively bonded).
- (3) In terms of the acetone cleaned adherends with no further surface activation, the joints formed using the thermosetting matrix CFRPs (carbon fibres reinforcing an epoxy matrix) showed much higher strengths than the joints formed using the thermoplastic CFRPs (carbon fibres reinforcing a thermoplastic matrix) as the adhesive employed in this study was epoxy based. However, after an appropriate surface pre-treatment was applied, the thermoplastic matrix CFRPs and the thermosetting matrix CFRPs were shown to have similar joint strengths.

7.1.4 Effect of the surface pre-treatments on CFRPs

The application of different surface pre-treatment techniques to the different types of composites prior to adhesive bonding was investigated. As mentioned above, the surface pre-treatments investigated were acetone cleaning (control condition), grit

blasting, and plasma treatment (with a range of plasma treatment parameters investigated). Based upon results of this study, the following conclusions are drawn.

- (1) Plasma treatment is an environmentally friendly technology. Atmospheric pressure plasma treatment has been frequently reported in previously published literature while low pressure plasma treatment on thermoplastic CFRPs has rarely been reported. In the present investigation, low pressure plasma treatment was used. It is found that this plasma treatment is highly effective on CFRP as a surface pre-treatment.
 - a. Plasma treatment effectively removed surface contamination. The F or Cl contamination, which can introduce interfacial failure and reduce the joint strength, can be reduced to below the limit of detection of an EDX or XPS apparatus.
 - b. Plasma treatment significantly improved the wettability. The water contact angle measured on the pre-treated adherends fell sharply (e.g., usually from a near-hydrophobic state to a near-superhydrophilic state).
 - c. Plasma treatment activated the surface chemistry. A sufficient plasma treatment remarkably increased the percentage of carbon-oxygen single or double bonds by several multiples, improving the adhesion.
 - d. Plasma treatment can allow the development of a highly desirable surface topography. On the thermoplastic CFRPs with optimised plasma treatment parameters, micro/nano-structures were created due to a nano-etching effect. This improved mechanical interlocking, contributing to the enhancement of the single lap shear strength of the joints.

In addition, the thermoplastic CFRPs usually required a higher power and longer duration of treatment compared to the thermosetting CFRPs due to their relative difference in initial surface chemistry and toughness. For example, considering the thermoplastic CFRPs, the adherends following a plasma treatment of 180 W for 5 min usually showed the highest joint strength. Considering the thermosetting CFRPs, an appropriate plasma

treatment was shown to be 100 W for 1 min. Raising the duration or power of the treatment led to a reduction in joint strength.

- (2) Grit blasting changes the surface topography of CFRP adherends, enhancing SLS strength by increasing mechanical interlocking; however, the integrity of the CFRP is sacrificed. An interlaminar failure mode (i.e., damage to the CFRP) in the joint can be observed in mechanical testing. Grit blasting also reduced the value of X_{max} in the SLS tests, indicating that the SLS joints had become less ductile.

7.1.5 A different mechanism found in hybrid joining

Hybrid bonding of CFRP to an aerospace-grade aluminium alloy (i.e., CFRP/Al joints) was studied in comparison with the homogeneous bonding of two CFRPs (i.e., CFRP/CFRP joints). The following detailed conclusions can be drawn.

- (1) In homogenous joining, the selection of the surface pre-treatment to optimise the surface chemistry, surface topography, and wettability was found to be the most significant factor in achieving high joint strengths. However, in hybrid joining, not only are the above factors important for each dissimilar adherend respectively, but another important factor affecting the joint strength is the dissimilarity between the two adherends. The dissimilarity between the surface topography or surface chemistry of the dissimilar adherends can encourage air retention during adhesive curing, increasing the likelihood of defects or stress concentrations being present, which finally reduces the hybrid joint strength.
- (2) The strength of a joint is controlled by the weakest interface according to the weak boundary layer theory. Strengthening an initially relatively-weak interface in a hybrid joint through surface pre-treatments leads to improved joint strength. In this study, results also show that strengthening an initially relatively-strong interface does not improve the joint strength but may even reduce it.
- (3) If a pre-treatment optimises the surface of an adherend for adhesive bonding

but increases the dissimilarity between the two adherends, the joint strength may not be increased, but can be decreased. In this case, the superiority of the surface properties of one adherend which can realise stronger interaction with the adhesive may not compensate for the greater dissimilarity between the two adherends.

7.2 Recommendations for future studies and for the industry

7.2.1 Surface pre-treatments on aluminium alloys

In terms of the aerospace use which usually requires a high joint performance, plasma treatment is a highly effective surface pre-treatment method when applied to either thermosetting or thermoplastic composites. However, plasma treatment was shown to only have a cleaning effect on aluminium alloys. Applied to aluminium alloys plasma treatment fails to alter the surface topography or activate the surface chemistry required for adhesive bonding.

The silane agent employed in this study is only effective when the aluminium alloys were bonded to some CFRPs. Alternative pre-treatments or alternative types of silane agents should be further investigated. Grit blasting is effective in optimising surface roughness for aluminium alloys; however, it is usually still insufficient due to its inability to activate the surface chemistry. Researchers or manufacturer focusing on metals should seek alternative environmentally friendly treatment methods (e.g., laser treatment) or combine these treatments.

7.2.2 Suggestions for further studies

- (1) Due to the research topic of the PhD programme and the background of the author, this thesis highlights the diverse interfacial characterisations for the pre-treated CFRP adherends. As for the mechanical performance of the joints, the SLS testing was carried out for evaluation. Future research may evaluate the adherends, the surface pre-treatments, and the joint performance via

some other mechanical testing avenues, e.g., testing the peel strength, testing the G_{IC} via double-cantilever-beam tests, or testing the strength of T-joints.

- (2) This thesis has investigated in detail the factors related to CFRP adherends and the surface pre-treatments. Researchers focusing on the adhesives may further investigate the effect of adhesives: (i) The difference between paste adhesives and adhesive films, the effect of viscosity of the adhesives, and the effect of curing temperature, pressure, or time for the adhesives should be further studied for better applications. (ii) Adhesives of diverse chemical composition should be included. For example, the effect of the “dissimilarity effect” in hybrid joining should be further evaluated when other types of adhesives/adherends are employed.

7.2.3 Recommendations for industry

- (1) The SLS strengths of homogeneous CFRP/CFRP joints were in the range 35-40 MPa while the SLS strengths of hybrid CFRP/Al joints were in the range 30-34 MPa. These high joint strengths indicate that i) the manufactured aerospace-grade CFRPs in this study were of high performance, ii) the optimised surface pre-treatments applied to the CFRP adherends were highly effective.
- (2) Thermoplastic composites are highly promising and are worthy of attention from academic researchers and from industry. An advantage is found in this thesis: thermoplastic CFRPs show high fault tolerance of SLS strength in surface treatment owing to their high toughness/impact resistance. They have scope for surface pre-treatment to improve joint strength. In addition, to ensure a relatively high joint strength, adhesives compatible for the thermoplastic CFRPs adherends should be developed.
- (3) This thesis found that the factors affecting the joint performance range from the carbon fibre production (e.g., the sizing agent, surface treatment on carbon fibre before making prepreg) to CFRP manufacturing (e.g., the technology, the moulding pressure) and surface pre-treatment on CFRPs for adhesive bonding. Hence, to obtain a high-performance joint structure

requires collaborative efforts from the upstream and downstream of the composites industry. A corporation which covers all these services may sustain a competitive advantage in this industry.

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Appendix 1

A.1 An additional study of manufacturing the CFRP-5: effect of the carbon fibre surface treatment and the moulding pressure

Before manufacturing the CFRP-5 for using as an adherend in this thesis, the effects of carbon-fibre surface treatment and moulding pressure were studied by the author and the collaborators in Zhongfu Shenying Carbon Fibre Co. Ltd and Donghua University. The additional study on CFRP manufacturing aims to obtain a CFRP with a higher 0° tensile strength in comparison with current commercial aerospace grade thermoplastic CFRPs. Also, the other mechanical properties should be competitive.

Hence, the materials used to manufacture the CFRP-5 was of higher grade in comparison with the materials in CFRP-1,2,3,4 in this thesis. For example, T800 grade carbon fibres (with a higher strength compared with the T700 grade in CFRP-1,2,3,4) was employed. A newly developed aerospace grade PAEK was used as matrix resin. In comparison to traditional PEEK resin, this PAEK show a higher stability of some physicochemical properties at processing temperature. In terms of the viscosity, this PAEK is more sensitive to the change of shear rate, which is beneficial to the melt impregnation process of prepreg manufacturing. More importantly, in this additional study the surface treatment on carbon fibre before making prepreg was optimised, so was the pressure in the compression moulding to manufacture CFRPs.

A.1.1 Effect of treatment on carbon fibre

Carbon fibres was treated via an electro-chemical method before sizing/making preregs. Charge concentration for this surface treatment was 12 C·g⁻¹ or 18 C·g⁻¹. Adjusting the charge was realised by changing the voltage, the current, or/and the concentration of electrolyte solution.

Interfacial characterisations of carbon fibres were carried out on the fibres without sizing agents, after the surface treatment process and before the prepreg was made. Figure A1-1 shows the morphologies of carbon fibres after the electro-chemical treatment of different charge concentration. Increasing the charge did not affect the dimensions of carbon fibre, but the surface conditions were different. As shown in Figure A1-1a, a single fibre which had been treated using $12 \text{ C}\cdot\text{g}^{-1}$ charge was around $5.1 \mu\text{m}$ in diameter. On some fibres, foreign bodies gathered. When it comes to $18 \text{ C}\cdot\text{g}^{-1}$ charge treatment (Figure A1-1b), the diameter of a single fibre was not changed. However, the foreign bodies were reduced, which were relatively uniformly disturbed rather than gathered on some fibres.

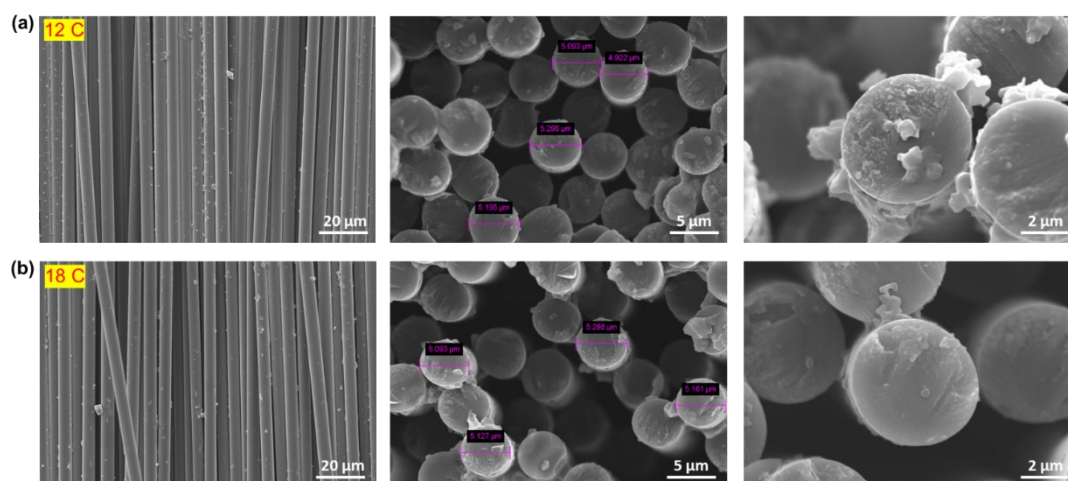


Figure A1-1. SEM images of carbon fibre after surface treatment. (a) $12 \text{ C}\cdot\text{g}^{-1}$ charge for surface treatment: around $5.1 \mu\text{m}$ in diameter, foreign bodies gathered somewhere; (b) $18 \text{ C}\cdot\text{g}^{-1}$ charge for surface treatment: around $5.1 \mu\text{m}$ in diameter, foreign bodies in less amount and frequency.

Chemistry of the two different fibres and the foreign bodies on them was further investigated (Figure A1-2). In the fibre areas, the carbon percentage of either was more than 99.3% (atomic). However, the chemical composition of the foreign bodies on the two fibres are different. On the $12 \text{ C}\cdot\text{g}^{-1}$ charge treated fibre, carbon and oxygen were the main elements of foreign bodies, which respectively accounted for 82-90% and 6-13%. Metallic contaminations, such as Na, K, and Ca, took up 1.2-1.7%, 0.5-0.6%, and 0.3-0.6%, respectively. As for the nonmetal, 0.8-1.1% Cl, 0.2-0.4% S, and around 0.1% Si were detected. When the charge concentration was raised to $18 \text{ C}\cdot\text{g}^{-1}$, more than 96%

foreign bodies were carbon. The percentage of oxygen was reduced to 0.2-2.8%. The percentage of Na, Cl, K, Ca, S, and Si also show noticeable decrease. Each of them only accounted for less than 0.3% of the foreign bodies.

The foreign bodies were brought in carbon fibre production [1-4]. For example, the Na, K, Ca impurities might be associated with the impurities in dimethyl sulfoxide (DMSO), which is the solvent for acrylonitrile polymerisation of carbon fibre precursor production. The S impurities may result from the use of DMSO or/and mercaptan (the chain transfer agent for acrylonitrile polymerisation). The Cl come from the water used in spinning stage, or/and the electrolyte used in fibre surface treatment. The Si was caused by the oiling agent used in spinning stage of producing carbon fibre precursor. The foreign bodies on carbon fibre are detrimental [3-6]. For one thing, the impurities which contains active elements and the low surface energy contaminations are harmful to the bonding of carbon fibre to matrix resin. For another thing, the irremovable gathered foreign bodies on carbon fibres may lead to a potential weak boundary or remarkable defects after CFRPs were manufactured.

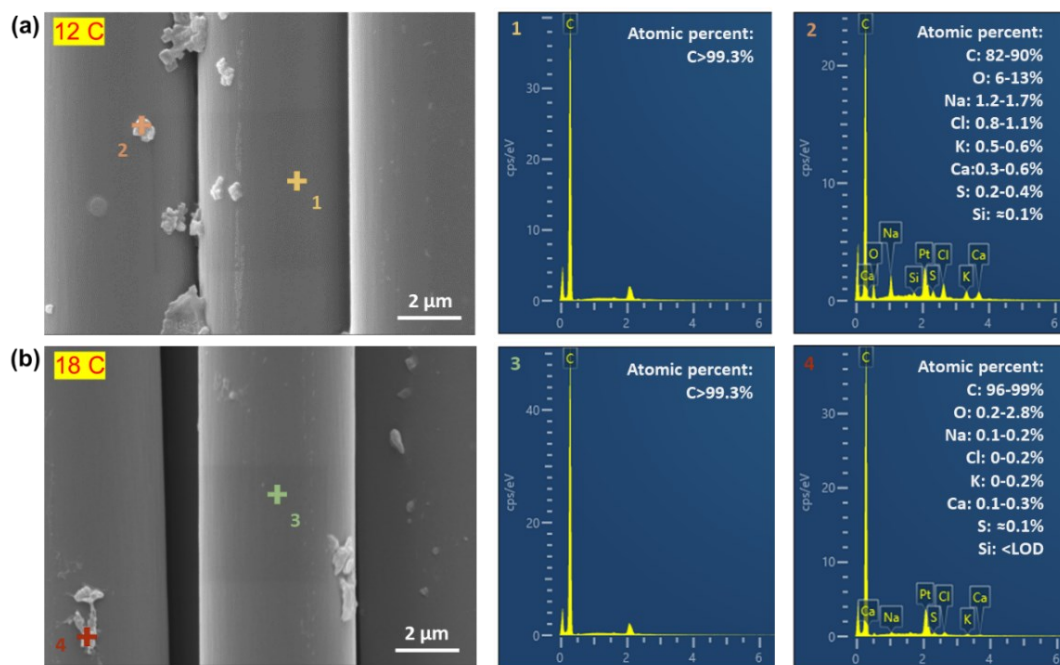


Figure A1-2. Surface chemistry of carbon fibre after treatment. (a) 12 C·g⁻¹ charge for surface treatment, point 1: a fibre area, point 2: a foreign object on the fibre. (b) 18 C·g⁻¹ charge for surface treatment, point 3: a fibre area, point 4: a foreign object on the fibres, less amount of detrimental chemical composition than point 2.

A.1.2 Mechanical performance and wettability of fibres

Table A1-1 sets up a comparison between the $12 \text{ C}\cdot\text{g}^{-1}$ and $18 \text{ C}\cdot\text{g}^{-1}$ treatment in terms of mechanical performance and wettability of carbon fibre tows. The two different carbon fibre tows showed a similar tensile strength (around 6000 MPa) and modulus (around 300 GPa). However, the interlaminar shear strength increased by 13.3% (from $113 \pm 2 \text{ MPa}$ to $128 \pm 2 \text{ MPa}$) when the charge concentration of surface treatment increased from $12 \text{ C}\cdot\text{g}^{-1}$ to $18 \text{ C}\cdot\text{g}^{-1}$. Also, the contact angle with EW800 resin dropped from $37.3 \pm 0.7^\circ$ to $30.6 \pm 0.5^\circ$.

The noticeable improvement in interlaminar shear strength and wettability indicates that the carbon fibres treated by $18 \text{ C}\cdot\text{g}^{-1}$ charge have a better interfacial performance. This interfacial performance can be significant when the carbon fibres are further processed to manufacture CFRPs, which ultimately affects the mechanical performance of CFRPs.

Table A1-1. Mechanical performance and wettability of the different carbon fibre tows

Properties	$12 \text{ C}\cdot\text{g}^{-1}$	$18 \text{ C}\cdot\text{g}^{-1}$
Tensile strength (MPa)	6010 ± 98	6066 ± 93
Tensile modulus (GPa)	300 ± 5	300 ± 6
Interlaminar shear strength (MPa)	113 ± 2	128 ± 2
Contact angle with EW800 resin ($^\circ$)	37.3 ± 0.7	30.6 ± 0.5

A.1.3 Effect of moulding pressure

Figure A1-3 shows the ultrasonic scanning images (PVA-AM 300, Questar, China) of CFRPs on which different moulding pressure was applied. When the moulding pressure was raised from 2 MPa to 4 MPa, the quality of CFRP laminates was improved. The area of low-quality edge (in red or green) showed remarkable decrease. Also, in the central part (in blue), less defects were detected. It is suggested that increasing moulding pressure can improve the fluidity of the thermoplastic resin, which reduces air retention during CFRP manufacturing, contributing to the better quality.

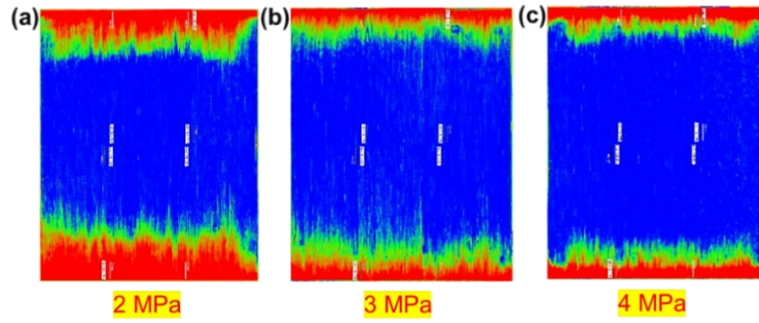


Figure A1-3. Ultrasonic scanning images of CFRP laminates. The moulding pressure for the CFRP manufacturing: (a) 2 MPa, (b) 3 MPa, (c) 4 MPa. Increasing moulding pressure can reduce the area of low-quality edge and reduce the defects in the central part.

A.1.4 Mechanical performance of the CFRPs

CFRP samples were prepared using different processing parameters. Table A1-2 shows the results of mechanical properties of these CFRP samples. The 0 ° tensile strength of the 18 C·g⁻¹, 4 MPa samples was up to around 3000 MPa, meeting the main aim of this additional study.

Table A1-3. Mechanical performance of CFRPs prepared using different processing parameters.

Mechanical properties	12 C·g ⁻¹ , 3 MPa	12 C·g ⁻¹ , 4 MPa	18 C·g ⁻¹ , 4 MPa ^c
0 ° tensile strength (MPa)	2058 ± 37	2770 ± 42	2932 ± 53
0 ° tensile modulus (GPa)	138 ± 3	152 ± 3	147 ± 3
0 ° compression strength (MPa)	1027 ± 71	1212 ± 89	1250 ± 43
0 ° compression modulus (GPa)	145 ± 3	140 ± 4	134 ± 2
0 ° bending strength (MPa)	-	1354 ± 52	1319 ± 58
0 ° bending modulus (GPa)	-	131 ± 3	135 ± 4
90 ° tensile strength (MPa)	37 ± 1	44 ± 2	68 ± 2
90 ° tensile modulus (GPa)	8 ± 1	9 ± 1	8 ± 1
90 ° compression strength (MPa)	-	139 ± 3	178 ± 2
90 ° compression modulus (GPa)	-	9 ± 1	10 ± 1
Interlaminar shear strength (MPa)	68 ± 2	89 ± 1	81 ± 1
G _{IC} (J·m ⁻²) ^a	-	2356 ± 113	2759 ± 49
Compression after impact (MPa) ^b	-	347 ± 10	388 ± 8

^a The testing was carried out according to the standard BS EN 6033 and HB 7402.

^b The testing was carried out according to standard ASTM D7137. The impact was 6.67 J·m⁻².

^c This sample is a final product of this additional study, which is the CFRP-5 used in this thesis.

It is evident that the mechanical performance was improved as the processing parameters were optimised. For example, the interlaminar shear strength increased from 68 ± 2 MPa to 80-90 MPa (increased by around 25%) when the moulding pressure increased from 3 MPa to 4 MPa. When the charge concentration was increased from $12 \text{ C}\cdot\text{g}^{-1}$ to $18 \text{ C}\cdot\text{g}^{-1}$, the 90° tensile strength increased sharply from around 40 MPa to 68 ± 2 MPa (increased by around 70%). The sample which employs $18 \text{ C}\cdot\text{g}^{-1}$ charge for carbon fibre surface treatment and 4 MPa for moulding pressure show a generally best mechanical performance. This sample is the final product of this additional study, which is the CFRP-5 used in this thesis.

Figure A1-4 shows the images of compression after impact (CAI) testing. CAI is a significant indicator for composites that shows the overall mechanical performance of a material. Usually it should be higher than 340 MPa for applications in aerospace industries. The results for the $18 \text{ C}\cdot\text{g}^{-1}$, 4 MPa sample is 388 ± 8 MPa, which meets the criterion for aerospace use.

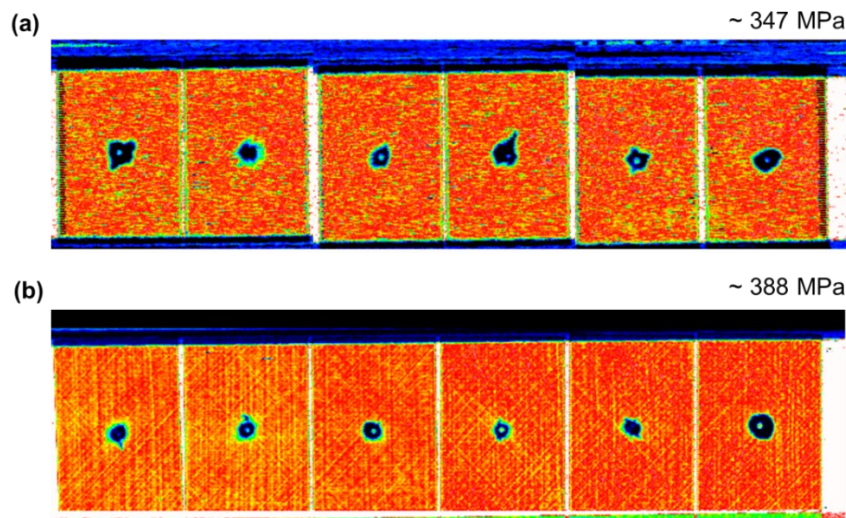


Figure A1-4 Compression after impact testing of CFRPs. (a) The $12 \text{ C}\cdot\text{g}^{-1}$, 4 MPa sample: around 347 MPa; (b) The $18 \text{ C}\cdot\text{g}^{-1}$, 4 MPa sample: around 388 MPa.

A.1.5 Mechanical performance of the prepared CFRPs

To explain why increasing the charge concentration of treating carbon fibre or increasing moulding pressure of manufacturing CFRPs can improve the mechanical performance of the CFRPs, the fracture interfaces after mechanical testing were

investigated. Figure A1-5a shows the fracture interfaces of CFRPs using $12 \text{ C}\cdot\text{g}^{-1}$ charge for carbon fibre treatment or using 2-3 MPa for moulding pressure. Many delaminated fibres were lacking in resin impregnation, where the fracture interfaces were relatively smooth. In addition, hole defects can be found especially in the sample using 2-3 MPa for moulding pressure. It is suggested that the hole defect was due to the air retention during CFRP manufacturing.

Figure A1-5b shows the fracture interfaces of CFRPs using the optimised processing (using $18 \text{ C}\cdot\text{g}^{-1}$ and 4 MPa). Most fibres became well-impregnated and the fracture interfaces were relatively rough. Such a better interfacial bonding should result from the better interfacial properties of carbon fibre, i.e., the lower percentage of detrimental elements as shown in section A.1.1 or/and the better wettability shown in section A.1.2. This stronger bonding ultimately led to the better mechanical performance of CFRPs as shown in section A.1.4.

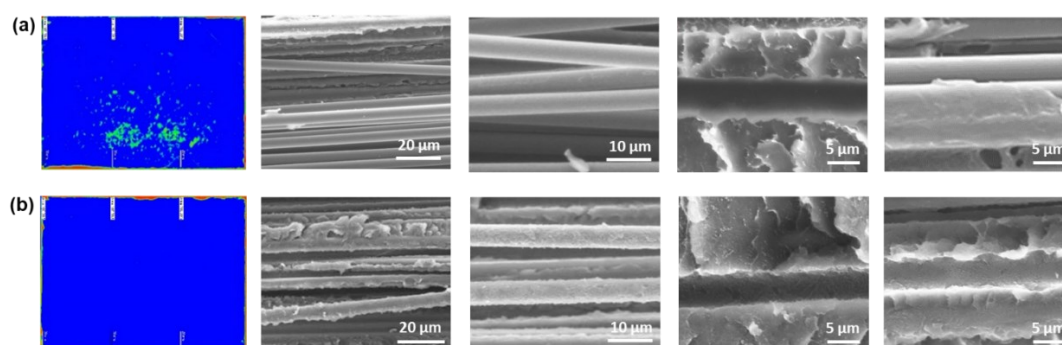


Figure A1-5. Ultrasonic scanning images of the CFRPs and SEM images of the fractured CFRPs after mechanical testing. (a) Samples using 12 C for carbon fibre treatment or 2-3 MPa for moulding pressure: remarkable defects detected by ultrasonic scanning, some fibres without resin, relatively smooth fracture interface, and hole defects; (b) Sample using 18 C for carbon fibre treatment and 4 MPa for moulding pressure: no remarkable defect detected by ultrasonic scanning, well-impregnated fibre, and rough fracture interface indicating a better combination.

A.1.6 Summary and the future work

Increasing the charge concentration of surface treatment of carbon fibres from $12 \text{ C}\cdot\text{g}^{-1}$ to $18 \text{ C}\cdot\text{g}^{-1}$, or increasing the moulding pressure of CFRP manufacturing from 2-3 MPa to 4 MPa, can ultimately result in a better mechanical performance of the

thermoplastic CFRPs. On the one hand, increasing the charge concentration of surface treatment can reduce the foreign bodies and prevent them from gathering on fibres. The detrimental elements were also remarkably reduced. Consequently, the wettability as well as the interfacial performance of fibres were improved, which benefits the bonding of fibres to resin. On the other hand, increasing the moulding pressure can improve the fluidity of the thermoplastic resin, which will reduce the hole defects in CFRPs through preventing air retention during CFRP manufacturing.

Future work should try more different processing parameters. e.g., other values of charge concentration ($12\text{--}18\text{ C}\cdot\text{g}^{-1}$ or over $18\text{ C}\cdot\text{g}^{-1}$ charge) for carbon fibre surface treatment, or other values of moulding pressure of (3–4 MPa, or higher than 4 MPa). In this way, not only can the effect of these processing parameters be further explored, but also some mechanical performance indicators can be further improved for specific aerospace use. Actually, the collaborating company and the collaborating university have got the plan to carry out the corresponding work.

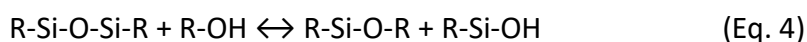
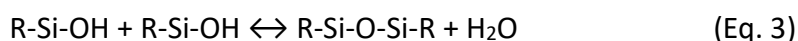
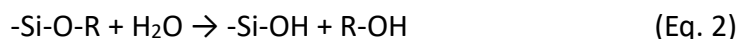
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Appendix 2

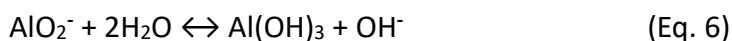
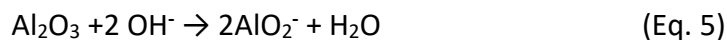
A.2 Effect of the silane treatment on AA2014

The details for the silane agent treatment are shown in section 3.4.4. In the silane solution, hydrolysis reactions and condensation reactions balance, according to the following chemical equations [1,2]:

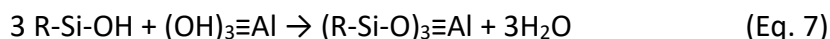


where R is a random group that do not influence the reactions.

The surface of an aluminium alloy is mainly cover by an Al_2O_3 layer. On the aluminium surface in the silane solution where the pH is 9-10, the following reaction may take place:



The Al(OH)_3 can react with R-Si-OH as shown in the following equation:



The alkoxy groups ($-\text{Si-O-R}$) are thus grafted on the aluminium surface. The alkoxy groups on the surface can usually contribute to a good interfacial adhesion to epoxy-based adhesives or composites [3-7].

A.2.1 Surface chemistry

Table A2-1 shows the elementary composition of as-received AA2014, which is adapted from the datasheet of AA2014 provided by the supplier (Smith Metal Centres Co., Ltd, London, UK). The AA2014 is deemed as an Al-Cu alloy, in which the element

aluminium and copper account for 90-95% and 4-5%, respectively. Si, Mn, and Mg is the minor alloying elements, respectively accounting for 0.5-2.1%, 0.4-1.0%, and 0.2-0.8%. The AA2014 may also contain <0.7% Fe, <0.25 Zn, <0.15% Ti, and <0.15% other elements.

Table A2-1. Elementary composition of as-received AA2014 (adapted from the datasheet provided by the supplier).

Weight %	Al	Cu	Si	Mn	Mg	Fe	Zn	Ti	Others
Minimum	95	3.90	0.50	0.40	0.20	-	-	-	-
Maximum	90	5.00	2.10	1.00	0.80	0.70	0.25	0.15	0.15

Surface chemistry of AA2014 before and after silane agent treatment were characterised via EDX, and the results are shown in Table A2-2. In terms of the acetone cleaned AA2014 samples, the result of aluminium and copper percentage were in accord with the datasheet above. The presence of oxygen element, which accounted for 2-4%, was due to the oxide layer on the aluminium surface (i.e., Al_2O_3). The presence of trace carbon element may come from the unremoved surface contaminations or the residual acetone after the acetone cleaning. In terms of the silane agent treated AA2014 samples, the percentage of oxygen, carbon, and silicon on the surface showed remarkable increased to around 20% each. This change indicates the -Si-O-R group were successfully grafted onto the aluminium surface.

Table A2-2. Elementary composition of AA2014 surface before and after silane agent treatment

Weight %	Al	Cu	O	C	Si
AC samples	90-92%	4-6%	2-4%	Trace	<LOD
SA samples	40-50%	Trace	17-22%	16-20%	15-21%

A.2.2 Surface topography

Surface topography of AA2014 before and after silane agent treatment were observed via SEM, as shown in Figure A2-1. The acetone cleaned AA2014 samples showed a relatively flat surface (Figure A2-1a). After the silane agent treatment as shown in Figure A2-1b, particles were observed on the surface when the scale bar is

200 μm . Increasing the magnification times till the scale bar is 2 μm , the rough structure of the silane composition on AA2014 surface were observed.

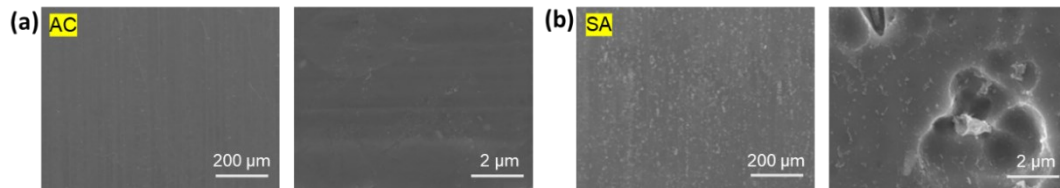


Figure A2-1. SEM images of AA2014 surface before(a) and after(b) silane agent treatment.

A.2.3 Wettability

The epoxy-resin contact angle on AA2014 surface before and after silane agent treatment are tested. The epoxy resin CA was $78.2 \pm 1.4^\circ$ after acetone cleaning, and it dropped to $69.8 \pm 2.5^\circ$ after silane agent treatment. Since the adhesive is epoxy based, such results demonstrate that silane agent treatment make the aluminium surface easier to be wetted by the adhesives.

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