

CRANFIELD UNIVERSITY

Lydia Frumosu

Atmospheric pressure plasma surface engineering to improve
polymer matrix composite bonding.

School of Aerospace, Transport and Manufacturing
PhD Manufacturing

PhD
Academic Year: 2019 – 2024

Supervisor: Dr Zhaorong Huang
Associate Supervisor: Professor John Nichols
Industrial Supervisor: Dr Tian-Long See
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ABSTRACT

This thesis explores the improvement of adhesive properties on carbon fibre reinforced epoxy composites, specifically MTM44-1, through the application of atmospheric pressure plasma (APP) treatments. The study aims to address the critical challenge of enhancing the adhesion of composite surfaces by investigating both thermal and non-thermal plasma techniques. A comprehensive analysis of plasma treatment uniformity, temperature effects, and treatment speeds has been conducted.

Special emphasis is placed on the removal of silicone contamination, from mould release agents, a common barrier to effective adhesion. Current industrial approaches often struggle to fully eliminate silicone contamination, which severely limits adhesive bonding on composite surfaces. Plasma has the potential to remove silicone contamination, while also improving the surface energy, prior to adhesion.

Another consideration in this study has been to the speed of plasma treatment. One of the barriers to using adhesion to bond composites in the industry is the time it takes to pre-treat surfaces prior to adhesion.

This study aims to also investigate the relationship between treatment time and surface energy, especially as APP can be easily integrated into a manufacturing processes, compared to traditional plasma surface treatment. This is due to the lack of vacuum which saves time, space and often energy in the process.

Various plasma generation methods were explored, including microwave, radio frequency (RF), and Dielectric Barrier Discharge (DBD), to treat the composite surfaces. This allowed for a variety of different plasma feed gases to be used including nitrogen, argon and a mixture of fluorinated gas and argon.

Surface characterisation was conducted using X-ray photoelectron spectroscopy (XPS) to assess the chemical composition of the treated surfaces, while water contact angle (WCA), surface energy measurements and lap shear testing were used to evaluate the effectiveness of the treatments in promoting adhesion. The results demonstrate that plasma treatments significantly enhance the surface

energy of the composites by removing surface contaminants, particularly silicon containing release agents, while also altering the surface chemistry to promote better adhesive bonding.

The work also evaluates the impact of processing parameters such as treatment speed and gas flow rates on surface modification efficiency and surface temperature, particularly when considering thermal radio frequency (RF) plasma.

Keywords:

Atmospheric pressure plasma, silicon contamination, composites, surface energy, adhesion, Surface Engineering, aerospace composites, non-thermal plasma, thermal plasma.

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LIST OF ABBREVIATIONS

ABS	Acrylonitrile Butadiene Styrene
AC	Alternating Current
AFM	Atomic Force Microscope
AFRP	Aramid Fibre Reinforced Polymer
BSE	Backscattered Electrons
CCI	Coherence Correlation Interferometry
CFRP	Carbon Fibre Reinforced Polymer
CM1	Drop Coating Method
CM2	Spin Coating Method
DBD	Dielectric Barrier Discharge
DLD	Delay-line detector
EDS	Energy Dispersive X-ray Spectroscopy
FIB	Focused Ion Beam
FTIR	Fourier Transform Infrared Radiation
GFRP	Glass Fibre Reinforced Polymer
IPA	Isopropanol (Isopropyl Alcohol)
MCCMD	Microwave Coaxial Capillary Micro Discharge
MEMS	Micro-Electro-Mechanical Systems
MIPP	Microwave Induced Power Plasma
NAP	Near-Ambient Pressure
OWRK	Owens-Wendt-Rabel-Kaelble Method

PLC	Programmable Logic Controller
PT1	Plasma Treatment Method 1
PT2	Plasma Treatment Method 2
RAP	Reactive Atom Plasma
RF	Radio Frequency
RF-ICP	Radio Frequency Inductively Coupled Plasma
RTP	Research Technology Platform
SE	Secondary Electrons
SEM	Scanning Electron Microscopy
SWL-MP	Surface Wave Launched Microwave Plasma
ToF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometry
ULE	Ultra-Low Expansion Glass
WCA	Water Contact Angle
XPS	X-ray Photoelectron Spectroscopy

1 Introduction

The aerospace industry is a key player in driving up advancements in engineering and technology, significantly influencing global transportation, defence, and economic development. In the UK alone, the sector boasts an annual turnover of £35 billion, largely driven by foreign exports, and employs over 120,000 skilled workers with wages significantly above the national average (1)

One of the critical challenges in aerospace engineering is the need to reduce the weight of aircraft to improve fuel efficiency and reduce environmental impact. This has led to a growing interest in the use of composite materials, which offer high strength and stiffness at a fraction of the weight of traditional metallic materials (2).

Composites have transformed the aerospace industry by facilitating the production of lighter, stronger, and more fuel-efficient aircraft. The application of composite materials has expanded beyond military use to become integral in commercial aviation, with modern aircraft such as the Airbus A350 and Boeing 787 incorporating substantial amounts (over 50% by weight) of these materials into their structures (3).

These materials provide several advantages over traditional metals, including superior strength-to-weight ratios (3-7 higher compared to steel, 80% lighter), enhanced fatigue resistance, and improved corrosion resistance (2,4).

The use of composites in aerospace applications also presents some challenges. Composites can often be expensive in raw materials. The manufacturing processes for composites can also be expensive and complex. Composite manufacturing can be labour intensive making it more expensive or simply take much longer to produce(5).

The aerospace industry is one of the few remaining industries that use machining in the final assembly (6). However traditional joining methods for metals, such as fastening can result in failure within composites (7).

The slow uptake of bonding to join components together is due to a number of reasons, a primary one is that surface adhesion can result in failure at the interface (8). As a result, when composite components are bonded together, they require extra material to be glued on top to reinforce the joint (9). This adds extra weight, material costs, complexity and time.

To prevent interface failure before adhesion, joining preparation is required. However, it can also be costly and time consuming to prepare the surface with the current techniques available (6,10). Surface contamination, from release agents used within the manufacturing process can also reduce the strength of bonds (11–14).

Surface treatments, particularly plasma treatments, could be effective in enhancing the adhesion properties of composites. While atmospheric pressure plasma (APP) treatments have already shown to be able to modify composite surfaces for improved adhesion (15–48) there remains a significant gap in fully understanding and optimising plasma removal of silicon and/or silicone containing release agents (47,48). Silicon based contamination, a persistent challenge in industrial settings, particularly in aerospace composites, hinders bonding processes and reduces the effectiveness of adhesive joints(49). Current methods, including plasma treatments, have not yet achieved complete removal of silicon contamination (47,48).

Additionally, research into the thermal effects of plasma treatments on the surface and bulk properties of composites is necessary. Plasma treatments, particularly at atmospheric pressure, generate heat, which could affect the integrity of composite materials. Studies involving continuous thermal monitoring during plasma treatments could help establish thresholds for safe operation while ensuring effective surface modification.

More studies are necessary to establish the ideal balance between processing speed, contamination removal, and surface energy modification. Additionally, understanding the aging effects of plasma-treated surfaces will be crucial for industrial applications. Plasma-treated surfaces can experience hydrophobic

recovery over time, reducing their improved adhesive properties, so long-term stability studies are essential (15,16).

1.1 `Aim

The aim of this work is to improve the adhesive quality of composite surfaces using atmospheric pressure plasma.

This involves evaluating both silicon contaminated and uncontaminated surfaces, considering the effects of temperature, treatment speed, the use of different plasma torches, and feed gases. The goal is to optimise plasma treatments for better removal of surface contaminants like silicon release agents, enhancing surface energy and improving adhesion.

1.2 Objectives

To achieve the above aim, several key objectives are outlined.

1. Investigate the use of both non-thermal and thermal plasma to increase the adhesion properties of composites.
2. Measure the impact of plasma parameters on surface energy through a series of liquid contact angle measurements.
3. Measure the impact of short and long term (hours/days/months) aging effect of plasma processing surface energy parameters through a series of liquid contact angle measurements.
4. To understand the ideal treatment speeds in plasma processing, in a trade-off between time of process and effectiveness and how this affects uniformity of plasma treatments, surface chemistry and adhesion strength
5. To investigate the use of plasma processing treatment to remove silicone contamination.

1.3 Overview of thesis

This thesis aims to contribute to the current research on aerospace composites by enhancing the adhesive quality of composite surfaces using atmospheric pressure plasma. The study will explore both silicon-contaminated and uncontaminated surfaces, examining the effects of variables such as temperature, treatment speed, different plasma torches, and feed gases.

The research aims to optimise plasma treatments for effective removal of surface contaminants like silicon release agents, evaluate treatment uniformity, and identify changes in surface chemistry. Shear strength testing will also be employed to assess the adhesion of samples post plasma processing.

1. Introduction

This chapter outlines the motivation and objectives of the study, highlighting the challenges in improving the adhesive properties of composite surfaces. It discusses the need to optimise atmospheric pressure plasma treatments for improved effective contamination removal, specifically focusing on silicon based agents. The chapter provides an overview of key research objectives, setting the context for the subsequent literature review, methodology, and experimental analysis.

2. Literature Review

This chapter explores published literature to provide a comprehensive review of the techniques currently explored to improve adhesion of aerospace composites. It begins with describing the role of composites in the aerospace industry, examining their evolution, applications, and benefits. It discusses fibre-polymer composites, including carbon-fibre-reinforced polymers (CFRPs) and the related adhesion challenges. Surface treatment techniques, with a focus on plasma based methods, are explored. The chapter concludes by identifying gaps in existing literature, such as the need for improved plasma treatments to remove silicon contamination and optimise surface energy.

3. Method

For materials used, the CFRP composite material substrates and silicone release agent employed are described, as well as the coating techniques. Various plasma generation methods (microwave, dielectric barrier discharge, and RF plasma) are outlined, along with their effects on surface topography. The chapter also describes the surface analysis techniques, such as XPS, SEM-EDS, ToF-SIMS, surface energy measurements, and water contact angle analysis. The study's approach to plasma treatment speeds and surface roughness evaluation is discussed, providing a framework for the experiments.

4. Results and Discussion

The results begin with the analysis of silicon contamination coating thickness and chemical composition using SEM-EDS and ToF-SIMS. The effects of microwave plasma treatments, including surface wave-launched microwave plasma (SWL-MP) and microwave-induced power plasma (MIPP), on composite surfaces are discussed, highlighting their impact on surface energy and exploring the possibility for contamination removal. The effectiveness of dielectric barrier discharge (DBD) plasma in modifying surface energy and removing silicon contamination is evaluated. The chapter also covers the role of RF-ICP plasma in surface modification, detailing changes in surface energy, silicon removal and adhesion. These results are then discussed and compared to previous studies and other literature which may explain, support or contrast this work. The mechanisms behind the results are discussed and how this impacted the study.

5. Conclusions

A summary of the key findings of this research. It emphasises the effectiveness of atmospheric pressure plasma treatments in improving the adhesive properties of composite surfaces. The study concludes that optimising plasma parameters, such as treatment speed and gas composition, significantly enhances contamination removal and surface energy, leading to better adhesion.

6. Future Work

Future research directions are covered in the section, including more detailed heat studies to understand thermal effects during plasma treatment. Further SEM and XPS analyses are recommended to explore the changes in surface morphology and chemistry. The chapter also proposes investigations into treatment speed optimisation, the effects of aging on treated surfaces, scaling up plasma treatment methods, and tailoring gas concentrations for more effective contamination removal.

2 Literature Review

This literature review aims to provide a comprehensive overview of the current state of research and development in the field of aerospace composites, the adhesion of these composites, surface preparation techniques for adhesion and plasma treatment.

The review will focus 4 key topics followed by an exploration of the research gap.

1. The Use of Composites in the Aerospace Industry

This section explores the significance of composite materials in aerospace, starting with their historical development and evolution. It discusses how composites have become integral to modern aircraft design due to their high strength-to-weight ratio, corrosion resistance, and flexibility in fabrication. The section also highlights the benefits and impacts of composites in enhancing aircraft performance, reducing fuel consumption, and offering innovative design solutions

2. . Fibre-Polymer Composites for Aerospace Applications

This section delves into the different types of fibre-polymer composites used in aerospace, focusing on

- Carbon-fibre-reinforced composites,
- Thermoset polymers
- Carbon fibre-epoxy composites.

It examines their unique properties, such as high tensile strength and thermal stability, which make them ideal for aerospace applications. The discussion also covers the manufacturing processes and the advantages of using these materials in high-performance aerospace components.

3. Joining and Adhesion of Aerospace Composites

This part reviews traditional and modern techniques for joining composite materials in aerospace. It highlights challenges in achieving reliable adhesion due to the surface chemistry of composites and introduces surface energy as a key factor influencing adhesive bonding. Additionally, it discusses barriers to adhesion, including surface contaminants and the use of silicone release agents, which can inhibit bonding effectiveness.

4. Surface Treatment of Composites

A review of the various surface treatment methods used to enhance the adhesion properties of composite materials is carried out. It focuses on plasma treatments, discussing their role in modifying surface chemistry and roughness to improve bonding. Recent advancements in plasma processing, including atmospheric pressure plasma, are examined for their potential in effectively removing contaminants like silicon containing release agents and enhancing composite surface energy.

5. Summary & Research Gap

The section summarises the key findings from the literature review, emphasising the importance of surface treatments in improving composite adhesion. It identifies gaps in current research, particularly the need for optimised atmospheric pressure plasma treatments to effectively remove silicon contamination and enhance surface energy. This sets the stage for the study's objectives to address these gaps through comprehensive plasma treatment investigations.

2.1 The Use of Composites in the Aerospace Industry

2.1.1 The Historical Context and Evolution of Composite Materials

The military were first to significantly use modern composites in Aerospace as early as the 1940s, in radomes which are dome-shaped structures, designed to protect radar equipment without interfering with signal transmission. They then moved on to secondary structures and internal aircraft components in the 1970s (50–53). These early applications demonstrated the potential of composites to provide unique solutions that traditional materials could not offer.

As the benefits of composites became more apparent, their use expanded beyond military applications. The aerospace industry began to explore the potential of composites for various structural components. The transition from metallic materials like aluminium, iron, and steel to composites was driven by the need for materials that offered high strength, stiffness, corrosion resistance, and fatigue resistance while being significantly lighter (2). This shift was crucial in addressing the industry's ongoing challenge of reducing the weight of aircraft to improve fuel efficiency and reduce environmental impact.

The Airbus A380, introduced in the early 2000s, airframe contains over 20% (by volume) composite materials, including wings, fuselage sections, tail surfaces, and doors made from carbon fibre and glass fibre reinforced polymer composites (50,54) The use of composites in the Airbus A320 also demonstrated substantial weight savings, with 800 kg saved compared to equivalent parts made with aluminium alloys (50).

It is estimated that for every kilogram reduction in weight of an aircraft, there is approximately £700,000 savings over the life of an aeroplane (55)

The economic and environmental benefits of composites have driven their adoption in the aerospace industry (56).

2.1.2 Current Applications of Composites in Aerospace

The aerospace industry has increasingly embraced composite materials due to their superior properties and the significant advantages they offer over traditional metallic materials. Composites, particularly fibre-reinforced polymers, have become integral to modern aircraft design and manufacturing, providing numerous benefits that enhance performance, efficiency, and sustainability(57).

The use of composites exists throughout an aircraft structure, including the airframe, interior components, engine and even secondary structures, as displayed in Figure 2-1.

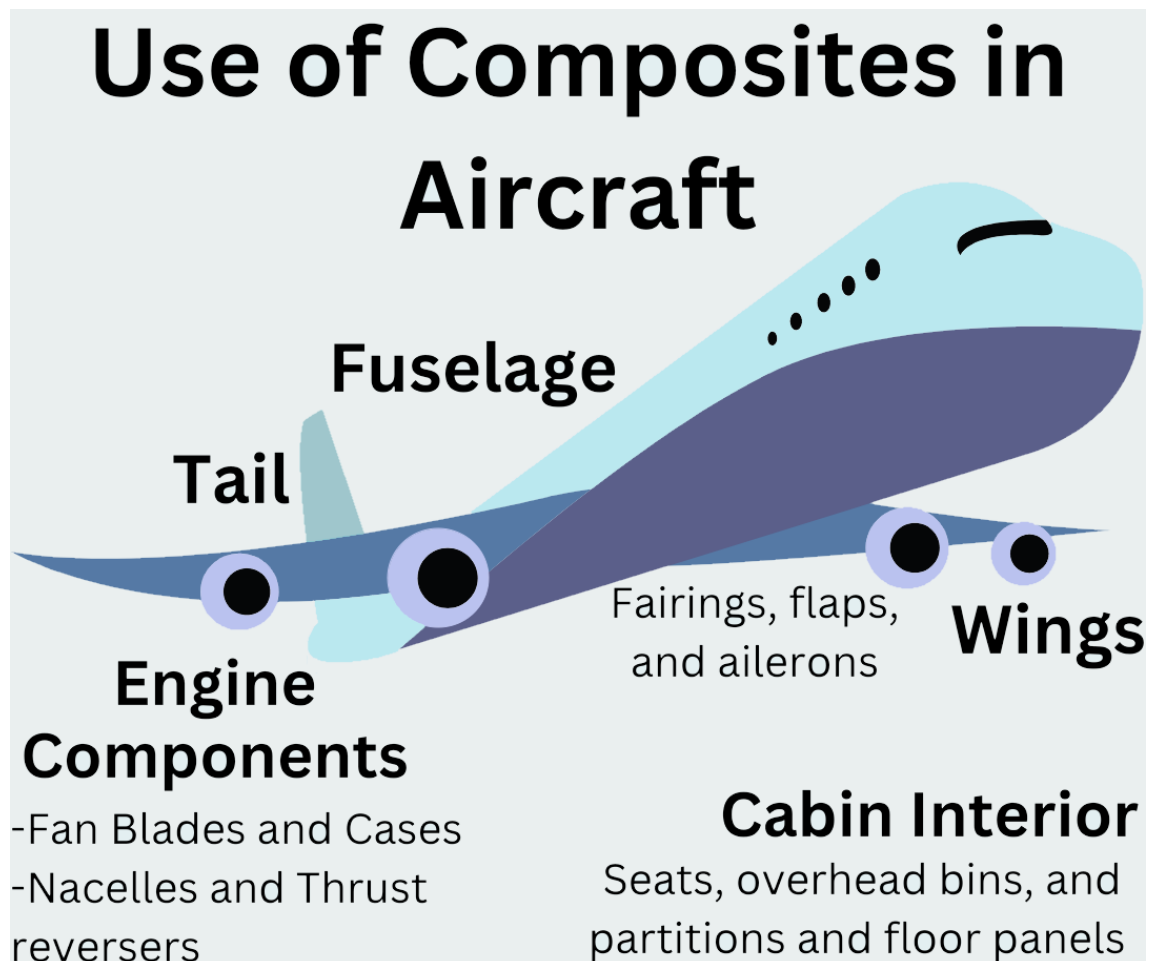


Figure 2-1 Diagram detailing locations of aircraft components which contain composites. Diagram drawn by the author using information from (58–61).

For instance, the Boeing 787 Dreamliner and the Airbus A350 XWB feature fuselages made predominantly from carbon fibre reinforced polymer (CFRP) composites (58,59).

Advanced composites are used in the fan blades and cases of jet engines. For example, the GE90 engine, used in the Boeing 777, features fan blades made from carbon fibre composites(61). Composites are also used in the construction of engine nacelles (thrust reversers). Composites are used in secondary structures such as fairings, flaps, and ailerons (60).

2.1.3 Impacts and benefits of the use of Composites in Aerospace

One of the most significant benefits of using composites in aerospace is the reduction in weight. Composites have a high strength-to-weight ratio, which means they can provide the necessary structural strength while being much lighter than traditional materials like aluminium and steel as detailed in Table 2-1. This weight reduction translates to improved fuel efficiency, lower emissions, and reduced operating costs(56,57).

Table 2-1 displaying the density and strength of various materials including composite fibres(62,63) .

	Density (kg/m ³)	Tensile Strength (MPa)
Polypropylene	900	400
Polyester	1,380	1,100
Titanium	4,500	950
Mild steel	7,800	450
High tensile steel	7,800	1,600
Glass fibre	2,550	3,000
GFRP	2,110–2,700	480–1,600
Aramid	1,450	3,000
AFRP	1,390–1,450	1,720–2,540
Carbon fibre	1,900	3,000
CFRP	1,550-1,760	1,720–3,690

While the initial cost of composite materials and manufacturing processes can be higher than traditional materials, the long-term cost savings are significant. This weight reduction translates to lower fuel costs and improved operational efficiency. The reduced weight of composite materials also contributes to efficiency and lower operational costs. Airlines can achieve higher payload

capacities and longer flight ranges without increasing fuel consumption. This efficiency is particularly beneficial for long-haul flights, where fuel costs constitute a significant portion of the operating expenses(3,64–66).For instance, the use of composites in the Airbus A320 resulted in a weight saving of 800kg (out of an average Maximum Zero Fuel Weight between 55300kg compared to equivalent parts made with aluminium alloys (58).

Composites offer superior mechanical properties, including high tensile and compressive strengths, excellent fatigue resistance, and superior stiffness. These properties enhance the overall performance of the aircraft, allowing for better manoeuvrability, higher payload capacity, and longer service life (58,59,61,67,68). Unlike metals, composites are resistant to corrosion, which is a significant advantage in the aerospace industry. This resistance to corrosion reduces maintenance costs and extends the lifespan of aircraft components, contributing to overall cost savings(59,61,67).

Composites can also be moulded into complex shapes and structures, allowing for aerodynamic designs (67). In addition to the benefits of composites in weight reduction and thus reducing usage and expense of fuel, composites can help aircraft operators save money on future maintenance costs, as the material is resistant to rust and corrosion. As a result, an Airbus A350 XWB requires 50% fewer structural maintenance tasks. The threshold for airframe checks is 12 years, compared to the A380 of 8 years (58,68,69).

It is also worth noting that composites have excellent impact resistance and energy absorption properties, which enhance the safety of aircraft. In the event of an impact, composite materials can absorb and dissipate energy more effectively than metals (67,70). For metals, a predominant single crack is the most common failure mechanism. On the other hand, in composite materials there are four basic failure mechanisms: fibre breakage, delamination, cracking and interfacial debonding(71). Considering failure tests on CFRP alone, beams have been able to withstand 20,000 up to 12,000,000 load cycles(4,72,73). They also have potential for self-healing or to be easily repaired with emerging technologies (74,75).

2.2 Fibre-Polymer Composites for Aerospace Applications

Regardless of the fibre material, two fundamental components define a composite's properties:

1. A reinforcement phase, whose orientation governs the mechanical attributes.
2. A continuous matrix, which provides the composite's overall shape, environmental resistance, and certain physical/chemical properties.

Reinforcements may be particulate, fibrous, or laminate (76–78), with fibres being the most common for high-performance applications. Fibre-polymer composites consist of a polymer matrix reinforced with fibres, producing materials that are both lightweight and strong. The matrix holds the fibres in place, facilitates load transfer, and provides protection from environmental factors. Meanwhile, the fibres impart strength and stiffness, making such composites especially valuable in aerospace applications where weight reduction and high performance are paramount.

Reinforcement agents can be aramid, basalt, carbon, glass, or polyethylene, among others, each conferring unique advantages such as corrosion resistance, conductivity, or high-temperature stability (79–82). For instance, glass fibres are widely chosen for larger-scale, lower-cost structures such as wind turbine blades; carbon fibres suit aerospace and transport sectors requiring high strength and stiffness; and aramid fibres excel in defence applications needing energy absorption (83). These differences are detailed in Table 2-2.

2.2.1 Carbon-fibre reinforced composites

Among fibre-reinforced composites, carbon fibres—often manufactured from polyacrylonitrile (PAN) or pitch via oxidation, carbonisation, and heat treatments—provide an optimal balance of high modulus, low weight, and excellent fatigue resistance (74,75). Consequently, they are the material of choice for primary and secondary aerospace structures and engine components, where elevated temperature tolerance and mechanical robustness are crucial.

Table 2-2 General comparison of Fibre Types commonly used in composites with data from (66,79,81,84)

Property	Carbon Fibres	Glass Fibres	Aramid Fibres
Strength-to-Weight Ratio	High	Moderate	High
Stiffness	High	Moderate	Moderate
Fatigue Resistance	Excellent	Good	Good
Impact Resistance	Moderate	Moderate	High
Thermal Conductivity	High	Low	Low
Electrical Conductivity	High	Low	Low
Cost	High	Low	High
Applications	Primary and secondary structures, engine components	Larger, lower-cost structures, secondary structures, interiors	Ballistic protection, rotor blades, structural components, interior components

2.2.2 Thermoset Polymers

Polymers play a crucial role in fibre-polymer composites, serving as the matrix that binds the reinforcing fibres together and transfers loads between them. The choice of polymer significantly influences the properties and performance of the composite material. In aerospace applications, two main types of polymers are used: thermoset polymers and thermoplastic polymers. Each type has distinct characteristics that make it suitable for specific applications. The material of the dispersed reinforcement agent can grant the composite desirable characteristics such as corrosion resistance, conductivity, and temperature resistance(79–82).

Thermoset polymers are a class of polymers that irreversibly cure to form a rigid structure. This curing process involves a chemical reaction, often initiated by heat, radiation, or a catalyst, which creates a cross-linked network of polymer chains. Once cured, thermoset polymers cannot be remelted or reshaped.

The matrix phase of a composite is usually a thermoset polymer (a plastic that is irreversibly hardened (85)), due to the high-performance output at a lower production cost.

Thermoset polymers can withstand high temperatures without deforming, are resistant to a wide range of chemicals, including solvents, have high mechanical strength and stiffness (due to polymer crosslinking) and maintain their shape and dimensions under load and temperature variations(86–88).

Epoxy resins are widely used in aerospace composites due to their excellent mechanical properties, adhesion, and chemical resistance. They are commonly used in primary and secondary structures, such as fuselage sections, wings, and control surfaces. They offer high strength, stiffness, and thermal stability. They also provide good fatigue resistance and environmental durability(87,89,90).

2.2.3 Carbon Fibre- Epoxy Composites

Carbon fibre reinforced polymer (CFRP) composites, particularly those with epoxy resin matrices, have gained widespread adoption across various industries due to their exceptional mechanical properties, lightweight nature, and corrosion resistance (91,92). These materials offer a unique combination of high strength-to-weight and stiffness-to-weight ratios, making them desirable for applications where weight savings and performance are critical factors.

Carbon fibres, the reinforcing phase in CFRP composites, are derived from precursor materials such as polyacrylonitrile or pitch. The manufacturing process involves oxidation, carbonisation, and high-temperature treatment to produce the desired carbon fibre properties (84). Epoxy resins, on the other hand, are thermosetting polymers that serve as the matrix material, providing a medium for transferring loads to the carbon fibres and protecting them from environmental factors (93).

Various manufacturing techniques, including hand lay-up, resin transfer moulding, vacuum-assisted resin transfer moulding and prepreg processing, can be employed to fabricate CFRP components. Prepreg processes involves impregnating the carbon fibre reinforcement with the epoxy resin, followed by curing under controlled temperature and pressure conditions. (94–96).

Carbon fibre epoxy composites exhibit exceptional mechanical properties, including high tensile and compressive strengths, excellent fatigue resistance, and superior stiffness. These properties make them suitable for a wide range of applications in industries such as aerospace, automotive, wind energy, and sporting goods (97–99)

In the aerospace industry, CFRP composites are used in the construction of aircraft components, including fuselage sections, wings, tail structures and landing gear, contributing to weight reduction and improved fuel efficiency (58–61).

The automotive sector has also embraced CFRP composites for manufacturing body panels, chassis components, and other structural elements, enabling lightweighting and enhanced performance(57,100,101).

Although there are many serious benefits for using CFRP, care needs to be taken as they are susceptible to various failure mechanisms, including fibre breakage, matrix cracking, delamination, and impact damage. These failure modes can significantly compromise the structural integrity and performance of the composite material (102,103).

It also potentially makes composites vulnerable with traditional joining methods. As heat can cause fibre breakage and delamination they may need to be also carefully managed for changes in heat. (100).

2.3 Joining and Adhesion of Aerospace Composites

The joining and adhesion of composite materials are critical aspects of aerospace engineering. As composite materials become increasingly prevalent in the aerospace industry, effective joining techniques are essential to ensure the structural integrity and performance of composite components. This section explores the various methods used to join composite materials, the challenges associated with these methods, and the advancements in adhesive bonding technologies that enhance the reliability and efficiency of composite structures.

The aerospace sector is a key player in the advancement of structural materials and processing. Due to large scale of aircraft, several components are needed to be joined together. There has been an increased interest in the joining of aerospace materials over the years due to the desire to improve the quality of joints while also reducing cost and lead times(104–106).

2.3.1 Traditional Joining Practices

Mechanical Fasteners and other traditional joining practices form a major role in the joining of aerospace components. With metallic aerospace materials, there are a variety of different welding options available to join two structures together. These include, but are not limited to, laser beam welding, friction stir welding, fusion joining, laser blown powder and laser powder bed fusion(106,107).

For composites, aerospace structures present unique challenges due to their inherent properties, such as anisotropy, low surface energy ($<60 \text{ mJ m}^{-2}$)(108), and susceptibility to delamination. Traditional joining techniques have been adapted and modified to accommodate the specific requirements of composite materials(100).

Mechanical fastening techniques, such as bolting and riveting, are widely used for joining composite components in aerospace structures. For the Airbus A320 each orbital joint combining the centre and fuselage sections with the tail, contained 3000 rivets(109). On the Boeing 777 fuselage, 60,000 rivets are used (110).

These techniques involve drilling holes through the composite laminates and securing them with fasteners. Drilling holes in composite laminates can introduce stress concentrations, delamination, and fibre breakage, potentially compromising the structural integrity (7) .

To mitigate the risk of delamination and stress concentrations, specialised fasteners and installation procedures are employed which increases cost and complexity. Additionally, reinforcing materials, such as metal or composite inserts, are often incorporated into the laminate during manufacturing to improve bearing strength and load transfer (111).

The mismatch in coefficients of thermal expansion between the fasteners and the composite material can lead to thermal stresses and potential joint failure under cyclical thermal loading conditions. When dissimilar materials are used (e.g., metal fasteners with carbon fibre composites), there is a potential for galvanic corrosion, leading to degradation of the joint over time. The use of mechanical fasteners adds weight to the structure, which is particularly undesirable in applications where weight efficiency is critical, such as in aerospace and automotive industries (111–114).

Welding techniques have been adapted for joining composite materials, particularly for thermoplastic composites. Techniques such as induction welding, resistance welding, and ultrasonic welding have been explored for joining thermoplastic composite components (111).

These techniques rely on localised heating and consolidation of thermoplastic matrix material to create a fusion joint. Welding techniques for composite materials, particularly thermoplastic composites, face challenges related to heat management and potential degradation of the matrix material or reinforcement fibres. Excessive heat input can cause matrix degradation, fibre damage, and residual stresses, adversely affecting the joint strength and integrity (115).

Additionally, welding of thermoset composites is generally more challenging, costly and may require specialised techniques, process control or surface preparation steps. Material compatibility is a key concern, as these techniques

are less suited to thermoset composites which cannot be remelted. Surface preparation, while not as demanding as for adhesive bonding, still requires attention to ensure cleanliness and compatibility, adding to the process time. Additionally, component designs must accommodate the welding process, considering the accessibility of the weld area to the energy source and the need for materials at the joint interface that are compatible with the welding method, which can sometimes limit design flexibility and material selection (111)

Hybrid joining techniques combine the advantages of different methods, however they can also inherit the disadvantages of each individual technique. For example, a hybrid joint combining adhesive bonding and mechanical fastening may still be susceptible to stress concentrations around the fastener holes and environmental degradation of the adhesive bond. Furthermore, the design and analysis of hybrid joints can be more complex, requiring careful consideration of the interactions between different joining methods (116).

2.3.2 Adhesive Bonding

Adhesive bonding is a widely adopted joining technique for composite materials in aerospace applications. It involves using structural adhesives to join composite components, offering uniform stress distribution, and minimising stress concentrations (111,117,118).

The adhesion properties of polymer composites are an important consideration in the manufacturing process due to their use in complex structures. Several mechanisms play a key role in the adhesion process including mechanical interlocking, diffusion, electrostatic attraction, adsorption, and molecular forces (111,117,118).

A key challenge in polymer adhesion is the need for adhesive pretreatment to improve the wettability properties of the surface(119). Proper surface preparation, such as peel-ply removal (120), solvent cleaning(121), or plasma treatment(47), is crucial for achieving strong and durable adhesive bonds with composite materials.

Moulding and other manufacturing techniques of composites produce silicon containing release agents at the surface (37,105,106). These agents hinder the bond strength at the surface and hence need removal before bonding techniques (47,122,123).

Many preparation techniques can be slow, difficult to apply uniformly, result in secondary contamination, such as solvent wipe or grit blasting, or require high power consumption, such as non-contact flame treatment or corona discharge(124) .

The ISO 17212:2012 (125) standard provides guidance on surface preparation of metals and plastics prior to adhesive bonding. For example, the standard proposes several methods of cleaning such as alkaline cleaners for oil removal, solvent use for paint removal and ultrasonic cleaning. They detail that to achieve optimum environmental durability for an adhered surface, three sequential steps are needed: removal of contaminants, physically induced modification of the surface and chemical treatment(125). Atmospheric plasma treatment has been

shown to either achieve, or eliminate the need for, one or more of these steps(126).

Composites UK produces several good practice guides for the handling and production of composites, useful for the aerospace sector. For example, 'Joining of fibre-reinforced polymer composites' Written by TWI Ltd and funded by the National Composites Centre. This document details advice on joining processes available and gives recommendations on how they should be carried out(126).

It states that energetic pretreatments of polymers and polymer composites are effective methods which change the material surface texture through interaction with highly energetic species. Inert gases, such as argon, are particularly advantageous in the plasma cleaning of surfaces. Other gases such as ammonia, nitrogen and oxygen can also be particularly advantageous(126).

If the plasma has enough energy, it may clean the surface through the displacement of surface contaminants. It can also ablate surfaces contaminated through surface degradation. Another advantageous treatment includes the cross linking of the surface preventing weak boundary layer formations. Plasma treatment of a surface may also lead to the introduction of oxygen containing groups such as carbonyl, increasing surface wettability(68,127).

2.3.2.1 Mechanisms of Adhesion

Adhesion describes the attraction between the two different phases of materials and there are multiple theories which explain adhesion. It can be assumed that adhesion occurs due to various factors including mechanical interlocking, physical, and chemical bonding. There are also various forces responsible for intermolecular interactions such as covalent bonds, weak van-der Waals forces, dipole-dipole interactions, etc (128). The adhesion properties of polymer composites are influenced by several mechanisms, including mechanical interlocking, diffusion, electrostatic attraction, adsorption, and molecular forces, as displayed in Figure 2-2.

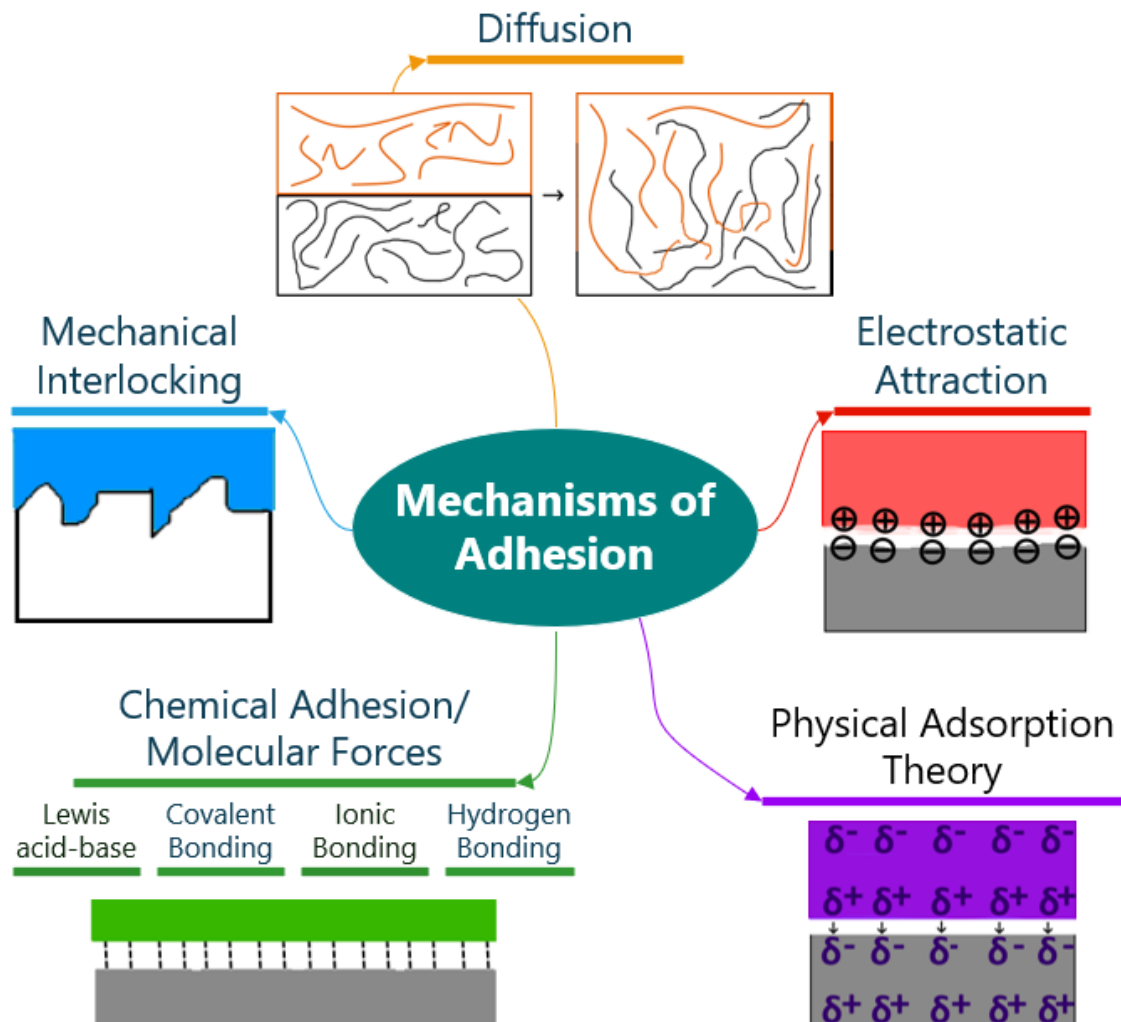


Figure 2-2 describing several key mechanisms of adhesion relevant to polymers and/or epoxy composites. Diagram drawn by the author with information from (128–132).

Diffusion is where polymers in contact interdiffuse, allowing an adhesive polymer to entangle with a polymeric substrate so that the initial boundary is eventually removed [92], [94]

Mechanical interlocking occurs when the adhesive fills into cavities at the surface of a material, creating a physical bond. This can be affected by the roughness of the composite material.

Electrostatic Attraction is when opposite charges on the adhesive and substrate surfaces attract each other, forming an electrostatic bond. Surface treatments that modify the surface charge can enhance electrostatic attraction and improve adhesion. (130,132).

The Physical Adsorption Theory, also known as dispersive adhesion, includes van der Waals forces across an adhesive-adherent interface. van der Waals forces involve attractions between permanent dipoles, induced dipoles, or temporary dipoles. A dipole refers to a pair of opposite electrical charges or magnetic poles that are separated by a small distance. In the context of molecules, a dipole occurs when there is an uneven distribution of electrical charge, leading to one part of the molecule being slightly positive and another part being slightly negative. This difference in charge creates a polarised molecule, with the two "poles" being the positive and negative ends, as displayed in Figure 2-2. Dipoles can arise from the way atoms share electrons in a bond, especially when different atoms have different attractions for electrons. There are three types of van der Waals interactions(129–132).

- Permanent Dipole-Dipole Interactions: Involve the attraction between two molecules with permanent dipoles. The potential energy depends on their separation distance.
- Dipole-Induced Dipole Interactions: A dipole in one molecule can cause a nearby non-polar molecule to develop a dipole. The strength of this induced dipole depends on how easily the non-polar molecule can be influenced and the strength of the electric field around it.
- Dispersion Forces: Arising from temporary dipoles caused by fluctuations in electron distributions

Lastly, the chemical bonding theory of adhesion explains that adhesion between materials occurs through the formation of chemical bonds (e.g. covalent, ionic, or hydrogen bonds) at the interface between the adhesive and the substrate. These bonds enable strong attachment at the molecular level, and their type and strength can vary based on the materials involved.

The strongest of these interactions would usually be the attraction between positive and negative ions, known as ionic bonding. In adhesives, ionic bonding can occur between charged groups in the adhesive and ions on the surface of the material. This type of bonding, however, is more relevant for adhesives used on metal surfaces, rather than composites, where charged carboxyl groups in the adhesive can form ionic bonds with metal ions.

The second strongest interaction would be the formation of covalent bonds. These occur when atoms share electrons. In adhesives, covalent bonds form between reactive groups in the adhesive and specific functional groups on the surface of the material (substrate). For example, silane coupling agents often form strong Si–O covalent bonds with surfaces like glass or metal oxides, which increases adhesion. Another example is isocyanate adhesives, which can form covalent bonds with hydroxyl groups in wood or paper. These bonds require a lot of energy to break, making them a reliable mechanism for adhesion.

Although weaker than both covalent and ionic bonds, hydrogen bonding works particularly well in materials such as wood, paper, or textiles which contain hydroxyl (–OH) groups. Another weaker interaction is the Lewis acid-base interactions, where an acid (electron acceptor) reacts with a base (electron donor)(128,132).

2.3.3 Surface Energy

Surface energy is the excess energy associated with the atoms or molecules present at the surface of a material compared to those within the bulk. This excess energy arises due to the unbalanced forces acting on the surface atoms or molecules, leading to different properties and behaviours compared to the interior of the material(133,134).

Surface energy plays a vital role in determining many physicochemical properties of materials, such as wettability(133), adhesion(135) and catalytic activity(134). It is a key factor in phenomena like capillary action and adsorption(136,137).

The concept of surface energy was introduced by Thomas Young in 1805(138), and it was further developed by Josiah Willard Gibbs in the late 19th century. Gibbs established the thermodynamic foundations of surface energy and introduced the concept of surface tension, which is directly related to surface energy(139).

Surface energy is typically expressed in units of energy per unit area (e.g. J/m² or mJ/m²). The surface energy of a material depends on various factors, such as the chemical composition, surface structure, orientation, and environmental conditions (e.g., temperature, pressure, and surrounding medium)(140–145).

The most common method to measure and calculate surface energy is liquid contact angle measurements. This method relies on the relationship between the surface energies of the solid and liquid phases, and the contact angle formed by a liquid droplet on the solid surface(146). This experimental method is explained further in section 3.6.2

Contact angle measurements are commonly used to characterise the surface energy of the reinforcement and matrix materials, as well as to assess their compatibility and wettability. A low contact angle indicates good wetting and a high work of adhesion, which is desirable for strong interfacial bonding. Surface treatments can modify the surface energy to improve compatibility(147).

Contact angle measurements and surface energy play a crucial role in the study and development of composite materials. In composites, the interface between the reinforcement (e.g., fibres, particles) and the matrix is of utmost importance, as it determines the overall mechanical properties and performance of the material(148,149).

The surface energy of the reinforcement and matrix phases governs their wettability and interfacial adhesion, which are key factors in achieving a strong and durable composite. Poor wettability and weak interfacial bonding can lead to poor stress transfer between the phases, resulting in reduced mechanical properties and potential failure of the composite bonding(128).

2.3.3.1 Surface Chemistry

The surface chemistry of a material is intrinsically linked to its surface energy. The surface energy stems from the imbalance of intermolecular forces experienced by surface atoms or molecules compared to those in the bulk, due to the termination of bonds at the surface. This imbalance is governed by the chemical composition, atomic arrangement, and bonding characteristics at the surface (150,151). Surfaces with highly polar functional groups, such as hydroxyl (-OH) or carboxyl (-COOH), tend to exhibit higher surface energies due to strong intermolecular interactions like hydrogen bonding (152).

Surface reconstruction and relaxation are phenomena associated with the rearrangement of surface atoms in materials to achieve a lower energy state. Surface reconstruction involves changes in the arrangement of atoms at the surface of a material compared to its bulk structure. This process can lead to new geometric and electronic configurations at the surface. Reconstruction can significantly alter the surface energy by creating a more stable surface configuration. The reorganisation of atoms reduces the overall energy of the surface, which is a driving force for the reconstruction process. Surface relaxation refers to the displacement of surface atoms from their ideal bulk positions, typically resulting in the contraction or expansion of the topmost atomic layers. Relaxation affects surface energy through changes in atomic spacing and coordination at the surface. In general, atoms at the surface seek to minimise

their energy by adjusting their positions, leading to a more stable surface structure with altered surface energy (153). This however is applied to metals, hence does not apply to polymer composites because the materials' structures and bonding characteristics are fundamentally different.

When considering polymer matrix composites, surface chemistry dictates the relative contributions of different intermolecular forces to the overall surface energy:

- Dispersive Forces: These are the non-polar interactions that emerge from momentary dipole-induced dipole attractions, primarily dictated by the material's surface composition.
- Polar Forces: Stemming from the electrostatic attraction between permanent dipoles, these forces are significantly influenced by the presence of polar functional groups or ionic species within the composite material(154).
 - Hydrogen bonding: Arising from the attractive force between a hydrogen atom, which is covalently linked to an electronegative atom (such OH or NH groups) within one molecule, and another electronegative atom (like O, N, or F atoms with a lone pair of electrons), either from a separate molecule (intermolecular) or within the same molecule (intramolecular). This type of bonding is a specific subset of polar interactions and is crucial in many polymer matrix composites(155,156).
- Acid-base interactions: Involving electron acceptor-donor interactions, the presence of acid or base sites on the surface of the composite components facilitates these interactions, which can significantly influence the interfacial bonding and, hence, the properties of the composite(157–159).

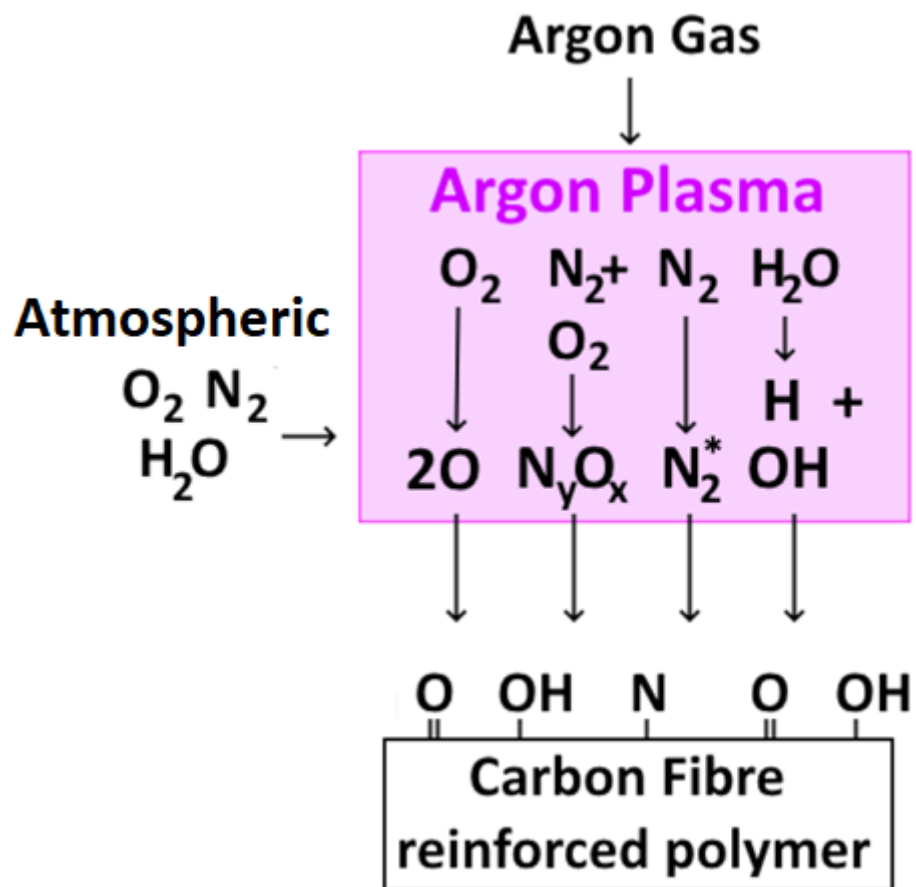


Figure 2-3 Displaying the interaction of Argon Plasma with atmospheric air and the effects this has on the surface composites. Adapted from Primc and Mozetič (160)

2.3.3.2 Surface Topography

The effect of surface roughness on surface energy is complex and can lead to various outcomes depending on the material, the scale of the roughness, and the environmental conditions.

An increase of surface area due to roughness can result in a higher surface energy, as more atoms or molecules are exposed. This is in line with Young's equation regarding the relationship between surface energy and contact angle on ideal, smooth surfaces. However, as detailed by Wenzel (161) when roughness is introduced, the actual area over which intermolecular forces act increases, potentially elevating the surface energy.

The presence of surface roughness can lead to different wetting regimes (Wenzel and Cassie-Baxter states), which are directly influenced by surface energy. In the Wenzel state, the liquid conforms to the rough surface, which can amplify the inherent surface energy characteristics of the material, making hydrophilic surfaces (Surfaces with water contact angles above 90°) more wettable and hydrophobic (Surfaces with water contact angles below 90°) surfaces less so. In contrast, the Cassie-Baxter state, where air pockets are trapped under the liquid, can effectively reduce the surface energy interaction with the liquid, enhancing hydrophobicity.

The chemical reactivity of a surface is significantly influenced by its surface energy, which is in turn affected by surface roughness. Increased surface area due to roughness can enhance the reactivity of a surface by providing more active sites for chemical reactions. The surface energy influences the types of reactions that can occur and their rates, as higher energy surfaces might be more reactive.

Surface roughness can influence adhesion and friction through mechanical interlocking and the modification of surface energy interactions at the interface. Rough surfaces can enhance mechanical interlocking, potentially increasing adhesion if the materials are able to conform to each other's roughness features(161–163).

2.3.4 Barriers to Adhesion

When bonding two composite surfaces together, several barriers can hinder effective adhesion and impact the integrity of the joint.

A difference in surface energy of two surfaces, as previously mentioned, can result in poor wetting and adhesion. This mismatch in surface energy can be attributed to the differences in surface chemistry between the two phases (108) The nature and strength of interfacial interactions, such as van der Waals forces, hydrogen bonding, or chemical bonding, play a crucial role in determining the adhesion strength. This can be due to the lack of compatible functional groups or the presence of contaminants at the interface. (108,164,165). Kim and Mai (148) highlighted that weak interfacial interactions between the composite surfaces and the adhesive can result in premature failure.

Surface topography and roughness play a crucial role in determining the adhesion strength when bonding composite surfaces. Proper surface roughness is essential for achieving good mechanical interlocking and increasing the effective contact area between the adherends, which enhances the adhesion strength. However, an inadequate or excessive surface roughness can act as a barrier to achieving strong adhesion.

In regard to composites specifically, it has been noted that surface pits or inadequate roughness can lead to poor adhesion, particularly in aerospace applications where composite bonding is widely employed. Mechanical pretreatments, such as peel-ply removal and plastic bead blasting, can significantly increase the surface roughness, leading to improved adhesion strength due to enhanced mechanical interlocking (166–168) .

The effect of surface roughness on adhesion strength is influenced by various factors, including the composite material properties, the adhesive used, and the bonding conditions. However, excessive surface roughness can also be detrimental to adhesion. Excessively rough surfaces can lead to a decrease in the real contact area between the adherends, resulting in reduced adhesion

strength. It has been proposed an optimal roughness range for maximising the interfacial shear strength in polymer composites(169,170).

The surface topography can also influence the wetting behaviour and the ability of the adhesive to penetrate and fill the surface irregularities. In addition to mechanical interlocking, surface roughness can also affect the formation of chemical bonds between the composite surfaces and the adhesive (165,171).

Environmental factors such as exposure to harsh environments, such as moisture, temperature extremes, or certain chemicals, can degrade the bonded interface and weaken the adhesion between the composite surfaces (172–174) The presence of impurities, such as oils, moisture, or other contaminants, at the bonding interface can act as barriers to adhesion, preventing direct contact between the composite surfaces (173)

During the bonding process or in service conditions, residual stresses can develop at the interface due to differences in thermal expansion coefficients or curing shrinkage of the adhesive. These residual stresses can lead to debonding and interfacial failure (175)

The compatibility between the composite surfaces and the chosen adhesive can significantly influence the adhesion strength. It is important to therefore chose appropriate adhesives and surface treatments to ensure strong and durable bonding between composite materials (117,176)

2.3.5 Release Agents as contamination preventing adhesion

In composite manufacturing, achieving a clean separation between the mould and the material is crucial to ensure the integrity and quality of the final product. Release agents are employed to prevent bonding between the composite material and the mould surface. These agents are vital in ensuring that composite components, such as those fabricated from carbon fibre, fibreglass, or various polymers, can be easily removed from moulds without causing damage. In the absence of release agents, materials would adhere to the mould surface, leading to defects and making part removal significantly more challenging.

The primary purpose of release agents is to form a non-stick barrier between the mould and the composite material. However, residual release agent that remains on the surface of the moulded part after demoulding can interfere with adhesion. This is particularly problematic in applications where the composite part must be bonded to another surface, painted, or coated(177).

Release agents are designed to be chemically inert or low-reactivity substances, which means that if any residue is left behind, it can prevent strong chemical or physical bonds from forming on the part's surface. Whether through contamination or a thin, invisible layer of the release agent, the adhesion properties of the surface can be compromised, leading to weaker bonds and/or coating failures(178,179)

Even when using high-quality, semi-permanent release agents, some amount of residue may be transferred from the mould to the composite part. This residue can inhibit surface wetting, which is essential for effective adhesion of paints, coatings, or adhesives. After demoulding, if the surface is not properly cleaned to remove all traces of the release agent, it can interfere with subsequent bonding processes. This is especially true for parts that require strong adhesion for structural purposes or surface coatings. In some cases, intricate or complex mould designs can lead to uneven application of the release agent, which might result in patchy coverage or excessive accumulation in certain areas. This can leave a thicker residue that is harder to remove, ultimately impacting adhesion(177,179,180).

2.4 Composite Surface Treatment

Surface treatment is a critical aspect of composite material processing, particularly in the composites industry. Proper surface treatment enhances the adhesion properties of composites, ensuring strong and durable bonds between different components(181) This section explores the various surface treatment techniques used for composites, the importance of surface treatment for adhesion, and the challenges and solutions associated with these processes.

The manufacturing processes of CFRP results in release agent contamination, this reduces the bonding strength of CFRP with an adherent(47). To completely remove the contaminant, a suitable pre-treatment method needs to be chosen.

2.4.1 Surface treatment techniques

Composite surface treatment involves modifying the surface of composite materials to improve their adhesion properties. This can be achieved through various techniques, each tailored to address specific challenges and requirements. The primary goal of surface treatment is to enhance the surface energy, cleanliness, and roughness of the composite material, thereby improving its ability to bond with adhesives, coatings, or other materials.

This method needs to be fast, easy to use and reproducible. It should result in a surface with high surface energy to be primed for good adherence to the surface(182). Common techniques for the surface treatment of composites include sanding, peel ply, plasma treatment and chemical etching.

2.4.1.1 Sanding

Sanding is a widely used mechanical abrasion method for surface preparation of CFRP composites before adhesive bonding or coating applications. The abrasive action of sanding helps to increase the surface roughness, which can enhance mechanical interlocking and improve adhesion strength.

In addition to mechanical interlocking, sanding can also influence the surface chemistry and wettability of CFRP composites, which can affect adhesion. However, excessive sanding or the use of coarse abrasives can also be

detrimental to adhesion. In addition, sanding produces dust, which is undesirable for bonding, so solvent cleaning is usually performed as an additional treatment step (183).

Prasad *et al* (36) in collaboration with the author, studied the effects of combining sanding with plasma treatment on the adhesion of CFRP to an epoxy adhesive. The results found that the combination of sanding and subsequent atmospheric plasma treatment significantly improved both the surface energy and lap shear strength compared to sanding alone.

2.4.1.2 Peel Ply

Peel ply can be used as a protective layer, or as a method of surface preparation. The use of a peel ply layer is to cover the surface of a composite prior to bonding to protect the surface from contamination and damage. The layer is removed before adhesion, modifying the surface in the process (169,182).

With the advantages of peel ply, comes disadvantages such as being difficult to remove and not producing a surface as appropriate for bonding as those pre-treated with mechanical abrasion. While the removal of the layer results in a roughened surface, the roughness shapes from the peel ply can in fact, negatively impact the adhesion process(169,184).

The surface roughness achieved by peel ply removal can be highly variable and dependent on factors such as the type of peel ply used, the curing conditions, and the removal technique. Inconsistent surface roughness can lead to inconsistent adhesion properties, making it challenging to achieve reliable and reproducible bonding performance(185).

The elemental composition of a surface treated with a peel ply layer depends on the composition of the peel ply itself, and the way it was applied. Polyester, polyamide and glass are the three main categories of peel ply. Some peel ply fabrics are surface finished with lubricating coatings. These include fluorocarbon or silicon containing compounds to ease the release of the layer from the composite surface. (169,184). The advantage of these surfaces becoming easier

to remove, can be outweighed with the disadvantage of these finishes being left on the surface as contaminant (169,186).

In some cases, additional surface treatments, may be required to activate the surface and promote chemical bonding between the composite and the adhesive or coating. While peel ply removal can provide some degree of surface roughness, the level of mechanical interlocking achieved may be insufficient for applications requiring high adhesion strength. In such cases, additional surface preparation techniques, such as abrasion or chemical etching, may be necessary to enhance mechanical interlocking and improve adhesion (187).

The removal of peel ply can sometimes lead to surface damage, such as fibre fracture or resin delamination, particularly in areas with complex geometries or sharp corners. This surface damage can compromise the structural integrity of the composite and adversely affect adhesion properties. Peel ply can also contain the use of release agents to counteract this effect, which further increases the need for further surface treatments(184,188).

The use of peel ply also results in further waste material, which may raise environmental concerns, especially as there still needs to be improvements and research to be conducted in the field of composite recycling(189).

2.4.1.3 Wet chemical etching

Wet chemical etching involves using chemical solutions to remove surface contaminants and modify the surface structure of materials(190). This process can increase surface roughness and improve the surface for bonding. Given its liquid based application, it can be suitable for complex shapes and surfaces(191).

The composite is immersed in a chemical solution, or the solution is applied to the surface. The chemicals react with the surface, removing contaminants and altering the surface structure(192). This can potentially remove contaminants and create a highly reactive surface(193,194). However, the chemicals used can be hazardous and pose both environmental and health risks. Proper safety measures and waste disposal procedures are essential(195–197).

2.4.1.4 Plasma Treatment

Plasma, a term to describe the fourth state of matter, is where not only do molecules can move freely akin to gas but are also ionised. Although in practice there will unlikely be complete ionisation of a gas. It consists of a complex mixture of electrons, ions, radicals, and neutral species, offering a unique environment for chemical and physical interactions with surfaces (198).

Plasma treatment involves exposing the composite surface to a plasma environment, which modifies the surface chemistry and increases surface energy. It can also introduce functional groups that enhance chemical bonding.

Contact-based processes, such as sanding or solvent cleaning can lead to uneven treatment and potential damage to the substrate. Solvent cleaning can leave residues and may not uniformly clean complex geometries. Plasma treatment is a non-contact process that can uniformly treat surfaces, including complex geometries and delicate materials(199). Other treatment methods are often limited in their ability to tailor surface properties for specific applications. Chemical etching, for example, is typically material specific and may not be suitable for all substrates (200).

Plasma processes can be accurately monitored using in situ plasma diagnostic instruments. Plasma treatment is versatile and can be customised by adjusting parameters such as gas composition, pressure, power, and exposure time. This flexibility enables precise control over surface properties(199).

Plasma treatment can be performed at both low and high temperatures, making it compatible with heat-sensitive materials. This is particularly important for applications involving polymers that may degrade or deform under high temperatures, or under the influence of certain chemicals or solvents (201–203).

Plasma treatment in the past typically took place inside a vacuum(204), however atmospheric pressure plasma has also been well researched and used in past few years, which will be further explored in section 2.4.3.

2.4.2 Plasma for Surface Modification

Surface modification techniques play a crucial role in tailoring the properties of materials for various applications across diverse industries, including biomedical, electronics, automotive, and aerospace (27,205). Among the available techniques, plasma treatment has emerged as a versatile and efficient method for altering the surface characteristics of materials without significantly affecting their bulk properties (206)

Plasma surface modification involves exposing the material's surface to a controlled plasma environment, where the energetic species present in the plasma can induce chemical reactions, etching, deposition, or crosslinking, depending on the specific process parameters and the nature of the material (207,208). This technique has gained significant attention due to its ability to modify surface properties such as wettability, adhesion, chemical functionality, and biocompatibility (209,210).

The effectiveness of plasma surface modification stems from the highly reactive nature of the plasma species, which can interact with the surface at the atomic or molecular level. These interactions can lead to the formation of new functional groups, the removal of contaminants, or the creation of a roughened or textured surface, all of which can significantly impact the material's performance in various applications (33,211,212)

Mechanical abrasion and chemical etching primarily increase surface roughness to improve adhesion. However, these methods may not introduce new functional groups that enhance chemical bonding. Plasma treatment can introduce a variety of functional groups (e.g., hydroxyl, carboxyl, amine) onto the surface, significantly enhancing wettability and adhesion properties(201–203).

New functional groups on the surface of the material form through chemical reactions with reactive plasma species, as displayed in Figure 2-3. Groups, such as hydroxyl (-OH), amine (-NH₂), carboxyl (-COOH), or fluorine (-F), can significantly alter the surface properties, including wettability and chemical reactivity(160). However, these functionalised surfaces are often not permanently

stable. The introduced groups may gradually become inactive due to surface rearrangement, contamination, or environmental exposure. Depending on storage conditions and material type, the activity of these groups can diminish within hours to days, with some studies reporting a half-life of surface functionality on the order of 24 to 72 hours.

Plasma crosslinking is a process where chemical bonds form between surface molecules due to plasma treatment, which enhances the material's mechanical strength, chemical resistance, and heat resistance. This technique is particularly beneficial for polymers surfaces making them tougher and more durable(213).

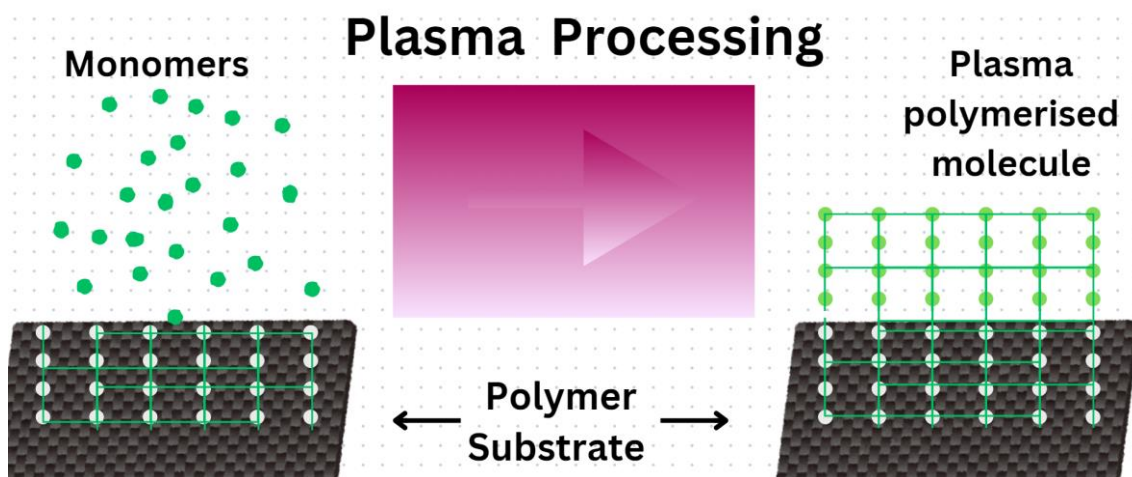


Figure 2-4 illustrating the process of plasma polymerisation. On the left, monomers are shown above a polymer surface enriched substrate, representing the initial phase before plasma processing. In the centre, the plasma field is highlighted, where the monomers are exposed to plasma energy. On the right, the result is depicted with a polymerised layer formed on the substrate, demonstrating how plasma processing transforms the surface by creating a stable, polymerised coating. Diagram drawn by the author using information from (214)

Plasma can also play a role in polymerisation at the surface, or deposition of materials. This involves depositing a thin film on the surface by breaking down precursor molecules in the plasma, as demonstrated in Figure 2-4. This can create a protective or functional coating that can make a surface water-resistant, chemically inert, or better suited to specific environments, depending on the material used (214).

2.4.2.1 Vacuum Plasma

The plasma sources and processes employed for surface modification are diverse, each offering unique advantages and capabilities. The selection of the appropriate plasma source and process depends on factors such as the material to be treated, the desired surface properties, and the scale of the application.

Low-pressure plasma systems operate at reduced pressures, typically below atmospheric pressure. These systems include glow discharge, capacitively coupled, and inductively coupled plasma reactors. Low-pressure plasmas are characterised by their high density of reactive species and controllable parameters, making them suitable for precise surface modifications (215,216).

2.4.2.2 Atmospheric Pressure Plasma

For composite surface treatment, time and cost are key players in choosing a surface treatment method. Atmospheric pressure plasma systems operate at ambient pressure, eliminating the need for vacuum chambers and offering advantages such as continuous processing, reduced equipment costs, and the ability to treat complex geometries (215).

The choice of plasma source and process parameters, such as gas composition, pressure, power, and exposure time, significantly influences the nature and extent of surface modification achieved. Careful selection and optimisation of these parameters are crucial for tailoring the surface properties to meet the specific requirements of the intended application (209).

2.4.2.3 DBD Plasma

Among the various atmospheric pressure plasma sources, dielectric barrier discharge (DBD) plasmas have gained significant attention for surface modification applications due to their versatility, scalability, and ability to operate at atmospheric pressure (217).

A DBD setup typically consists of two electrodes separated by one or more dielectric barriers, such as glass, quartz, or ceramic materials. When a high voltage (typically a few kilovolts) is applied between the electrodes, the dielectric barrier prevents the formation of a direct spark or arc discharge. Instead,

numerous short-lived micro discharges are generated, forming a uniform glow-like plasma (218).

The dielectric barrier acts as a current limiter, allowing for stable and uniform plasma generation without the need for complex external circuitry. DBD plasmas can be operated in various configurations, including planar, cylindrical, or coplanar geometries, allowing for treatment of diverse substrate shapes and sizes (219).

The plasma chemistry in DBD systems is highly dependent on the feed gas composition, which can range from inert gases (e.g., helium, argon) to reactive gases (e.g., oxygen, nitrogen, air) or precursor gases for specific surface modifications. The energetic electrons in the plasma ionise and dissociate the feed gas, generating a complex mixture of reactive species, including ions, radicals, and excited molecules (220).

These reactive species can interact with the surface of the material being treated, leading to various surface modification mechanisms, such as etching, activation, functionalisation, and deposition. The low-temperature nature of DBD plasmas allows for treatment of heat-sensitive materials, making them suitable for applications in the biomedical, packaging, and textile industries (25).

DBD systems can be scaled up for treating large surface areas or continuous web processing. By varying the feed gas composition and process parameters, DBD plasmas can achieve a wide range of surface modifications, including wettability alteration, Functionalisation, and deposition of thin films.

One of the primary benefits of oxygen DBD plasma is its ability to remove contaminants and weak boundary layers from surfaces, thereby improving roughness and reactivity. This process significantly enhances surface adhesion, making it ideal for industries like electronics, coatings, and automotive, where strong material bonding is essential.

One of the standout benefits of DBD plasma is its antimicrobial and sterilisation capabilities. The combination of reactive species, UV radiation, and charged particles in DBD plasma treatments effectively inactivates a wide range of

microorganisms making it a highly efficient tool in healthcare environments. Although the antimicrobial properties are less relevant to composite adhesion, the high UV content itself can benefit the effects of polymer crosslinking, and surface functionalisation (202,221).

Air Plasma

Among the various gas compositions used in DBD systems, air plasmas have gained significant interest due to their cost-effectiveness, environmental friendliness, and the ability to generate a wide range of reactive oxygen and nitrogen species (222).

Air DBD plasmas are generated by applying a high voltage (100v and above) across a gap filled with ambient air. The plasma ionises and dissociates the molecular oxygen and nitrogen present in air, leading to the formation of various reactive species, including ozone (O_3), atomic oxygen (O), hydroxyl radicals ($OH\bullet$), singlet oxygen ($^1O_2$), nitrogen oxides (NO_x), and excited nitrogen species (N_2^*) (223).

Oxygen containing DBD plasma is also highly effective at introducing functional groups, such as hydroxyl ($R-OH$), carbonyl ($C=O$), carboxyl ($-COOH$) and amine ($R-NH_2$), to material surfaces. DBD plasma also induces crosslinking within polymeric materials (224).

Nitrogen Plasma

Nitrogen DBD plasmas, generated by using nitrogen gas or nitrogen-containing gas mixtures as the feed gas, offer unique advantages and capabilities for surface modification applications.

In nitrogen DBD plasmas, the high-energy electrons collide with nitrogen molecules (N_2), leading to their dissociation and ionisation. This process

generates a variety of reactive nitrogen species, including atomic nitrogen (N), excited nitrogen species (N_2^*), and nitrogen oxides (NO_x) (223,225).

Other nitrogen-containing species include amine groups ($R-NH_2$), imines ($C=N$) (226), and nitro compounds ($R-NO_2$). Arnold *et al* (227) found that introducing nitro groups to the surface of carbon fibres significantly increases hydrophobicity. The water contact angle of fibres rose from 98.4° to 123.1° , after being functionalised with nitrophenyl groups. When these nitro groups were reduced to amines, the WCA decreased to around 99.9° , which was more hydrophilic than the nitrophenyl enriched surface, but similar to that of virgin fibres. Despite the increase in hydrophobicity due to nitro and perfluorinated alkyl groups, all surface chemistries demonstrated an increase in interfacial shear strength. The study challenges the belief that increased surface polarity always directly correlates with enhanced adhesion. The presence of these groups, especially amines, can facilitate cross-linking with polymer matrices, enhancing adhesion properties

Ren *et al* (228) used hydrazine hydrate to modify glycidyl methacrylate (GMA) grafted polyacrylonitrile (PAN) fabrics. Hydrazine reacts with the epoxy groups in GMA, resulting in a more hydrophilic surface due to the introduction of amino groups.

2.4.2.4 Microwave Plasma

In recent years, microwave plasma has emerged as a promising technique for surface modification, offering unique advantages over traditional plasma sources. Microwave plasmas are generated by the interaction of microwave electromagnetic radiation with a gaseous medium, typically at a frequency of 2.45 GHz (229)

Microwave plasma systems typically consist of a microwave source (e.g., a magnetron or a solid-state generator), a waveguide or resonant cavity for transmitting and confining the microwave energy, and a plasma chamber where the gas is ionised and sustained as a plasma (230).

Microwave plasmas offer several advantages over other plasma sources. They produce a high-density plasma, typically in the range of $0.1\text{--}10\text{ mm}^{-3}$, enhancing the reactivity and efficiency of surface modification processes. Operating at lower pressures, from tens of millitorr to a few torr, allows for more efficient control of plasma chemistry by minimising collisional deactivation of reactive species. Another significant advantage is their electrodeless operation, which avoids contamination from electrode materials and allows for the treatment of complex geometries. Additionally, microwave plasmas achieve a high degree of ionisation, resulting in a substantial concentration of reactive species, such as ions, radicals, and excited molecules, further enhancing their effectiveness in surface treatment applications (231–234).

Microwave plasmas can induce various surface modification mechanisms, such as etching, activation, functionalisation, and thin film deposition, depending on the process parameters and precursor gases used. These mechanisms can be useful for a variety of applications, including those previously mentioned in section 2.4.2 and 2.4.2.3.

2.4.2.5 Radio Frequency Thermal Plasma

Radio frequency (RF) plasmas, operating at frequencies typically in the range of kilohertz to megahertz, have emerged as versatile tools for surface modification across various industries. The ability to generate high-density plasmas and the wide range of operating pressures make RF plasmas suitable for a variety of surface treatment applications.

RF plasmas are generated by applying an alternating current (AC) electromagnetic field at radio frequencies, typically 13.56 MHz (the industrial standard frequency) or its harmonics, across two electrodes in a vacuum chamber (235)

The oscillating electric field accelerates the electrons in the gas, which gain sufficient energy to ionise the gas molecules through collisions, leading to the formation of a plasma. The electrodes in an RF plasma system can be configured

in different geometries, such as parallel plate, cylindrical, or more complex shapes, depending on the application and the desired plasma characteristics.

RF plasmas are characterised by their high plasma density, typically in the range of $0.001 - 1 \text{ mm}^{-3}$, and their ability to operate over a wide range of pressures. The plasma density and the flux of reactive species can be controlled by adjusting the applied power, pressure, and gas composition. (230,236)

The reactive species generated in an RF plasma, such as ions, radicals, and excited molecules, can interact with the surface of the material being treated, enabling various surface modification mechanisms.

RF plasmas are used for surface cleaning, activation, and functionalisation in various industries, such as automotive, aerospace, and packaging (203,204,237) in the fabrication of integrated circuits, microelectromechanical systems (MEMS), and optoelectronic devices (230,238)

Argon Plasmas

Argon, being an inert gas, has long been used as a carrier gas or a diluting agent in various plasma processes. However, argon plasmas themselves can also play a crucial role in surface modification.

Argon plasmas are typically generated by ionising argon gas using various plasma sources, such as capacitively coupled, inductively coupled, or microwave-based systems. The primary reactive species in argon plasmas are argon ions (Ar^+), metastable argon atoms and energetic electrons (230).

Argon plasmas can induce physical etching/sputtering, surface activation and thin film deposition (24,238,239)

Silicon contamination, often from silicone based mould-release agents like Chemlease EZ 41-90, significantly affects the surface chemistry of epoxy samples, particularly when subjected to plasma treatments. These contaminants can interfere with the plasma's ability to modify the surface, influencing the outcomes of XPS analyses and the material's overall properties(49).

Silicon-based groups such as Si-O and Si-CH₃ dominate the surface(240), creating a hydrophobic layer. The Chemlease layer impacts wettability and adhesion(240–242), reducing the effectiveness of plasma treatments. Argon plasma may have a marginal etching effect [64]. partially when increased temperatures is involved(243–245).

Fluorinated Argon RF Plasma

Fluorinated argon plasmas are created by introducing fluorine-containing gases, such as CF₄ or SF₆, into argon plasma. The reactive fluorine species generated in these plasmas, including fluorine radicals (F•) and fluorine ions (F⁻), offer unique surface modification capabilities (246) as demonstrated in Figure 2-5.

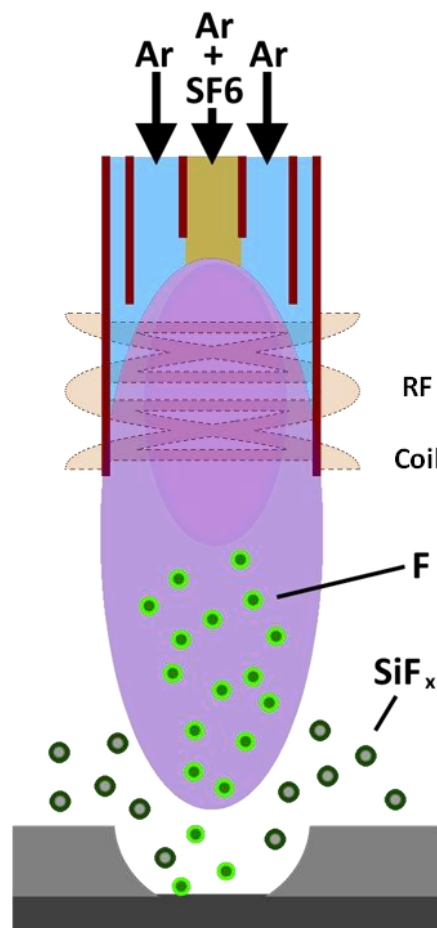
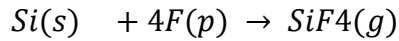
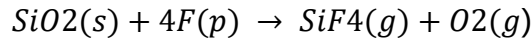


Figure 2-5 Displays a RF plasma (from an argon with fluorinated argon feed gases) removing silicon layers from a surface. The Fluorine in the plasma interacts with the silicon to produce SiF_x compounds (247–249).

When clean silicon is exposed to atomic fluorine, a surface layer of fluorine forms around it that may penetrate the top 1-5 monolayers. It may attack subsurface Si-Si bonds, which will eventually release silicon in gaseous form of either SiF₂ (a free radical) or SiF₄ (a stable product) as described below.



In the case of Si being masked by organic polymer layer, Argon ions can sputter this layer, although care needs to be taken to ensure the argon does not sputter, burn or delaminate the epoxy (247–249).

Fluorinated argon plasmas are highly effective in inducing several key mechanisms on material surfaces. First, they enable etching and surface modification by using reactive fluorine species to effectively remove material, making them particularly valuable in the semiconductor industry for etching applications. In addition to this, fluorine species introduced through plasma can lead to surface functionalisation, where fluorine-containing functional groups are added to the surface, thereby altering properties such as hydrophobicity, chemical resistance, and surface energy. Lastly, fluorinated argon plasmas are useful for the deposition of fluorocarbon-based thin films, which act as protective coatings against corrosion, wear, and chemical attack on various substrates, providing long-lasting surface protection(250–252).

2.4.3 Notable Advancements of Plasma Processing for surface treatment

Plasma surface treatment offers several significant advantages over traditional surface treatment methods, making it an increasingly popular choice in multiple industries, including the aerospace, automotive, electronics and biomedical field. These benefits stem from the unique properties of plasma and its ability to modify surfaces at the atomic or molecular level (253).

ISO standards on the methods of surface preparation before adhesion state a 3-step process; contaminant removal, physical surface modification and chemical treatment (125)

The 3-step process can often involve the use of abrasive cleaners and other chemical treatments that are not only complicated but also time consuming (254). Atmospheric pressure plasma offers an alternative treatment that has the potential to functionally replace not just one but possibly all of these steps while also being a relatively simple non-contact treatment method (255).

As composites often have a polymer matrix, it is important to review the effect of plasma on both composite and polymer surfaces.

2.4.3.1 Polystyrene

Polystyrene composite is a promising, light weight polymer composite for the aerospace industry (256,257) For example, thin film composites can be explored to produce super hydrophobic and super paramagnetic surfaces. (258)

Arinda et al (39) modified the surface of polystyrene films using a radio frequency oxygen plasma at 40 Pa pressure. The treatment saw a decrease in water contact angles, especially in cases of high RF voltage. A linear trend formed where an increase in voltage resulted in a decrease in contact angle.

Aging studies showed that across almost all voltages the contact angles were still lower even after 5 and 10 days post treatment. RF oxygen plasma treatment resulted in an initial decrease in contact angle ranging from 55° to 75°. The aging

is an indication of the formation of polar groups at the polystyrene surface, C-OH and C-O, increasing dipole-dipole interactions.

A reason for aging could be due to the air humidity allowing water to come into contact with the surface and creating non-polar bonds. Surface morphology measurements indicate that there is a decreased surface roughness during treatment but not after recovery which could be the result of the contact angle effects. Similar results have been observed in other studies. (259,260)

2.4.3.2 Acrylonitrile butadiene styrene (ABS)

Abenojar *et al* (261) used an atmospheric pressure air plasma of 17kHz and 20kV to modify the surface energy of ABS. The treatment time was controlled by placing the sample upon a speed controlled platform and changing that speed to 1, 5 or 10 m/min. An optical pyrometer measured the temperature on the material to be less than 27°C, with there being 6mm between the torch nozzle and the substrate. Aging was measured over 30 days for the 1m/m and 10m/m trails at room temperature.

The results show that even at the fastest processing speed the surface water contact angle measurement dropped about 20°. At 1 m/min the contact angle decreased from over 70° to under 40°. Aging studies showed that 30 days had little effect to the contact angle of the 10 m/min sample although had a large effect on the 1 m/min sample after 20 days where contact angle rose by 10°. This however seems to be similar to the contact angle of the 10 m/min samples. This would imply that, if a sample would need to maintain a low contact angle over an extended period of time, a faster treatment speed of 10 m/min would be just as adequate as a slower treatment time.

XPS analysis shows a decrease in carbon and an increase in oxygen at the surface of plasma modified ABS, with the 1m/min speed having a significant effect. Even after 26 days of aging, treated samples still retain a higher O/C ratio although this is significantly less in the case of the 1m/min sample. This is likely a result of the degradation of carboxylic groups, carbonyl groups, C-O-H, R-O-C=O, C-O and C-N polar species over time.

The prevalence of oxidation may indicate that modification is not just restricted to the surface. Attenuated Total Reflection Fourier transform (ATR-FTIR) infrared spectroscopy analysis indicates that the abundance of C=O, C=C and C-O groups increases with an increase in plasma treatment. When the –CN group reforms to N₂ and N₂O the modification is permanent. Here, the nitrogen based molecules disappear as gas, and the carbon remains on the surface, contributing to the formation of other carbonyls. Although active chemical groups remain on the surface, new bonds are formed after plasma resulting in a decrease in surface energy. SEM images indicate that surface treatment increases the surface roughness of the ABS sample.

2.4.3.3 Styrene-butadiene rubber

This synthetic copolymer has similar characteristics to natural rubber. It has a high impact strength and tensile strength. The 10-25% styrene content results in good bonding characteristics. Styrene butadiene has improved strength, and abrasion resistance over polybutadiene. The sulphur vulcanisation process is a method to increase strength and stiffness by cross linking elastomer molecules. This process is open to additional additives such as carbon black, fibre glass and silica.

Romero-Sanchez and Martin-Martinez (119) used atmospheric air plasma to modify the surface of synthetic sulphur-vulcanised styrene-butadiene rubber. Two nozzle-to-surface distances were used: 5 mm and 10 mm. The speed of the sample passing under the torch was set to 1m/min and the two distances compared. The shorter distance was shown to improve wettability while also removing paraffin wax from the surface.

Further study was carried out by altering the speed of the substrate as it passes under the nozzle, thus altering the treatment time, with a 5 mm distance. Despite the slower treatment increasing the degree of surface oxidation through the creation of C-O bonds, the adhesion properties did not improve. This was further supplemented though the migration of zinc stearate to the surface.

2.4.3.4 Nylon

Nylon, particularly nylon 6, 6,6 and 12 are a group of synthetic polymers known well in the textile industry but more recently show promise in 3D printing and aerospace. Nylon 12 is made from either ω -aminolauric acid or laurolactam monomers. The '6' or '12' denote the number of carbons contained within the monomers (124) Nylon 6,6 is a polyamide, a polymer derived from the condensation reaction of carboxylic acid (-COOH) and amine (-NH₂) group containing monomers. The amide linkages form hydrogen bonds with one another in nylon fabric (126).

Zhu *et al* (262) used an RF atmospheric pressure helium plasma at 10 and 13.56MHz. 2mm distance was kept between the nozzle and the sample with a flow rate of 10 l/min and the sample was placed under the nozzle at a rate of 3mm/s. The nozzle temperature was kept at 100°C. The result was an improvement in the hydrophobicity, adhesion to dye and surface roughness. As expected, XPS showed that treated fibres have higher levels of oxygen content than untreated fibres. Tensile strength tests indicated that plasma processing had negligible effect.

Pappa *et al* (22) used either an acetylene or nitrogen atmospheric pressure plasma to modify the surface of nylon 6. The study showed that both plasma treatments resulted in an increase in surface tension of nylon fabric from 34.62 mN/m to 45.07 mN/m and 48.56 mN/m in acetylene and nitrogen treatment respectively.

Nylon films were exposed to N₂/He plasma for 9.6 seconds, where the water contact angle, 15 days post treatment, decreased from 76.13° (in the untreated samples) to 58.22°.

Through the addition of new reactive chemical groups such as -COOH and -OH on the nylon 6 fibres, the wettability of the surfaces was improved. This leads the surface to be affected by hydrophobic recovery. The results also note that samples with longer treatment times will still have lower contact angles one month

post treatment. Even samples exposed for just 0.6 and 2.4 seconds still resulted in lower contact angles after one month than the control film.

Surface roughness was significantly increased with 876 nm for the control film to 1769nm for the nitrogen-helium plasma treated sample after 4.8seconds.

Cui *et al* (263) used DBD for the treatment of nylon 6,6. Where the results indicated that there were two stages to surface oxidation. The first stage involved single carbon-oxygen bonds. The second stage saw these carbons double bonded. As a result, a large drop in contact angle was observed.

2.4.3.5 Hydrophobic recovery of Carbon fibre reinforced polymers.

Liang *et al* (18) conducted an aging study of the long-term effects of both argon and helium gas plasma on polypropylene membrane separators. In this case it is the result of diffusion of low molecular weight organic matters towards the bulk of the polymer as well as the reorientation of polymer chains. Their results taken over 700 hours, just under a month, display the need for short term studies. Here the bulk of the hydrophobic recovery occurred within the first 50 hours/ 2 days. It can be observed that post 100 hours, the water contact angles plateau. This displays the need for an extensive 'secondary' study over a 24 hour and 4-day period.

Cheng *et al* (264) studied the aging effect of polypropylene and polyethylene terephthalate fibres post treatment by atmospheric cold argon plasma. The gas temperature was between 25-30°C and the treatment time was varied. This study displays the intricacies between the treatment times and type of polymer. It also highlights the need for longer term studies as even after 60 days some of the samples still appear to be in the stage of hydrophobic recovery.

2.5 Summary & Research Gap

The aerospace industry has made significant strides in the development and application of composite materials. These advancements have been driven by the need for lighter, stronger, and more fuel-efficient aircraft

2.5.1 Summary

Composites have enabled the production of lighter and more efficient aircraft. Modern aircraft like the Airbus A380 and Boeing 787 incorporate significant amounts of composite materials, leading to substantial weight savings and improved performance.

Fibre-polymer composites, particularly those reinforced with carbon, offer high stiffness-to-weight ratios, excellent fatigue resistance, and improved corrosion resistance. These properties make them ideal for various aerospace applications, including primary and secondary structures, engine components, and interior parts.

Effective joining techniques, including mechanical fasteners, welding, and adhesive bonding, are crucial for ensuring the structural integrity of composite components. Adhesive bonding, in particular, offers uniform stress distribution and weight reduction but presents challenges related to surface preparation including contamination removal.

Surface treatments, especially plasma treatments, are essential for enhancing the adhesion properties of composites. Techniques such as Dielectric Barrier Discharge (DBD) Plasma, Microwave Plasma, and Radio Frequency (RF) Plasma have been explored for their effectiveness in modifying surface properties and improving adhesion. Plasma can also be a tool for the etching of glass with the potential to use this ability to further remove silicon based contamination without damaging the composite itself.

Despite these advancements, several research gaps remain that need to be addressed to further optimise the pretreatment composite manufacturing.

2.5.2 Identification of Gaps in the Literature

The challenge of removing silicon contamination from composite surfaces, crucial for enhancing adhesion in manufacturing processes, is well observed in industry. While existing studies have explored various plasma treatment methods, there remains a notable gap in understanding the comparative effectiveness and efficiency of different plasma technologies. The specific gases used in plasma treatments appear to significantly influence the outcomes, although there is little knowledge out there on specific silicone removal with plasma.

Contact-based processes, such as sanding or solvent cleaning can lead to uneven treatment and potential damage to the substrate. Solvent cleaning can leave residues and may not uniformly clean complex geometries. Plasma treatment is a non-contact process that can uniformly treat surfaces, including complex geometries and delicate materials.

The speed of plasma treatment is another crucial factor in industrial settings where time efficiency directly impacts production costs and throughput. However, the literature often overlooks this aspect, focusing more on the qualitative outcomes of surface treatments. There is a need for detailed studies that quantify the treatment times of various plasma technologies and correlate these with their effectiveness in silicon removal. Silicon contamination can cause significant bonding difficulties, leading to delays and inefficiencies in production.

Dighton *et al* (48) used an atmospheric plasma treatment method involving a PlasmaTreat OpenAir single rotating flame jet to remove silicone containing release agent. The blown-arc plasma system used clean dry air as the feed gas. This treatment was found to not completely remove the contaminant layer. Instead, the plasma transforms the silicon contaminant into a more stable inorganic form, namely a thin layer of silicon dioxide (SiO_2). This transformation was detected through X-ray photoelectron spectroscopy (XPS), which showed a chemical shift in the silicon present on the surface after plasma treatment.

There has been limited research into the detailed effects of plasma treatment on the surface chemistry of carbon fibre/epoxy resin systems with surface

contamination. As a result, the mechanisms behind the improvements in strength need to be thoroughly investigated.

Fluorinated plasma has been used to etch silicon wafers and silicon-oxide based glass material, but there has been no research to date regarding the ability to use fluorinated plasma to remove silicon contamination on composites, nor the effect fluorinated plasma may have on the structural effects of composites, and the risk of over-etching, burning or delamination.

Finally, while existing research focuses on the immediate effects of plasma treatments on surface properties, the long-term stability and durability of these treatments, are not as well-documented.

3 Methodology

3.1 Introduction

This study compared multiple atmospheric plasma systems, both thermal and non-thermal, for the improvement of composite surface adhesion. Initial studies attempted to utilise non-thermal plasma systems, using a mixture of argon and nitrogen plasmas. To do this three plasma systems were explored: two microwave systems of different powers, and one dielectric barrier discharge (DBD) system.

Mould release agents are commonly used in the manufacturing process to facilitate the separation of moulded parts from the mould. These agents form a barrier between the mould surface and the material, reducing surface energy and preventing adhesion(265,266). Comparing coated and non-coated samples allows for a comprehensive evaluation of how these agents interact with plasma-treated surfaces and affect adhesion properties. For instance, the inclusion of release agents can influence the surface chemistry and topography, which in turn impacts the effectiveness of plasma treatment in enhancing adhesion.

Through the measurement of surface energy, it is possible to infer the wettability and the potential for adhesion of different materials to the treated surface. High surface energy indicates better wettability and potential for stronger adhesion, which is desirable in many applications, such as in coatings and adhesives. Plasma treatments are known to alter the surface energy by introducing functional groups that can increase or decrease the surface tension. Thus, studying surface energies before and after plasma treatment provides insights into the effectiveness of the treatment in modifying surface properties to achieve the desired adhesion outcomes.

XPS and surface chemical analysis in general will provide some insight into the surface effect of plasma, shining light on the science behind how plasma increases surface adhesion. Lap shear strength studies, although a time-lengthy intensive and material destructive testing method, further quantify the improvement in adhesion properties. These tests measure the shear strength of

adhesives by applying force until failure, thus providing direct evidence of the enhanced adhesion due to plasma treatment.

Temperature is a critical parameter in plasma treatment processes. It affects the kinetics of chemical reactions on the surface, the stability of the plasma itself, and the physical properties of the materials being treated. In plasma treatments the increased surface (between 50-200°C) can enhance the mobility of surface atoms, promoting more uniform surface modifications and improving the bonding strength between surfaces. Excessive temperatures (>200°C) however can lead to thermal degradation of sensitive materials. Therefore, maintaining an optimal temperature range is essential for achieving the desired surface modifications without damaging the substrate(253,267).

The study employs a variety of plasma torches to manage temperature effects and achieve desired surface modifications:

- 1) Dielectric Barrier Discharge (DBD) Non-Thermal Plasma: This type of plasma operates at near-room temperatures, making it suitable for treating temperature-sensitive materials. It is effective in introducing surface functional groups without causing thermal damage.
- 2) Microwave Non-Thermal Plasma: Microwave plasmas provide high electron densities and energy, which can be beneficial for achieving deep surface modifications and enhancing the activation of chemical reactions on the surface.
- 3) Radiofrequency (RF) Thermal Plasma: RF plasmas can generate higher temperatures, which are useful for applications requiring significant surface restructuring or for treating materials that are less sensitive to heat.

Further studies explored the use of Thermal Radio Frequency (RF) Plasma processing. Plasma processing has been shown to remove silicon material in the presence of Sulphur Fluoro Hexane (SF_6) s-linking an(40,268–271). As silicon is a major component of silicone, for this study SF_6 inductively coupled RF plasma was explored with the potential to remove silicone contamination on composite samples (while also increasing surface energy to result in improved adhesion).

3.2 Composite Materials

Two composite materials were used to investigate the ability of plasma to increase the surface energy of composites; C 420, a thin carbon fibre reinforced epoxy laminate, sourced from Goodfellows, and MTM44-1, an aerospace grade carbon fibre composite with an epoxy finish, sourced by BAE Systems. The former was chosen due to a lower cost, being readily available and appropriate for use in measurement devices where MTM44-1 could not be used. For example, MTM44-1 was too thick to be observed under AFM, and the surface texture made measurement under a CCI inappropriate.

3.2.1 C420 Laminate

The C420 carbon fibre- epoxy resin matrix samples had a thickness of 0.25mm. The sample was composed of a cross-hatched carbon fibre layer with a surface epoxy layer. These samples were used for early stage studies, and for studies where the thicker and more textured MTM44-1 samples would not be appropriate, e.g. AFM, FTIR and CCI.

3.2.2 MTM44-1

MTM44-1 is a high-performance composite material designed specifically for the production of primary and secondary aircraft structures. It is a toughened epoxy resin that cures at 180°C (356°F) and offers exceptional mechanical and thermal properties. This material can be processed using both low-pressure vacuum bag Out of Autoclave (OOA) moulding and autoclave moulding methods.

It meets NASA's stringent outgassing requirements, making it suitable for use in space structures. The cured resin has a density of $1.18 \times 10^3 \text{ g/mm}^3$, and its mechanical properties include high tensile and compressive strength, making it ideal for aerospace applications.

MTM44-1 is a two-part epoxy formulation consisting of a resin component and a hardener component. The resin component is a blend of epoxy resins and reactive diluents, while the hardener component contains amine-based curing agents and additives. The unique formulation of MTM44-1 allows for a wide

processing window, with a recommended cure cycle ranging from 120°C to 180°C, depending on the desired properties and production requirements.

One of the key advantages of MTM44-1 is its ability to achieve high glass transition temperatures (T_g) after curing. This high T_g of 190°C ensures excellent thermal stability and dimensional stability of the cured composite parts, making them suitable for applications in high-temperature environments. It comes in either a fabric configuration or one of two unidirectional modes. This includes a twill fabric at 285g/m², “UD HTS 5631 12K 145 gsm” which is a unidirectional prepreg using a high-tensile-strength fibre in 12K tow form, weighing 145 g/m² and, “UD IMS 5131 24K 268 gsm” which uses an intermediate-modulus fibre in 24K tow form and weighs 268 g/m². For this study, the UD HTS 5631 12K 145 gsm form of MTM44-1 was used.

The mechanical properties of MTM44-1 composites are suitable for high-performance applications, particularly in the aerospace industry. It is worth noting that these performance metrics may refer to systems using high-modulus fibres such as M55J carbon fibre, and values can vary depending on the specific reinforcement used. These properties include an impressive 0° tensile modulus, ranging from 62.6 GPa to 174.6 GPa, and a tensile strength between 927 MPa and 2738 MPa, depending on the specific reinforcement used. The compressive modulus ranges from 59.4 GPa to 147.2 GPa, with compressive strengths spanning 729 MPa to 1459 MPa. MTM44-1 also demonstrates robust shear properties, with an in-plane shear modulus of up to 4.11 GPa and shear strengths reaching 133 MPa. Additionally, its flexural modulus and strength are noteworthy, ranging from 57.1 GPa to 154.9 GPa and 1181 MPa to 1958 MPa, respectively. The interlaminar shear strength, essential for maintaining structural integrity under stress, ranges from 75.4 MPa to 109.4 MPa. These mechanical attributes make MTM44-1 appropriate for environments where high strength, stiffness, and durability are required.

3.3 Chemlease 41-90 EZ Silicone Containing release agent

Chemlease 41-90 EZ is a semi-permanent, silicone release agent specifically designed to improve the ease of demoulding in composite manufacturing while minimising surface contamination. However, like many release agents, it has potential to affect surface adhesion. While Chemlease 41-90 EZ is formulated to leave minimal residue on the moulded part, careful attention must still be paid to ensure that the surface is adequately prepared for any bonding, painting, or coating operations that may follow.

The agent is optimised for applications where a matte or satin finish is required, making it particularly suitable for the manufacture of MTM44-1. It also exhibits excellent thermal stability, allowing it to perform effectively in high-temperature manufacturing environments. This could cause issues however with its removal as high temperature treatments may not have an effect on breaking it down or possibly would require very high surface temperatures in order to achieve this, potentially disrupting the integrity of the composite in the process.

The release agent is typically applied by wiping it onto the surface with a clean cotton cloth. The process typically requires 4 to 5 coats, with 15 minutes of drying time between each coat.

One of the most significant drawbacks of Chemlease 41-90 EZ is that it is a silicone-based release agent, meaning it contains silicone compounds that are chemically resistant and hydrophobic. While this provides excellent thermal stability and chemical resistance, it also makes complete removal from moulded parts challenging. Even trace amounts of silicone residues left behind after demoulding can create low-surface-energy films, which interfere with bonding, painting, and adhesion processes. Proper cleaning and surface preparation are essential to mitigate these adhesion issues.

Standard cleaning methods may not always be effective in removing silicone residues, requiring several aggressive surface treatments such as abrasion, plasma treatment, or chemical etching to ensure that the surface is free from contaminants.

3.4 Coating of Release Agent

To simulate contamination within laboratory settings, an even and consistent layer of release agent contaminant needs to be applied to sample surfaces. This needs to be in a way that would be consistent with contamination found within the manufacturing process, while also leaving areas of too high/low contamination so that proper sampling cannot take place.

When considering coating techniques there are many to consider with various up and downsides to each technique. Coating techniques include dip coating(272), electro spraying(273), layer by layer deposition, optical deposition (274), plasma spraying (275) and spin coating(276). For this study two coating methods were explored, offering different advantages for each approach. These include a drop coating method and a spin coating method. The first coating method (CM1) was used due to its simplicity, ease of use, lack of resources required, and vitally, having already been used in a similar study. The second coating method (CM2), although slightly more labour and equipment intensive, was chosen to increase the possibility of producing a thin, even coating.

3.4.1 Drop Coating Method (CM1)

The drop coating method is a simple method adapted from similar work for the same composite and contaminant (47) This method requires only a pipette, an operator, and the use of a vacuum oven.

The process commenced with the preparation of a Chemlease 41-90 EZ solution, as described in section 3.3, diluted with isopropyl alcohol at a ratio of 1:2. A rotary mixing machine was employed to ensure a homogeneous mixture, operating at a speed of 1500 rpm for a duration of 1 minute.

A pipette was used to apply 10 μ L of mixture per 10mm² of composite. The Chemlease 41-90 EZ solution was applied starting from one end of the composite surface to the other, ensuring even coverage.

Subsequent to the Chemlease 41-90 EZ solution application, the composite samples were immediately transferred to a vacuum oven to prevent the uneven spread of the contaminant due to solvent evaporation at ambient conditions.

A vacuum oven was preheated to 60°C. The samples were dried in the oven for 1 hour to ensure the deposition of the solid uniform Chemlease 41-90 EZ layer on the composite surfaces.

3.4.2 Spin Coating Method (CM2)

Spin Coating allows for the deposition of thin coating layers while also being low cost and relatively easy to use (277,278). First the material intending to be deposited is diluted into a solvent. Then the sample which is to be coated is spun at high speeds and the solution is dispensed on the surface of the substrate, which spreads out across the surface using centrifugal force. The solvent is evaporated during the spinning process and can be further removed with heat. Although in practice contamination events are rarely uniformly distributed across a sample, this method allows for an even coating which is appropriate for scientific analysis. It also allows for the deposition of very thin contaminant layers (as detailed in 4.1.1). The thickness of the resulting film is determined by the spin speed, surface tension and solution viscosity(277,279,280).

The samples were coated with a spin coater provided by Electronic Micro Systems Ltd as displayed in Figure 3-1. The spin coater was set to 100rpm for 2 minutes, with an additional 30s loading stage where 10µL of mixture per 1cm² of composite was deposited. The ideal spin speed, time and dilution for spin coating was determined by a series of experiments on composite, glass (displayed in 6A.1) and mylar samples, where a microscope was used to determine the presence of contamination on the sample. Samples were placed in a vacuum oven preheated to 60°C. The samples were dried in the oven for 1 hour.



Figure 3-1 Spin Coater used for CM2

3.5 Plasma Generation

Four plasma systems were used to generate a plasma for the treatment of composite samples, which were placed on an Aerotech A32000 two-axis motion stage. The stage was programmed to move the samples in a raster pattern at predefined speeds and distances to ensure uniform exposure. In plasma treatment, forward power refers to the energy transmitted from the generator to the plasma, while reverse power (or reflected power) is the portion of energy that is not absorbed by the plasma and instead reflected back toward the generator.

3.5.1 Microwave Plasma Generation

To produce an argon plasma, two separate microwave plasma torches which operate at different powers are compared regarding their effect on surface energy. Initial studies investigated the higher-powered 200-100W surface wave launched system, with a second additional 50W Microwave induced power system which was used to observe the potential effect that a lower powered system may have.

3.5.1.1 Surface Waved Launched Microwave Plasma

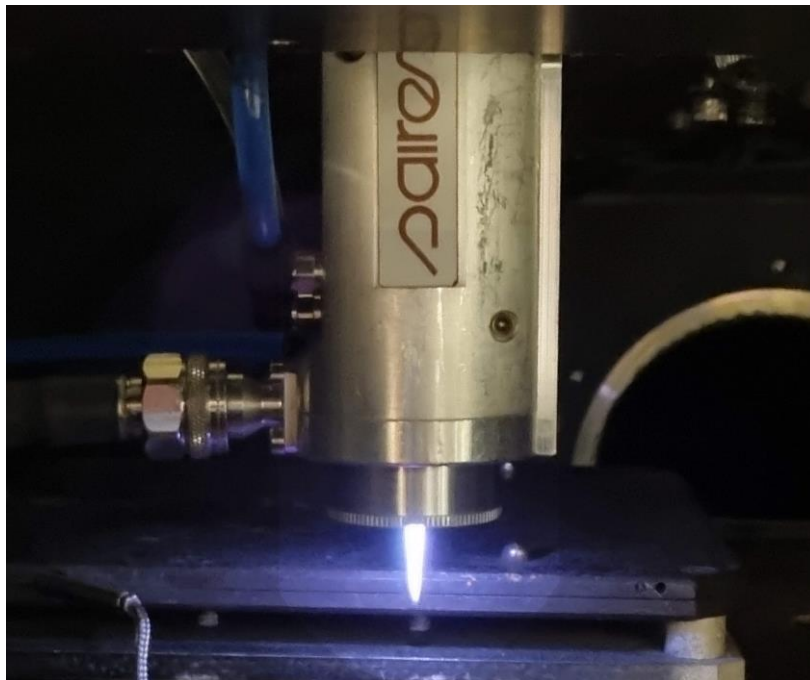


Figure 3-2 The Sairem microwave surface wave launched plasma torch mounted in position for plasma treatment.

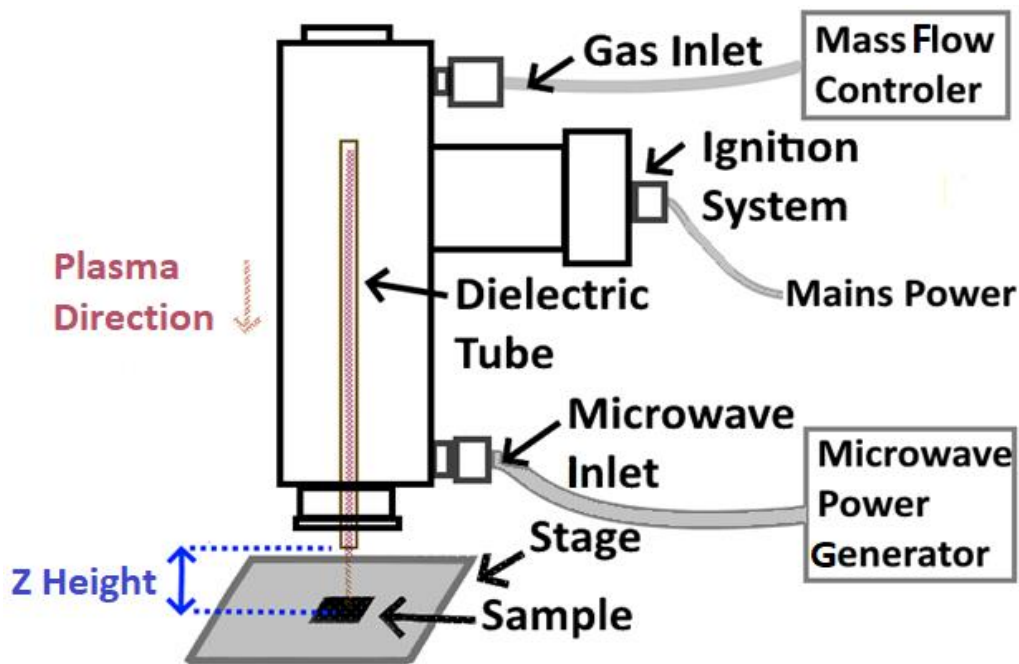


Figure 3-3 Diagram of Plasma Processing Set up.

The first studies within this work looked into a surface wave launched plasma system. These studies are detailed also in a paper by the author (30). A Sairem surface wave compact plasma torch was adapted for atmospheric applications. A microwave electromagnetic field propagates longitudinally at the interface between a dielectric quartz tube and a plasma is created within the tube. The plasma then flows out of the torch as a jet as displayed in Figure 3-2. A DBD ignition system is added to ensure the plasma ignites under atmospheric conditions. The inductively coupled torch was mounted vertically so that the plasma flows downwards towards the sample (See Figure 3-3 and Figure 3-4).

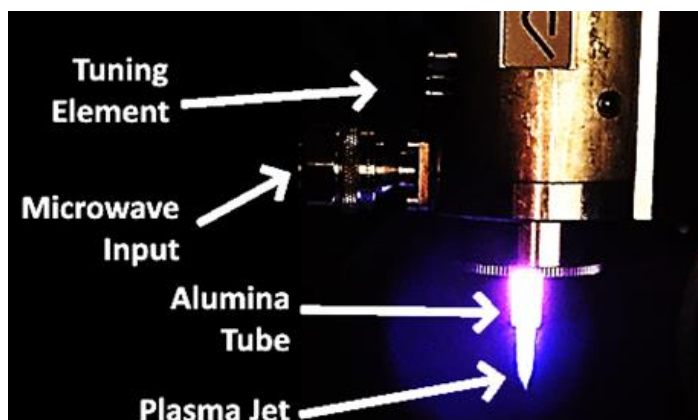


Figure 3-4 Displaying a Sairem plasma torch in operation

The 2.45GHz microwave plasma torch was operated at a total power of 137W $\pm$ 3W (150W forward power with 13W reflected). The samples were placed directly under the torch, a raster pattern was used to ensure even plasma processing across the sample. A 4 mm stand-off distance was used which was determined to be the optimal distance for effective plasma treatment. A continuous flow rate of 30Lmin⁻¹ was used to create the plasma.

3.5.1.2 Microwave Induced Power Plasma



Figure 3-5 front face of the Plasma Tact 50W Microwave induced power plasma system

A 50W microwave induced power system was used being a PlasmaTact50 by AdTec Plasma Technology, as shown in Figure 3-5. The total power for this torch was an average of 48W $\pm$ 2W (50 W forward power, 2 W reflected power), 2.48 GHz frequency, 10 L/min gas flow rate, a 3 mm stand-off distance, as shown in Figure 3-6, and a processing speed of 1m/min.

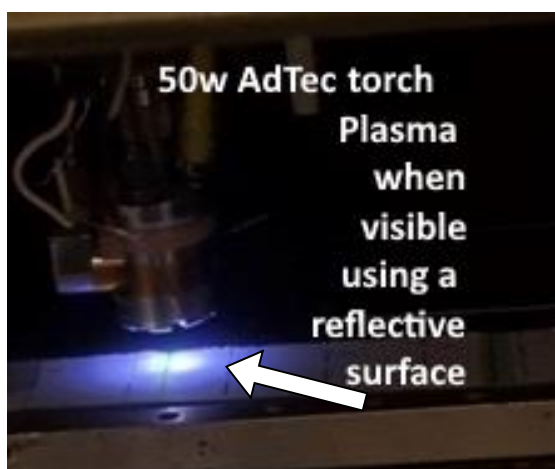


Figure 3-6 Displaying a AdTec plasma torch.

3.5.2 Dielectric Barrier Discharge Plasma (DBD)

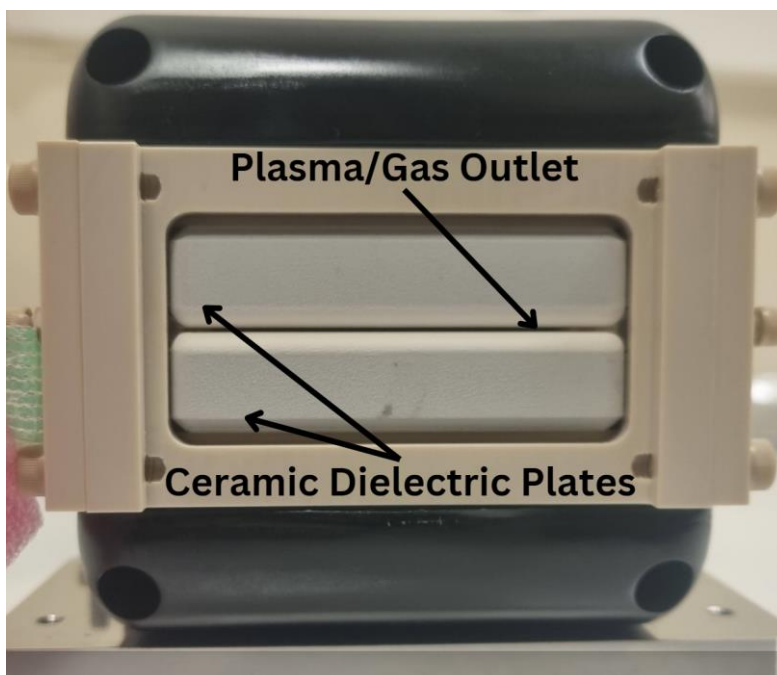


Figure 3-7 The underside of the MCCMD DBD plasma torch by Adtec Plasma Technology. The plasma is created in between the plates and passes out of the torch.

An atmospheric pressure DBD plasma system, developed by Adtec Plasma Technology, was used to investigate the effects of non-thermal Air, Oxygen, and nitrogen plasma. This system, known as MCCMD (Multi Capacitively Coupled Modified Discharge) distributed an even gas flow in between two separate ceramic dielectrics, as displayed in Figure 3-7. This torch did not need a coolant system, and as such was less susceptible to creating instability in the plasma. In addition to this, the even plasma treatment area (60mm across) reduced the need for raster patterning, creating a more even plasma treatment.

Electrodes, connected to a generator via coaxial cables, were embedded into the dielectric to transfer energy to gas, thereby generating the plasma at a current of 0.3A. The generator had a maximum power output of 300W and delivered a 50 kHz signal with a peak voltage of 2.8 kV, or 5.6 kV peak-to-peak.

Processing was conducted with a flow rate of 40L/min. A 10mm standoff distance was used between the samples and the plasma torch.

3.5.3 RF-Plasma Generation

The RAPT300, a thermal Radio Frequency inductively coupled plasma (RF-ICP) prototype torch, developed by RAPT Industries, was used for reactive atom plasma (RAP) etching. This was originally developed as a surface correction technique of silicon carbide optics, to be placed in the European Extremely Large Telescope (282)

Figure 3-8 displays schematics of the enclosure where the torch was contained, including the exhaust outlet, which allows for hazardous biproducts to be removed from the processing areas to a scrubber where they are mixed in water. The plasma torch remains stationary at the centre of the processing chamber, while the sample workpieces are moved through the plasma plume on an Aerotech precision motion stage, displayed Figure 3-9.

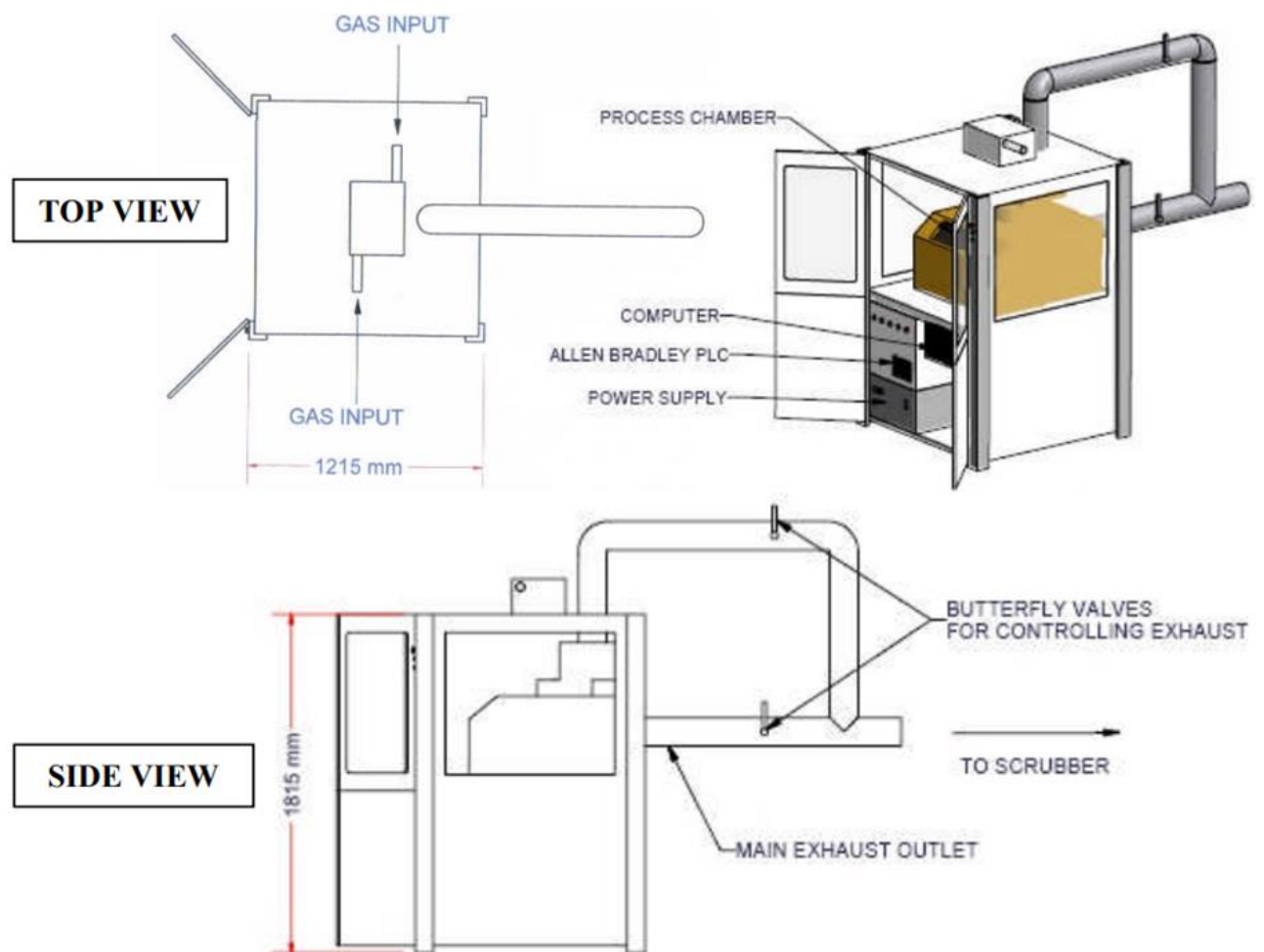


Figure 3-8 Schematics of the RAPT300 machine



Figure 3-9 Precision motion stage used to pass samples under the plasma torch for both RF, MW and DBD plasma systems.

The flow of argon and reactive gases is regulated by mass flow controllers, which include a mass flow sensor and a proportional control valve to set the desired flow rate. An Allen Bradley PLC (programmable logic controller) manages the power supply, Tesla ignition coil (shown in Figure 3-10), and mass flow controllers. The motion stage is controlled using G-code and run on the computer. The vertical position is manually adjusted using a micrometre, as can be seen in Figure 3-9. A water cooling system runs through the generator and copper RF coils of the torch, to prevent overheating.

The RAP process uses an inductively coupled argon plasma, where the reactive gas is atomised within a coil zone. A 27.12 MHz, 1kW plasma was produced using 17Lmin⁻¹ of argon gas flow. For RAP studies, between 0.1Lmin and 0.3Lmin of SF₆ was added to the argon gas, through a small inner coaxial quartz tube as shown in Figure 3-11, to produce a fluorinated plasma. Gases are atomised so that fluorine radicals chemically target the material resulting in a Gaussian removal shape. SF₆ has a low enthalpy of atomisation, with a bond energy at just 285 kJ/mol making it suitable for efficient processing(283).

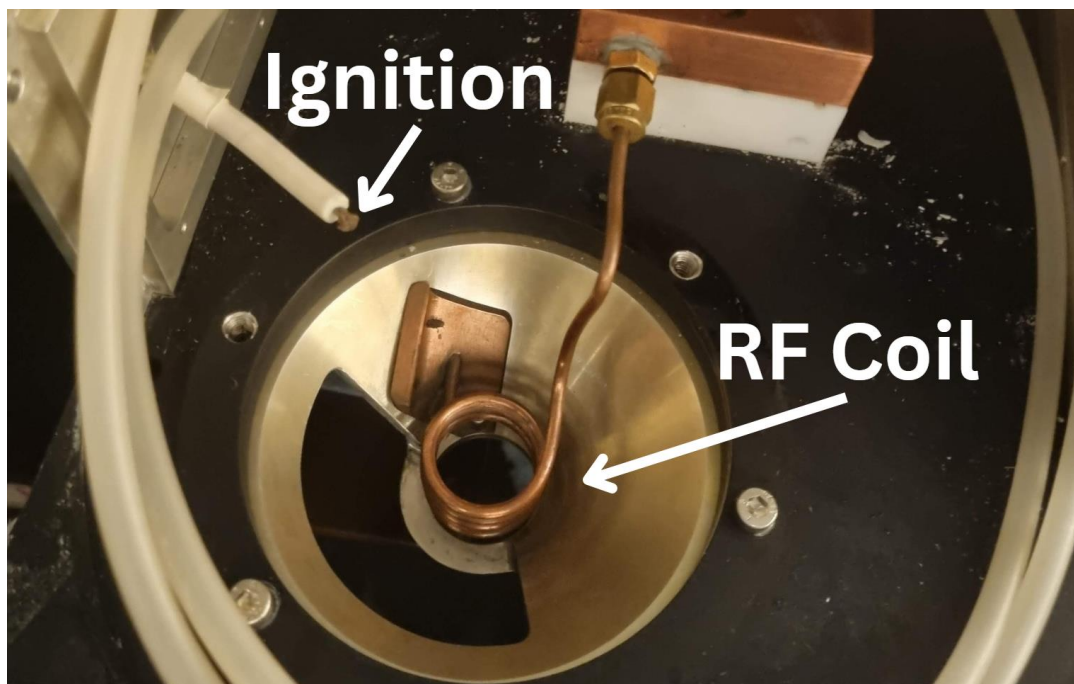


Figure 3-10 displaying the RF coil and ignition tesla coil for the RAPT300 torch.

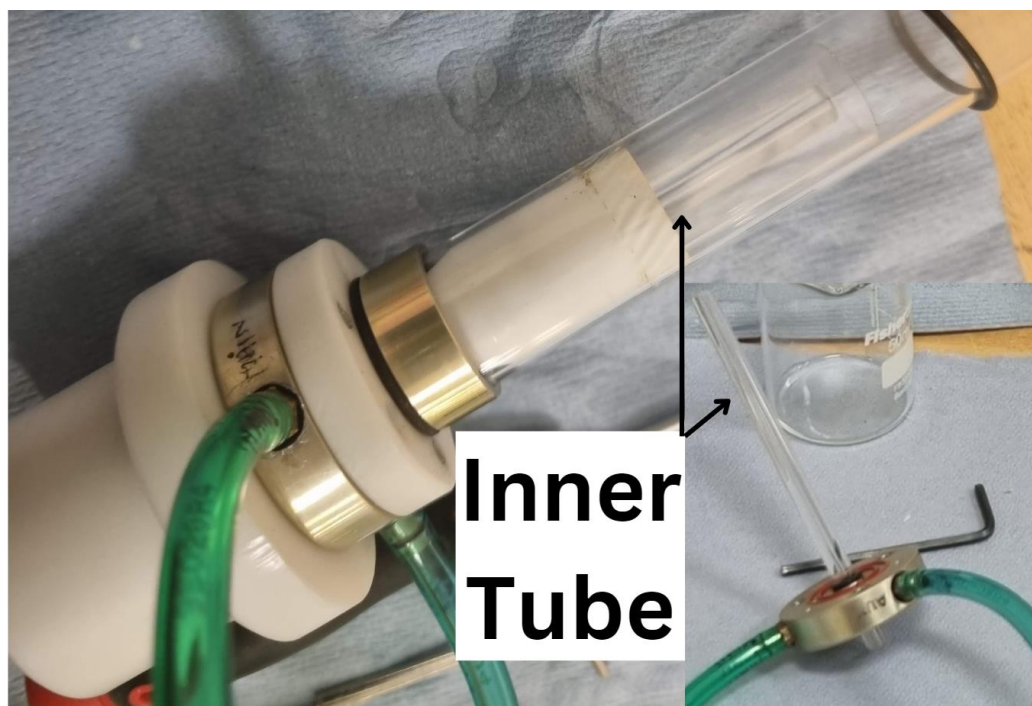


Figure 3-11 displaying photos of the RAP ICP torch during maintenance. The main photo displays the three coaxial quartz tubes from the torch with the two outer tubes for argon, with the most centre tube reserved for reactive gas. Bottom left of the photo displays just the inner tube mounted to the gas delivery section for the main argon feed gas.

3.5.4 The effect of RAP on the Surface Topography of MTM44-1

Increased temperatures were a concern when choosing to work with thermal RF plasma. O'Brien (283) measured the temperature of the argon jet produced by RAP300 via spectroscopy. The temperature of the argon jet itself reached temperatures of almost 6000°C, reducing to just over 5200°C when a reactive gas is injected into the mixture. However, this does not mean that this heat will be the temperature transferred to the sample itself.

When O'Brien (283) found that when ULE was tested through the use of a thermal imaging camera, the temperature of the ULE ranged between 250-300°C. A previous study on this machine by the author (284) was conducted to measure the temperature of the argon plasma plume using a glass Fibre Bragg grating sensor. In this study, measured temperatures of this torch were shown to reach nearly 1000°C.

When considering the effect using this plasma source on samples of silicon containing release agent of carbon fibre reinforced epoxy, it is important to consider the thermal degradation temperature of the silicone elastomer. Amorphous silicone elastomers typically begin to degrade between 200–300 °C (285) which is comparable to or slightly below the degradation temperature of some epoxy resins (286), and carbon fibre which can degrade between 300-1000°C depending on the fibre type (287).

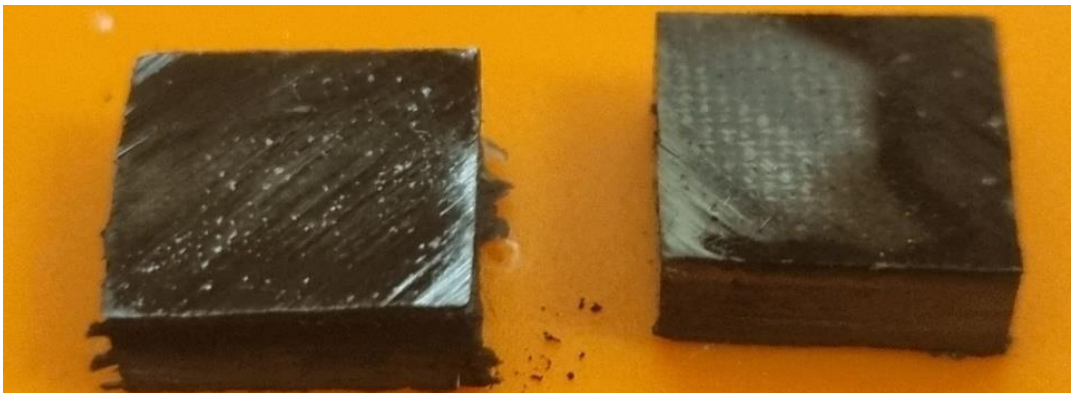


Figure 3-12 MTM 44-1 Samples burnt after treatment from RAP.

Therefore, care must be taken to ensure that the duration and intensity of plasma exposure do not lead to degradation of the epoxy matrix, breakdown of the silicone release agent, or delamination of the composite material.

During this study, samples had been burnt from the effect of increased temperatures, when using a 1mm distant raster pattern. This resulted in composite samples with fully removed epoxy finishes and exposed fibres. In order to reduce the sample temperature under the plasma beam, it is necessary to reduce the time the sample is exposed to the plasma beam. The experiment found that this can be achieved when the sample is moving at a high speed of 1000 mm min^{-1} and a 6mm gap in between passes, as displayed in Figure 3-13.

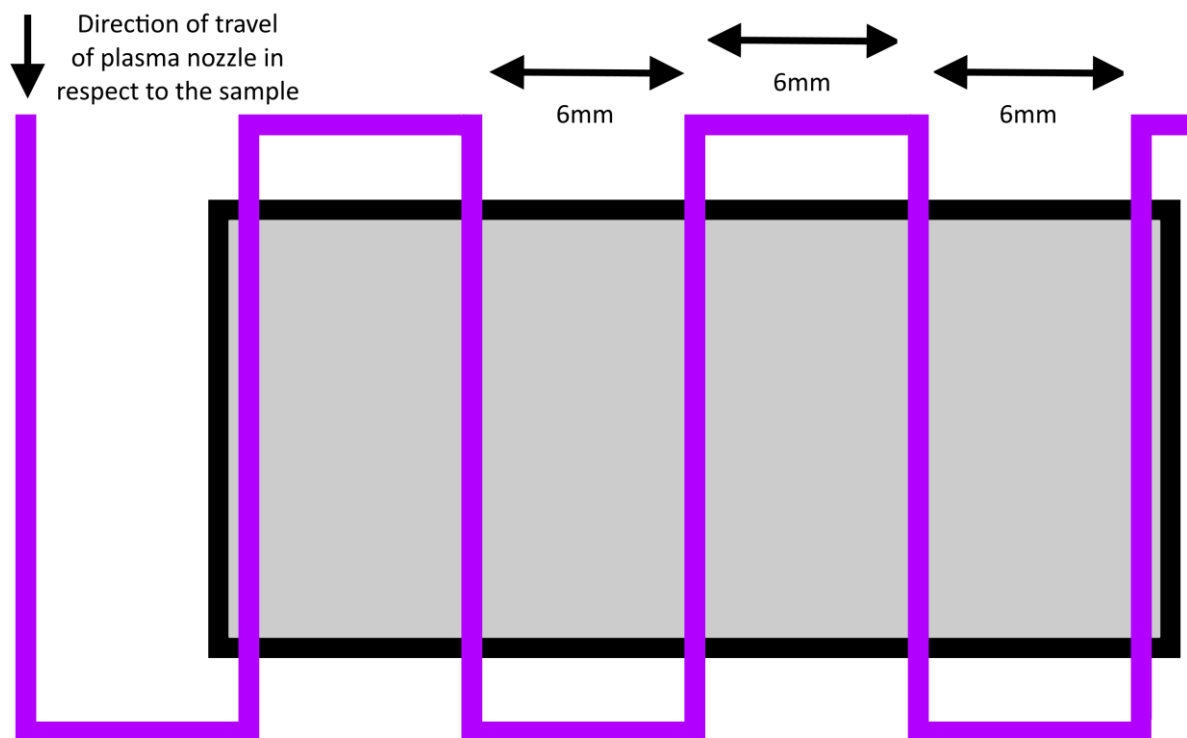


Figure 3-13 Conventional raster pattern of plasma process with 6mm space between passes.

After the results of work found in sections 4.2, 4.3 and 4.4, a more intense plasma treatment was determined to be an avenue to consider in order to remove contamination from the surface. However, slowing down the treatment speed

would result in burnt samples, with possibly little advantage in material removal, as was found in previous work conducted by O'Brien (283) As a result, 1mm spacing between plasma passes was considered as a method to increase intensity of plasma treatment. This allows the sample enough time to cool In between processing passes at any particular position.

As displayed in Figure 3-14, the pattern moves forward by 20mm and then subsequently returns backwards by 19mm, resulting in 1mm between the passes. This allows heat to be conducted away before any position is exposed to the plasma beam again, so that the composite sample will not be burnt during the plasma process.

SEM was used to observe any effects to the surface treated with fluorinated argon plasma. The effect of the plasma treatment was compared to that of sandpaper, an alternative surface pretreatment. During the study, sandpaper of different grain sizes, P80 and P240, were used to roughen the surface of composite samples, by hand, for 30 seconds.

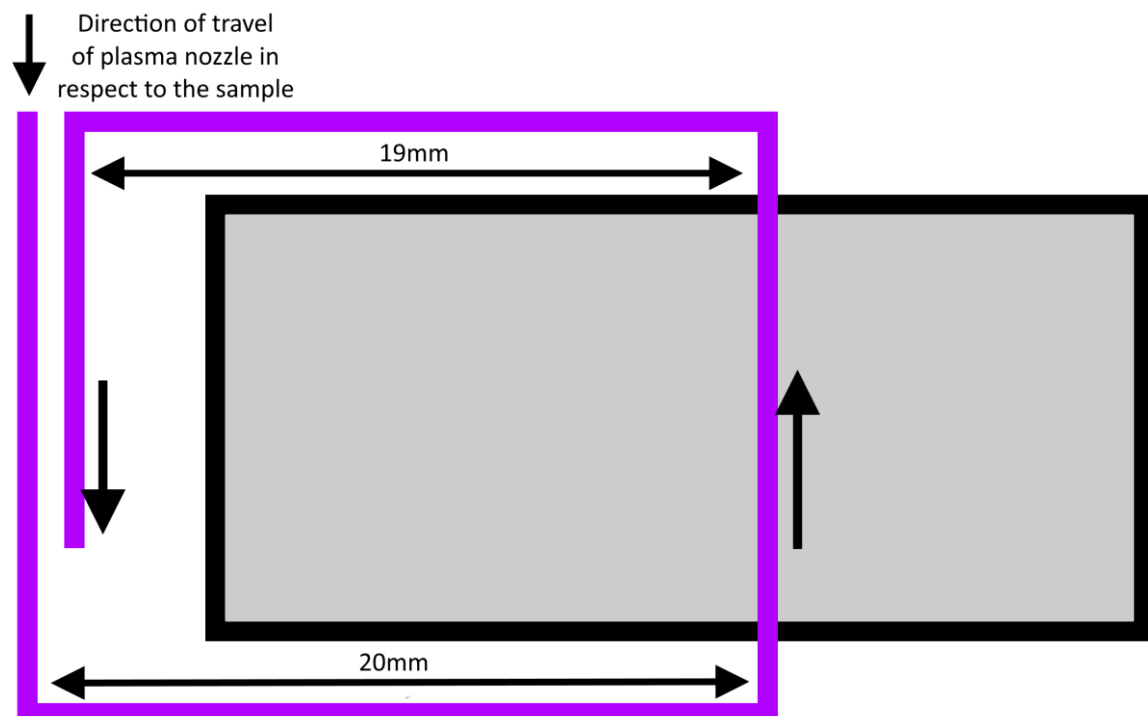


Figure 3-14 Adapted Raster pattern for treatment every 1mm.

No noticeable difference was seen between samples that had not undergone surface treatment (other than cleaning) and samples that had undergone plasma surface treatment, as displayed in Figure 3-15. In the sandpapered samples, by contrast, parts of the epoxy finish were worn away, revealing the fibre underneath. In some parts of the sample, as can be observed in Figure 3-16 , there was breakage of the fibre below.

In summary, the plasma process, when using an adapted raster pattern, was deemed appropriate for the surface treatment of epoxy based composites in respect to possible high temperature damage.

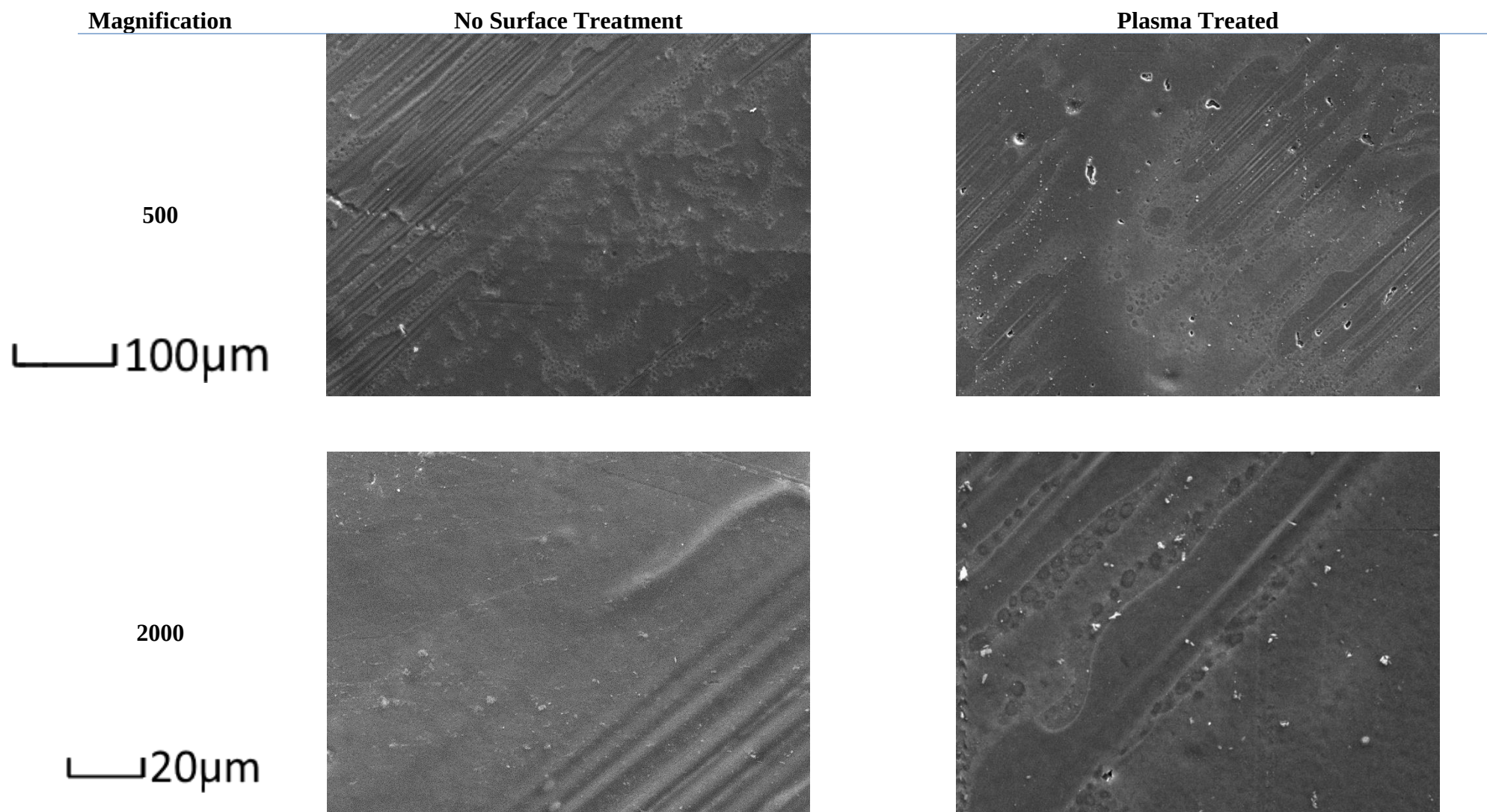


Figure 3-15 SEM images of unprocessed and plasma processed samples, treated from an alternative raster pattern.

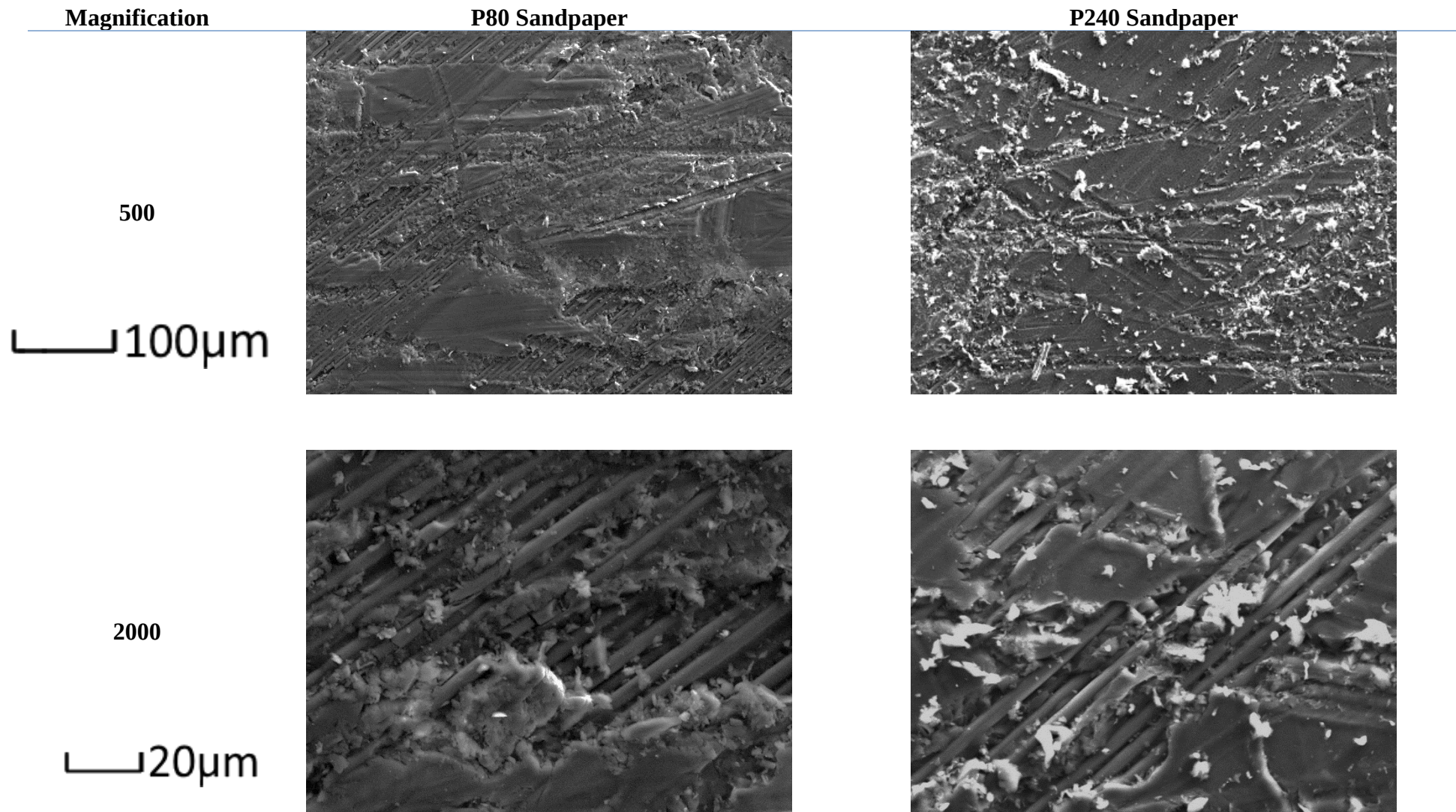


Figure 3-16 SEM images of Sandpapered samples

3.6 Surface Chemistry Analysis Techniques

Several surface analysis techniques were compared and trialled for this study. A long period of initial study was conducted using Fourier Transform Infrared (FTIR), in both reflectance and attenuated total reflection (FTIR-ATR). FTIR has a varied analysis depth between 500nm to 5000nm, depending on the material and mode of FTIR used. This analysis was used to understand the surface chemistry effects of nitrogen DBD and argon microwave plasma on the surface of clean, uncoated composite samples, but the results of this study showed no significant change in surface chemistry. Raman and EDS spectroscopy were also trialled but provided similar results. This is likely due to the analysis depths of these techniques being too deep to provide noticeable change in chemistry. As a result, XPS was sought after to understand these changes. EDS and FIB TOF-SIMS were used to observed chemistry effects on coated samples only.

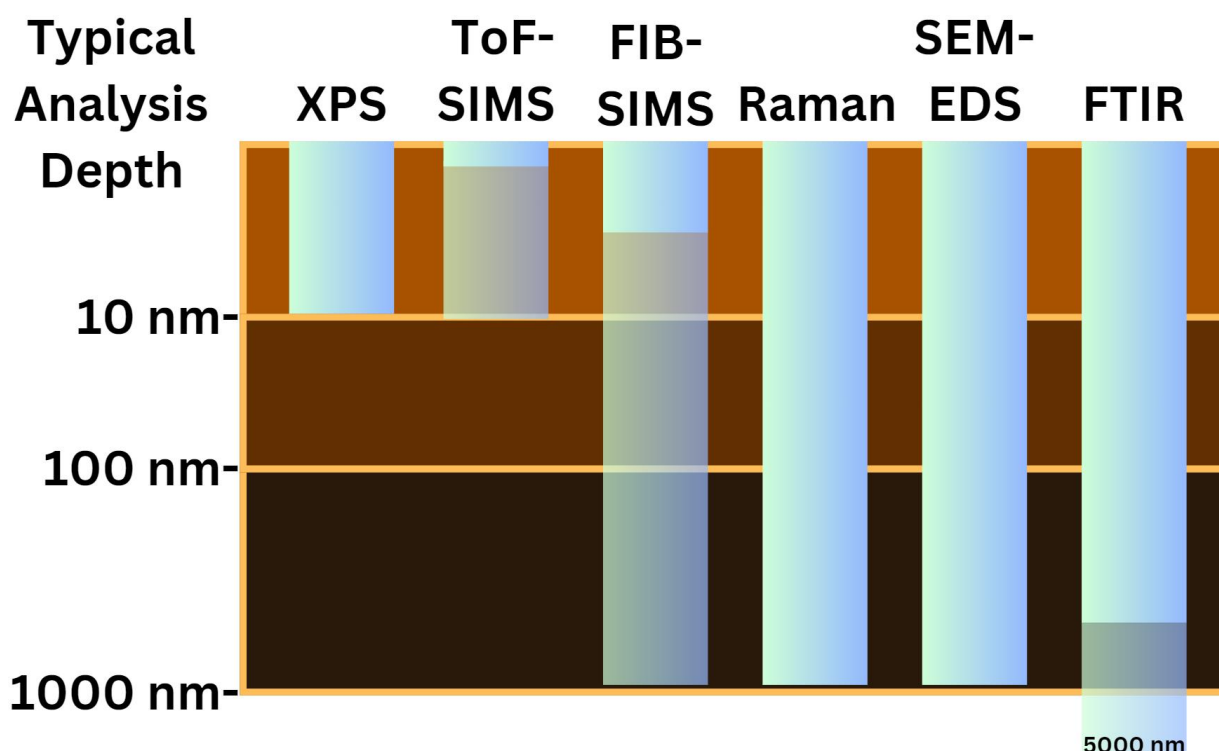


Figure 3-17 Typical analysis depths of various surface chemistry analytical techniques tried in this study. The data for FIB-SIMS assumes a Xe ion source as found in the equipment at Cranfield University adapted from (288–299).

3.6.1 XPS

X-Ray photoelectric spectroscopy was conducted at two facilities. Initial set of results were conducted with thanks to SEEDCORN access funding at Warwick University, with further research conducted with the Henry Royce Institute access funding at the University of Leeds. Data was collected with either a 6mm or 1mm gap between plasma passes.

3.6.1.1 Kratos Axis Ultra DLD spectrometer (University of Warwick)

X-ray photoelectron spectroscopy (XPS) data, for 6mm spaced samples, were collected at the Photoemission RTP, University of Warwick (Figure 3-18). The samples investigated in this study were attached to electrically conductive carbon tape, mounted on to a sample bar with a layer of filter paper between the samples and the sample bar to ensure electrical isolation and hence differential charging, before being loaded into a Kratos Axis Ultra DLD spectrometer which possesses a base pressure below 1×10^{-10} mbar. XPS measurements were performed in the main analysis chamber, with the sample being illuminated using a monochromatic Al K_{α} x-ray source ($h\nu = 1486.7$ eV). The measurements were conducted at room temperature and at a take-off angle of 90° with respect to the surface parallel.

The core level spectra were recorded using a pass energy of 20 eV (resolution approx. 0.4 eV), from an analysis area of $300 \mu\text{m} \times 700 \mu\text{m}$. The work function and binding energy scale of the spectrometer were calibrated using the Fermi edge and $3d_{5/2}$ peak recorded from a polycrystalline Ag sample prior to the commencement of the experiments. To prevent surface charging the surface was flooded with a beam of low energy electrons from a charge neutraliser throughout the experiment and this necessitated recalibration of the binding energy scale. To achieve this, the C-C/C-H component of the $C1s$ spectrum was referenced to 285.0 eV. The data were analysed in the CasaXPS package using Shirley backgrounds and mixed Gaussian-Lorentzian (Voigt) line shapes. For compositional analysis, the analyser transmission function has been determined using clean metallic foils to determine the detection efficiency across the full binding energy range.

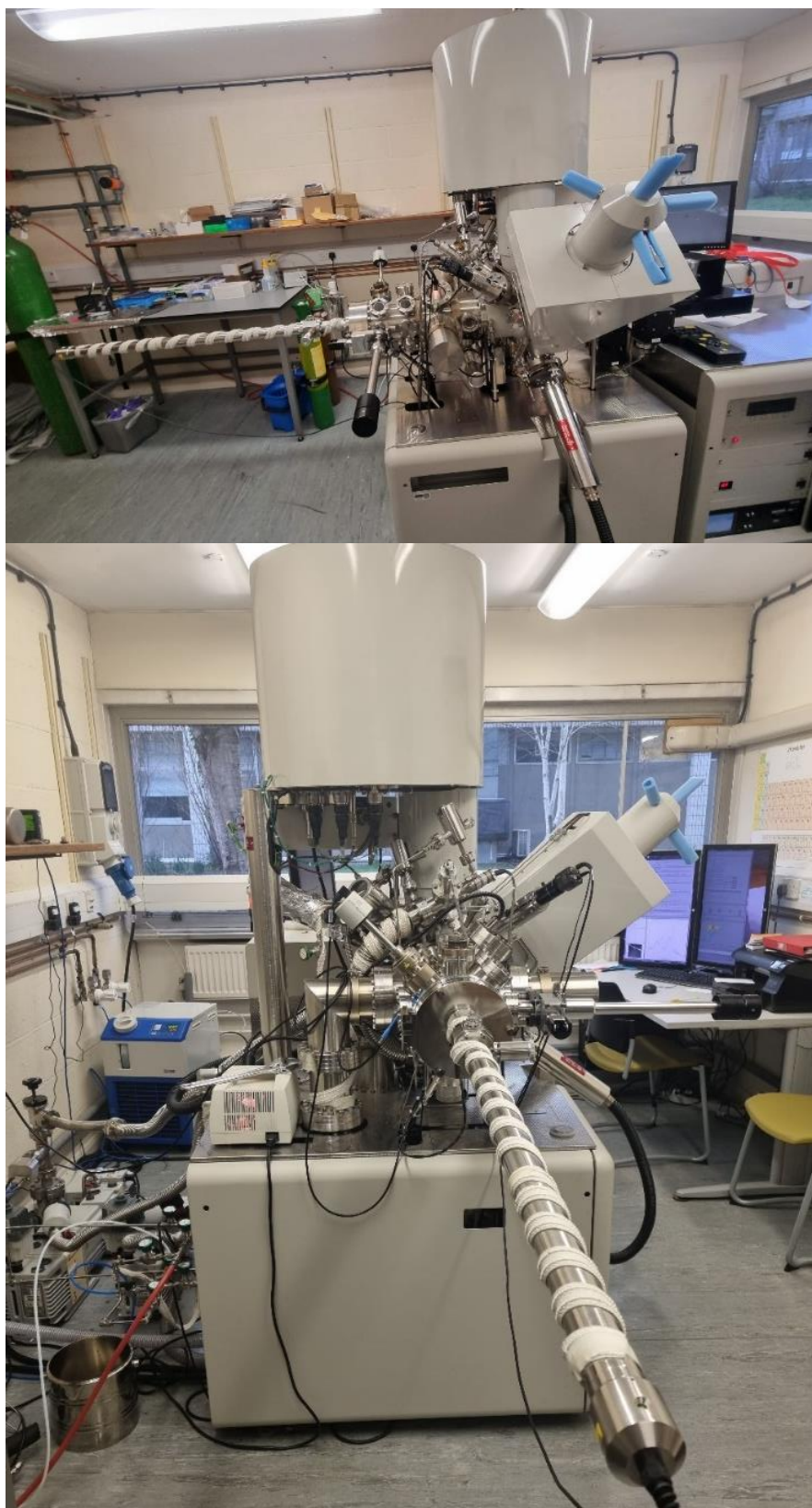


Figure 3-18 XPS facilities at Warwick University, featuring the side view (top) and front view (bottom) of the Kratos Axis Ultra DLD spectrometer

3.6.1.2 SPECS Group EnviroESCA Near Ambient Pressure XPS Analyser (University of Leeds)

The x-ray photoelectron spectroscopy (XPS) data were collected at the Versatile x-ray spectroscopy facility, at the University of Leeds. The samples were attached by carbon tape to a sample plate in the SPECS Group EnviroESCA Near Ambient Pressure (NAP) XPS Analyser. The initial setup survey was done at 5 mbar of nitrogen and the final measurements were done in 10 mbar of nitrogen to better charge neutralise the sample.

Samples were illuminated using a monochromatic Al K α x-ray source with a Slit width of 4:7x20 from a carbon fibre grid. Fixed analyser transmission mode was used with an Excitation Energy of 1486.71 eV. The Detector Voltage was 1725 V, with a Bias Voltage of 90.00 V. The spot size is 300 μm (analysis area). Measurements were conducted at room temperature.

The nozzle was at normal incidence to the sample with the source-Analyser angle being 55 degrees. Transmission function is calibrated using a silver sample via the SPECS prodigy software. Pass energy of core-hole spectra is 50 eV and of the survey is 100 eV. Binding energy was calibrated by setting the C 1s main C-C peak to 285 eV.

The data were analysed in the CasaXPS package, using U2 Tougaard backgrounds and mixed Gaussian-Lorentzian (Voigt) line shapes. An example of a spectra survey presented in CasaXPS is presented in Figure 3-19

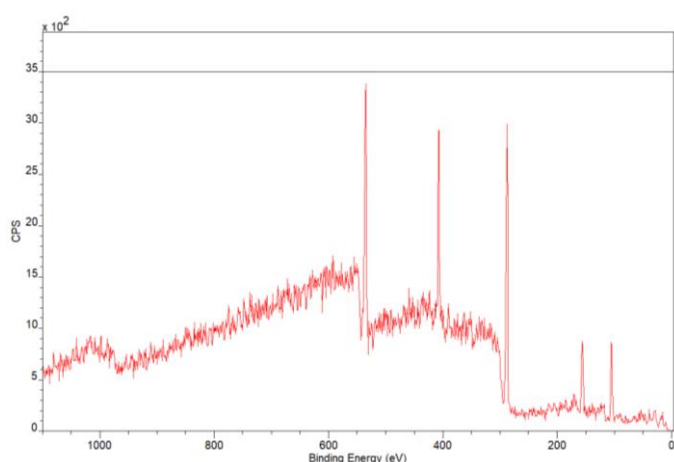


Figure 3-19 A survey spectrum presented in the CasaXPS package

3.6.2 Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS)

A TESCAN VEGA3 Scanning electron microscope (SEM) was used to take SEM images, in order to detect changes in surface topography before and after processing. The microscope, displayed in Figure 3-20, has the capability to produce images from both secondary electrons and backscattered electrons. It also includes a detector in order to perform Energy Dispersive Spectroscopy (EDS) to allow for chemical composition analysis.

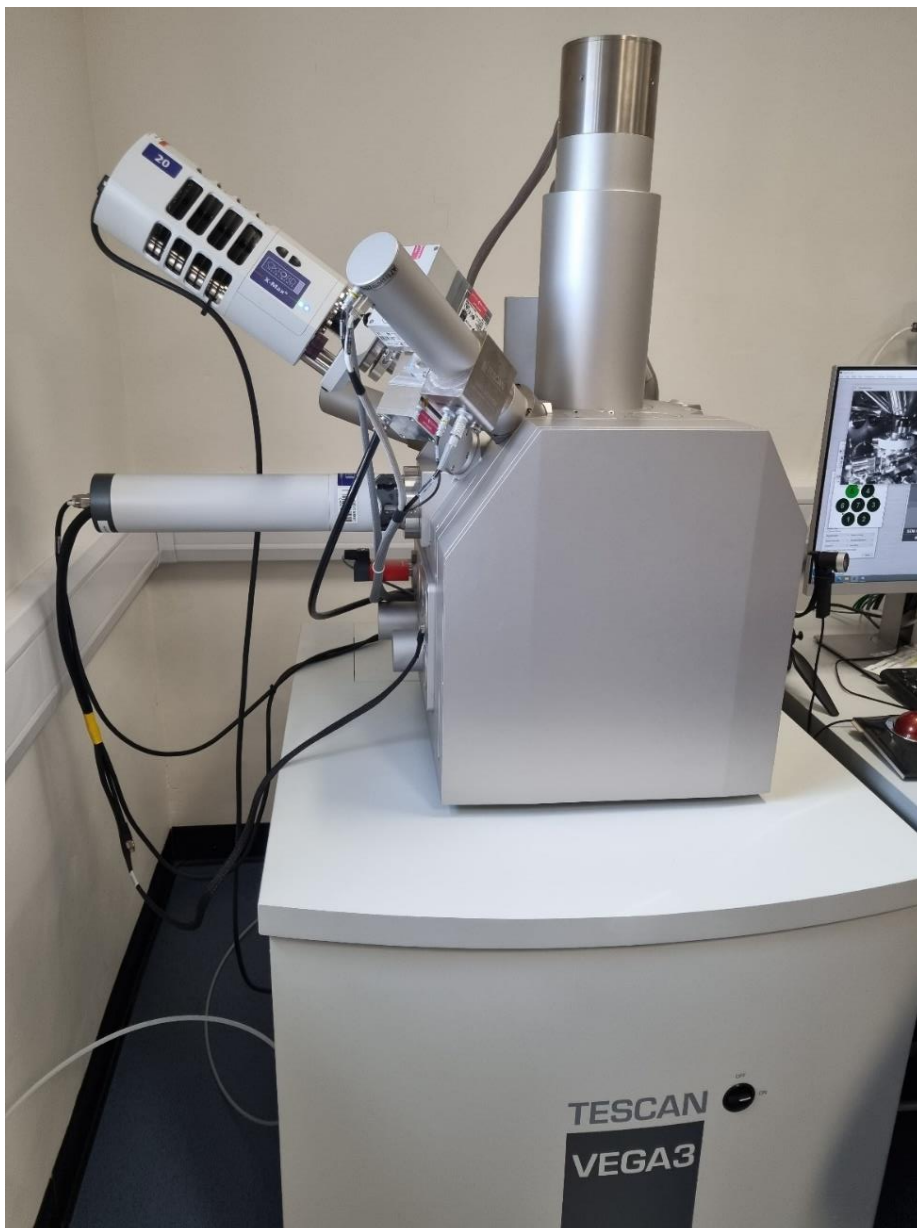


Figure 3-20 displaying the TESCAN VEGA3 scanning electron microscope

The SEM was operated under low vacuum with beam intensities ranging from 5 kV to 20 kV. Lowering the beam intensity enhances the SEM's sensitivity to the surface. Both secondary electron and backscattered electron imaging were used.

Secondary electrons (SE) come from the atoms within the sample due to inelastic interactions with the beam, while backscattered electrons (BSE) are reflected after elastic interactions between the electron beam and the sample.

BSE originate from deeper within the sample, while SE come from the surface, providing different types of information. SE images capture electrons emitted directly from the substrate, providing surface morphology details, while BSE images detect electrons scattered back from the beam, offering information from deeper within the sample compared to SE images.

EDS was used to determine the elemental composition. The peaks in the obtained spectra were initially identified using the auto-assign feature from the TESCAN AZTEC software. Any peaks misidentified by the software were manually corrected.

EDS results were also used to estimate the thickness of the coated Chemlease layer on the sample. A 2 nm gold layer was deposited on all samples before analysis. When the high-energy electron beam interacted with the coated composite sample, the scattering and energy loss of electrons were carefully monitored. The compositional data from EDS enabled the estimation of the silicone layer's thickness by comparing it to the known thickness of the gold layer, as described further in section 4.1.1.

3.6.3 Time of Flight Secondary Mass Spectrometry

A TESCAN S8000, displayed in Figure 3-21 integrated with a Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), has the potential to provide detailed surface analysis as well as elemental or molecular composition mapping at the micro and nanoscale. In this case analysis was performed by bombarding the sample surface with a focused ion beam (FIB) of xenon plasma to raster across selected areas of the sample surface before being recorded. This process causes the ejection of secondary ions from the sample, which are then detected based on their mass-to-charge ratio. The elements, isotopes and any molecular ions produced can then be selected (by knowledge of their mass/charge ratio) to plot as an image distribution display on screen.



Figure 3-21 featuring a TESCAN S8000 FIB-SEM with attachment capability for FIB and ToF-SIMS.

3.7 Surface Energy and Water Contact Angle Analysis

Surface energy effects were explored using Water, Glycerol and Diiodomethane contact angle measurements. A fully automatic measuring device, OCA 50 by Data Physics Instruments GmbH, was used to ensure uniform droplet size and repeatable measurement (Figure 3-22).



Figure 3-22 OCA 50 by Data Physics Instruments GmbH used to measure liquid contact angles.

Surface energy refers to the extra free energy present at a material's surface, attributed to surface molecules having fewer neighbouring molecules to bond with. This results in unbalanced forces and additional energy. There are various methods to measure surface energy, tailored to the material type and the chosen liquids. A fundamental method used is Young's equation, Equation 1, which establishes a connection between contact angle ($^\circ$), liquid surface tension, interfacial tension (Nm^{-1} or J/m^2) between a solid and a liquid (γ_{sl}) and the solid's surface free energy. Figure 3-23 further demonstrates these forces acting on a liquid droplet on a surface.

Equation 1: Young's Equation

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta$$

The choice of the model for determining surface energy depends on factors like the sample's energy level (high or low) and whether it is polar or non-polar. Liquids with different dispersive and polar properties are often selected for this measurement. The chosen model significantly influences the results, making the selection process complex and critical(300)

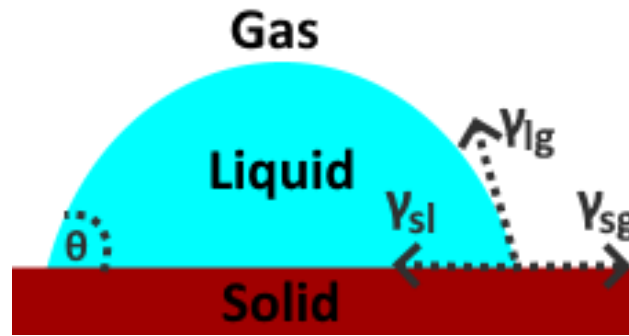


Figure 3-23 The diagram describes the components needed for Young's equation in relation to a liquid droplet measurement, where γ_{sl} is the surface tension between a solid and a liquid, γ_{sg} is the solid and gas interfacial tension and γ_{lg} is the liquid and gas surface tension and θ is the contact angle of the liquid.

The Owens, Wendt, Rabel and Kaelble(OWRK) method (301–303) is a prominent technique for assessing the surface energy of polymers and surfaces with moderate polarity. This method integrates the Young-Dupre equation, which is displayed in Equation 2. The OWRK method further extends this concept by dividing the work of adhesion into polar and dispersive forces, following the principles outlined in the Fowkes model, Equation 3 (38,304) .

Equation 2: Young-Dupre Equation

$$W_{sl} = \sigma_l(1 + \cos \theta)$$

Where W_{sl} is the work of adhesion, σ_l is the surface tension of the liquid (both in J/m^2) and θ is the contact angle ($^\circ$).

Equation 3: Fawkes Model

$$W_{sl} = s \left(\sqrt{\sigma_l^P} \cdot \sigma_s^P + \sqrt{\sigma_l^D} \cdot \sigma_s^D \right)$$

Where σ_l^P and σ_l^D are the polar and dispersive components of the liquids surface tension and σ_s^P and σ_s^D are the respective solid components.

The Fawkes method employs two liquids with known polar and dispersive characteristics to calculate the interfacial tension between solids and liquids(44). For example, water, with a surface energy of 72.8 mJ/m², consists of 51 mJ/m² polar energy and 21.8 mJ/m² dispersive energy. Ethylene glycol, on the other hand, has a total energy of 48 mJ/m², split into 19 mJ/m² polar and 29 mJ/m² dispersive components(300).

The OWRK model, see Equation 4, is derived so that the interactions of the dispersive and polar components of the liquid can be represented linearly as $y = mx + c$.

Equation 4: OWRK Model

$$\frac{\sigma_l(1 + \cos \theta)}{2(\sqrt{\sigma_l^D})} = \left(\sqrt{\sigma_s^P} \right) \frac{\sqrt{\sigma_l^P}}{\sqrt{\sigma_l^D}} + \sqrt{\sigma_s^D}$$

In this equation, the y-axis represents the left side of the equation, while the x-axis plots the square root of the liquid's polar forces over its dispersive forces,

$\frac{\sqrt{\sigma_l^P}}{\sqrt{\sigma_l^D}}$. This requires first plotting the polar and dispersive energies of 2 or more

liquids, although ideally more to provide a better fit. By analysing the slope ($m = \sqrt{\sigma_s^P}$) and intercept ($c = \sqrt{\sigma_s^D}$) of this linear relationship, the polar and dispersive components of the surface energy are determined.

As the surface energy of a solid sample is considered a component of its polar and dispersive forces, we may add these forces together to produce our total surface energy, σ_s .

$$\sigma_s = \sigma_s^P + \sigma_s^D$$

3.8 Surface Roughness Studies

Surface Roughness evaluation was performed using a coherence scanning interferometer (CSI) (Talysurf CCI 6000, Taylor Hobson Precision) as displayed in Figure 3-24.



Figure 3-24 Coherence Scanning Interferometer

In measuring surface roughness, the standard deviation of the surface heights from the mean plane was measured to produce an 'Sq' value. Sq refers to the root mean square roughness. It is a statistical measure used to quantify the roughness of a surface, providing an indication of how much the surface deviates from being perfectly smooth.

Higher values of Sq indicate a rougher surface, while lower values suggest a smoother surface. It's commonly used in 3D surface roughness measurements and provides a more comprehensive understanding of roughness than those taken from a roughness profile.

3.9 Lap Shear Testing

Lap shear test conditions were adapted from ISO 4587:2003(305) where the samples were cut into 25mm x 100mm sized samples and the sample overlap was 12.5mm. Sample thickness of this study was thicker than standard, at 4mm, as this is the thickness of the as manufactured MTM44-1 panels.

FM 300K Thin Film adhesive, procured from Solvay, was used to bond the samples. The FM 300K had a nominal weight of 244gsm and a nominal thickness of 0.2mm with a wide open knit carrier. This adhesive was used to ensure a consistent bond line thickness across all samples. A precision rig was used to ensure sample overlap was consistent and aligned correctly, as displayed in Figure 3-25.

Two Lap Shear testing studies were conducted over the course of this research project. The initial study was conducted to explore the use of microwave plasma treatment as produced from the Surface Wave Launched Microwave plasma system. Araldite 420 adhesive was used to bond the samples. In further studies looking at RF and DBD plasma, FM 300 adhesive film by Solvay was used to ensure a uniform bond line thickness of 0.33mm.



Figure 3-25 showing composite lap shear samples placed on a precision rig, prior to bonding.

For lap shear strength testing, an Instron 5500R was used which is equipped with a 30kN load cell and wedge grips to hold the specimens in place. At the start of testing, samples were subject to a 10N preload, at a speed of 1mm/min. Loading rate was 13mm/min. Load vs displacement was measured until specimen failure.

Interface Failure



Cohesive Failure



Substrate Failure



Figure 3-26 describes the different failure methods of adhesively bonded lap shear samples. An Interface, or adhesive, failure is where there is a clear separation between the adherend and the adhesive. A cohesive failure shows a failure within the adhesive layer, causing it to separate with both sides of the adhesive still adhered to the adherend. A substrate, or adherend, failure is when the substrate itself breaks under force, leaving damaged adherend remaining onto the adhesive after separation.

To better understand the failure mechanisms in adhesively bonded lap shear samples, the breakage types were analysed post-failure. The images provided in Figure 4-48 display evidence of the different failure modes, for each sample type. As displayed in Figure 3-26 there are three distinct failure modes observed in the lap shear tests:

Interface/Adhesive Failure: Separation occurs at the adhesive-substrate interface, indicating poor adhesion.

Cohesive Failure: The failure happens within the adhesive layer, leaving the adhesive bonded to both substrate surfaces.

Substrate/Adherend Failure: The substrate itself fails, leaving fragments of the substrate adhered to the adhesive.

3.10 Microwave Plasma Study Sample Treatments

MTM44-1 carbon fibre reinforced epoxy samples were cleaned using an ultrasonic bath in warm isopropanol (IPA) followed by a drying step in a vacuum oven at 80°C. Contaminated samples were coated with Chemlease 41-90 EZ release agent supplied by Chem-Trend GmbH.

Samples were classified into 4 categories.

- Original: These are unprocessed samples that have been cleaned but not processed with plasma treatment nor contaminated.
- Plasma processed: These are samples that have undergone atmospheric pressure plasma treatment.
- Contaminated: These are samples that have undergone surface contamination Method 1 (CM1).
- Contaminated then Plasma Processed: There are samples that were contaminated using CM1 and then subsequently treated with atmospheric pressure plasma.

3.11 Plasma Treatment Studies used in Radio Frequency Plasma Study & DBD plasma study

A variety of different treatment options were explored for this study, the details of which are displayed in Table 3-1. These parameters were determined through a mixture of prior experimentation and review of previous studies by the same torch(283). The flow rate considered the best coupling of the gas, with power.

Table 3-1 detailing the shorthand names for various treatment regimens used.

Name	Treatment Details
PT1	Argon plasma treatment with 6mm raster between scan
PT2	Argon and SF ₆ 0.01Lmin ⁻¹ plasma treatment with 6mm raster between scan
PT3	Argon and SF ₆ 0.01Lmin ⁻¹ plasma treatment with 1mm raster between scan
PT4	Argon and SF ₆ 0.03Lmin ⁻¹ plasma treatment with 1mm raster between scan

4 Results & Discussion

The aim of this study is to improve the adhesive quality of composite surfaces using atmospheric pressure plasma treatments. This section explores the results of using various plasma treatment methods for both plasma surface modification to improve adhesion, as well as to remove contamination in the process. To achieve this, samples were treated with different types of plasma and some of these were coated with release agents to simulate a contamination event.

This section starts by exploring coating methods, and ways to quantify contamination at the surface of the sample, as silicone contamination was found undetectable both to the naked eye, microscopy and even some spectroscopy methods such as FTIR and FTIR-ATR.

4.1 Silicone Contamination Coating

Samples of epoxy carbon fibre composite MTM44-1, supplied by BAE Systems, were coated with the silicone-based release agent Chemlease 41-90 EZ supplied by ChemTrends. The release agent was mixed with Isopropanol (IPA) at a ratio of 1:2. Two main methods were developed for applying a coating of the silicone based contamination.

Method 1 (CM1) follows the coating method used by Dighton(47) which was adapted to ensure an adequate and equal coating of silicone solids. This required placing a controlled value of mixture onto the composite surface and moving the composite until an even coat could be viewed to the eye. The coated mixture was then placed into a vacuum oven at 60°C for half an hour. Previous work by Dighton *et al* (48) found the contaminant thickness to be in the range of 0.5–3 nm.

Although this method was stated by Dighton *et al* (48) to produce an even contamination layer, scanning electron microscopy (SEM) images (Figure 4-1) conducted show signs of beading of silicone at the surface. It also featured occasional build-up of contaminant at the surface of the composite.

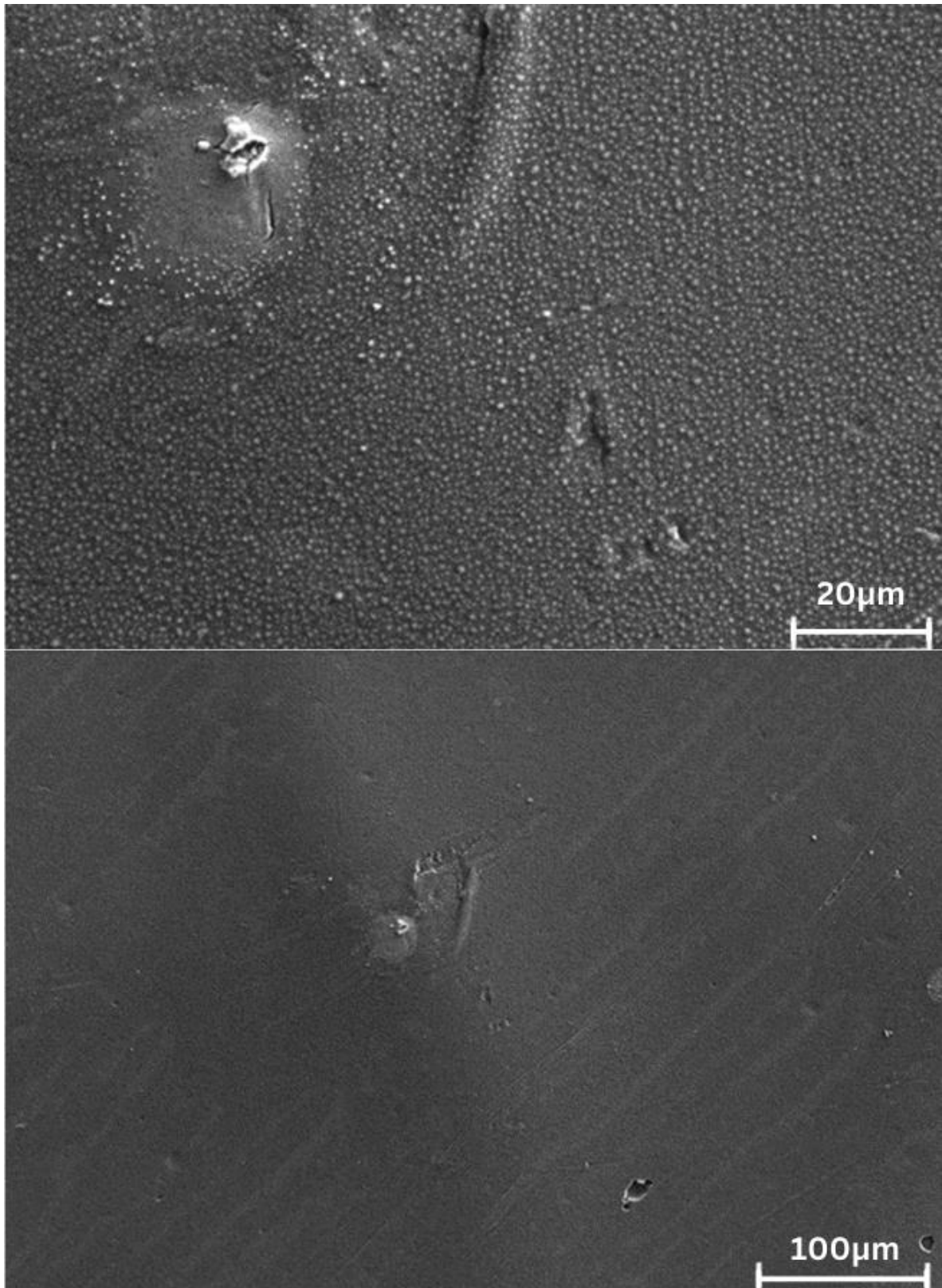


Figure 4-1 SEM Figures of MTM44-1 samples coated with CM1 at 2000x magnification (top) and 500x magnification (bottom), respectively.

Method 2 (CM2) attempts to create a more uniform and thinner coating of the release agent by using a rotary spin coater to apply a coating to the surface of each composite. 1 μ L per cm² was applied to samples spun at 100 rpm. Method 2 was developed through exploration of spin speeds and concentrations of Chemlease and IPA as shown in Appendix A.

Under SEM, no clear patterning of the coating could be observed on composite samples. As a comparison, coating onto a titanium wafer is shown in Figure 4-1 where the surface can be considered nearly featureless

For the composite sample, some surface features can be observed, as shown in Figure 4-2. Unlike for titanium, it does not show uniformity across the sample surface.

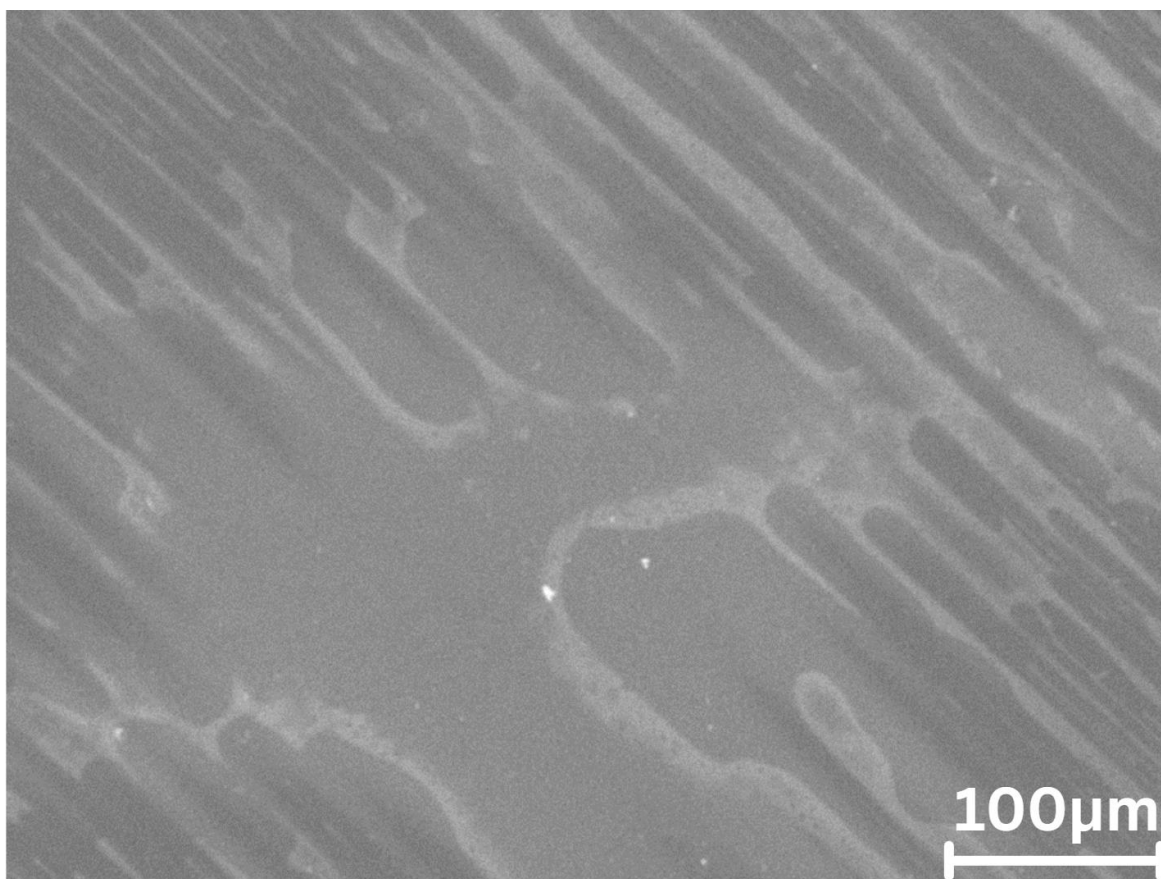


Figure 4-2 SEM image of a composite sample after coating of Chemlease 41-90 EZ using CM2. MAG: 500x, 10kV, BSE, WD:14.85

Energy dispersive X-ray spectroscopy (EDS) was used to investigate the chemical composition of the coating and to confirm presence of elemental silicon and carbon (and thus silicone). Figure 4-3 shows an EDS spectrum for a 6-times coated composite sample. The purpose of multiple coating is to increase the thickness of the Chemlease 41-90 EZ layer. It is apparent that the top layers contained a high concentration of carbon (61.7% wt), oxygen (25.2% wt) and silicon (9.2% wt). Low concentrations of F (2.7% wt) and S (1.2% wt) were also observed. Figure 4-4 shows the EDS area map of the same sample; from these it can be observed that Si was uniformly distributed across the area.

The chemical concentrations are unlikely to be solely the chemical composition of the contaminant Chemlease 41-90 EZ. The contribution from the composite (mainly carbon fibre and epoxy polymers) cannot be ignored. This is due to the thickness of the coated layer being no more than a few tens to hundreds of nanometres, whilst the penetration depth of the electron beam during EDS was much larger.

Figure 4-5 shows a typical EDS results for an original (uncoated layer of) composite sample. The main concentrations are of C, O, and S, with traces of Cl. No peak for Si was observed for this composite without a coated layer. Figure 4-6 shows a SEM image (a) and its corresponding element maps, clearly showing the dark contrasted regions are mainly Carbon in the fibres, and Sulphur existing mainly in the bright contrasted matrix regions of the composite. Further EDS area maps suggest the element S comes from the matrix component of the composite, displayed in Figure 4-7.

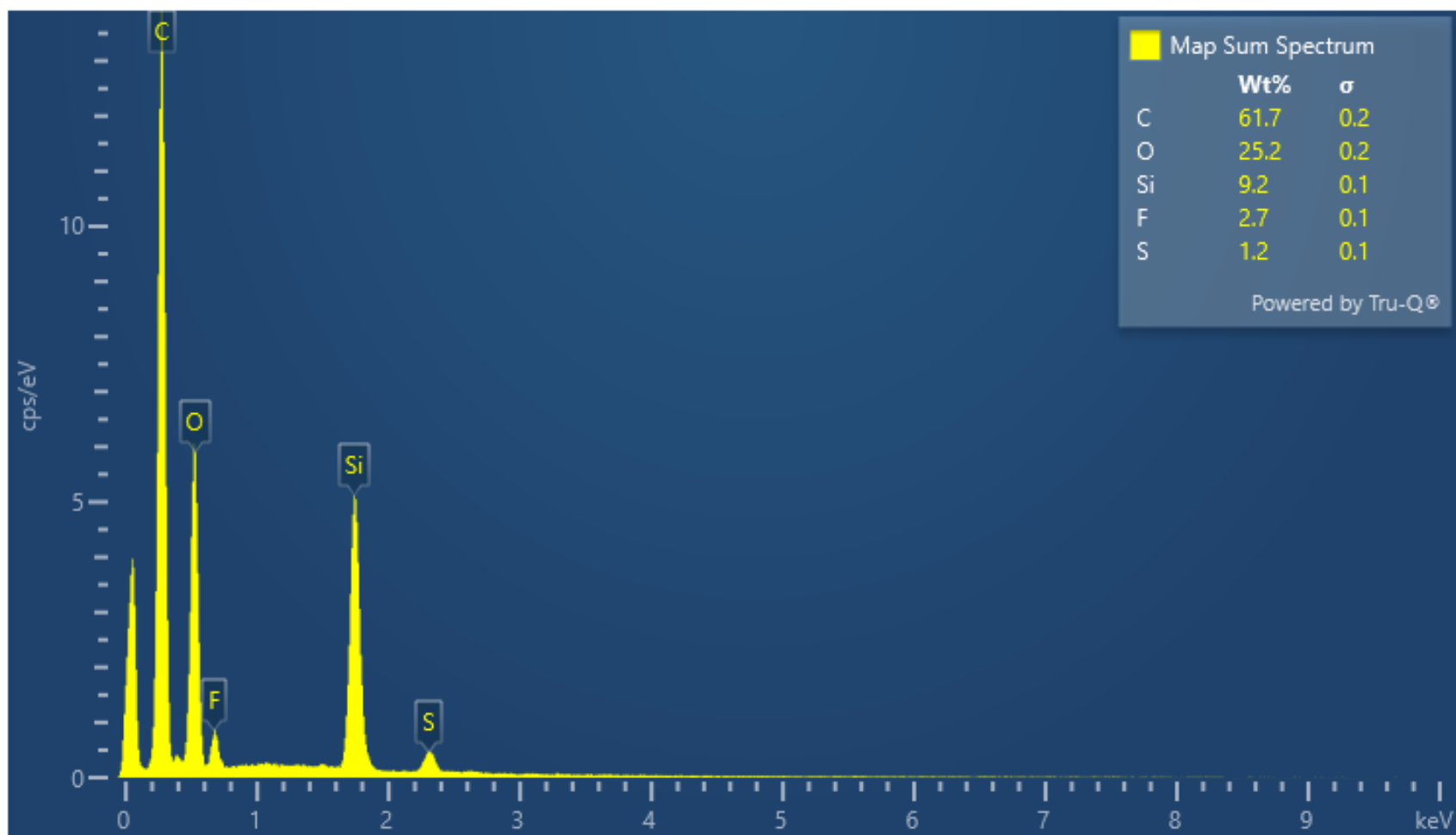


Figure 4-3 SEM-EDS pattern for a composite sample coated with the Chemlease 41-90 EZ by 6 times. The inset displays the chemical composition results.

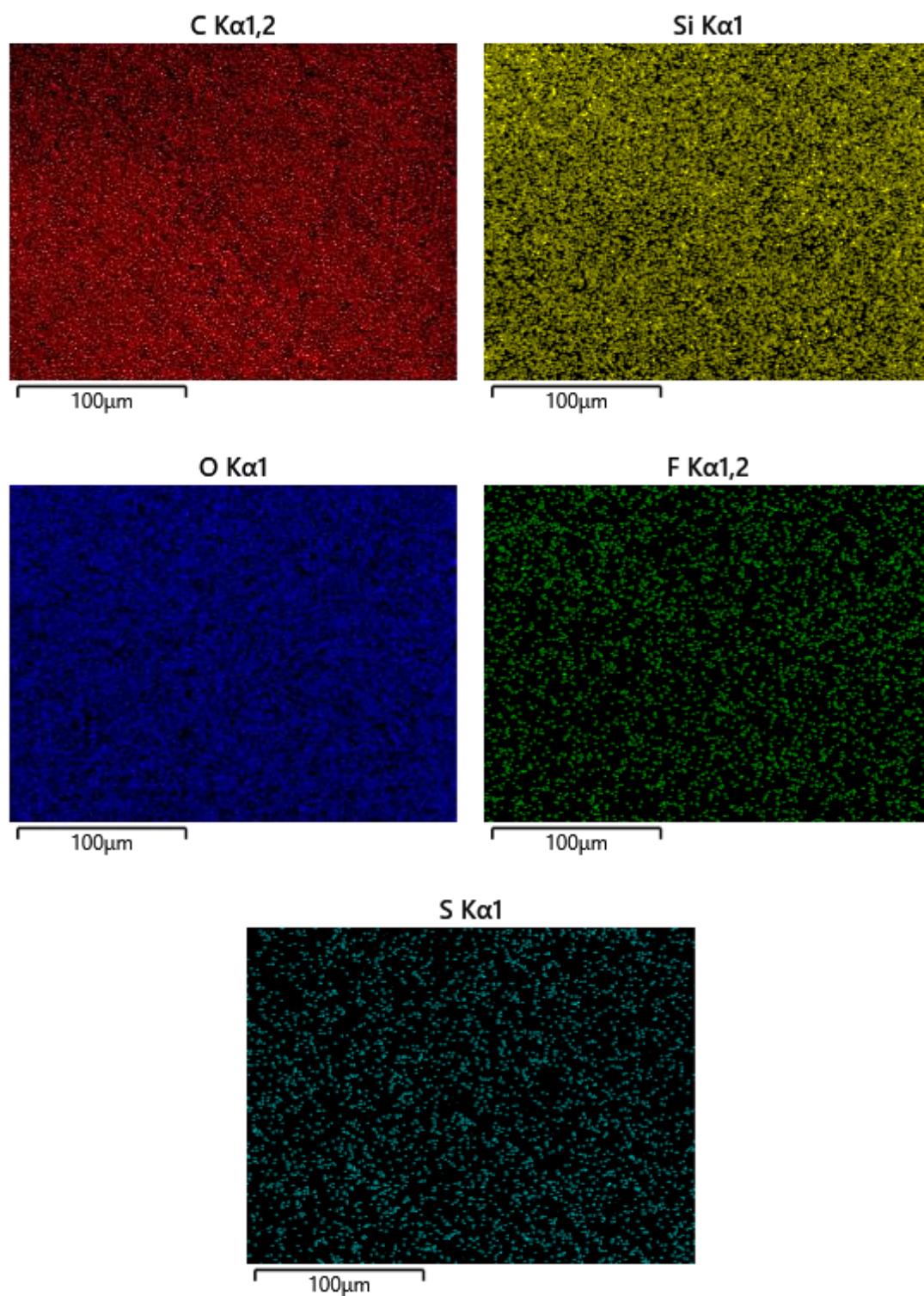


Figure 4-4 SEM-EDS area map for a composite sample coated with the Chemlease 41-90 EZ by 6 times. Area maps include Carbon (C); Silicon (Si); Oxygen (O); Fluorine (F); Sulphur (S).

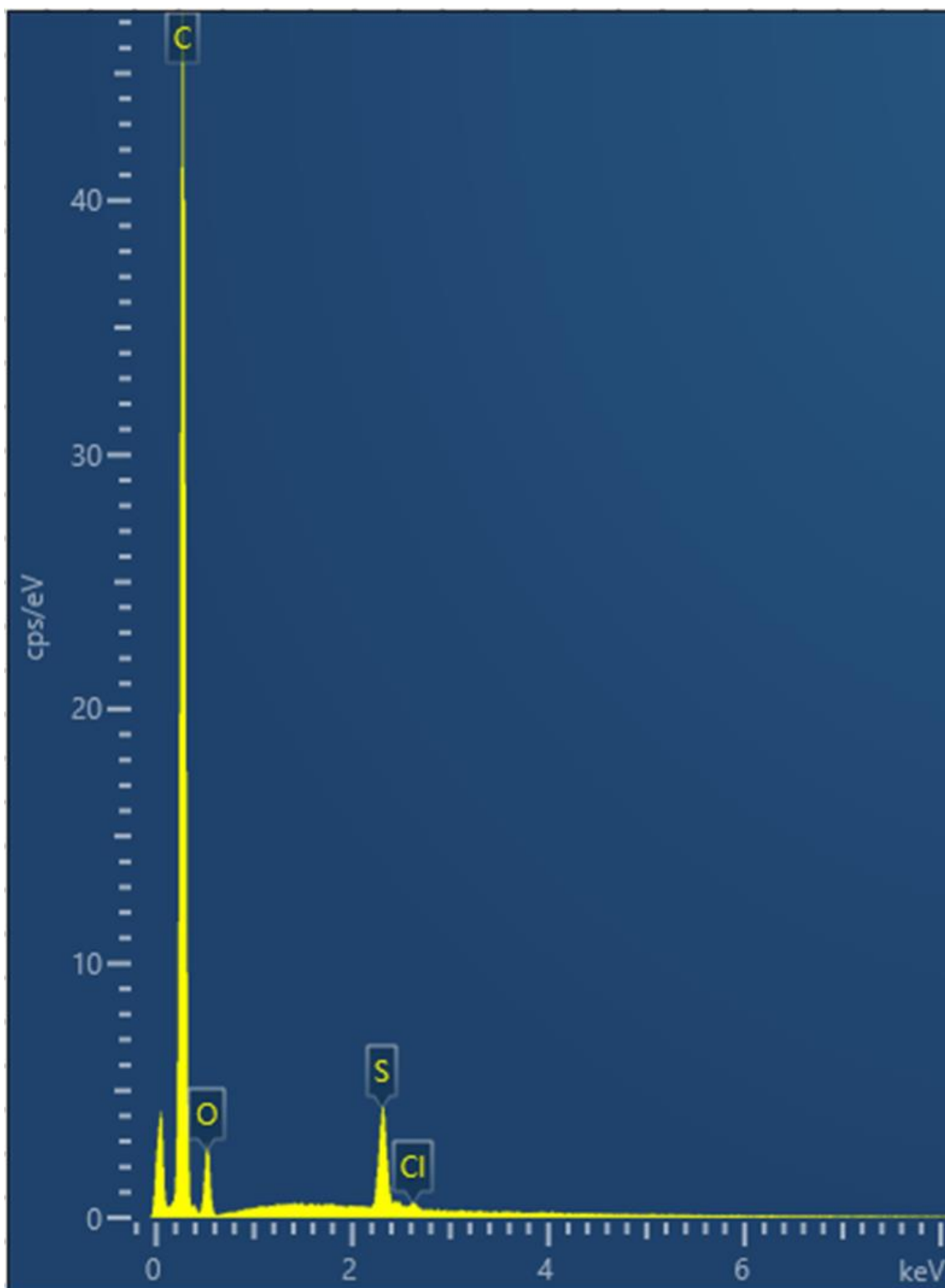


Figure 4-5 Typical EDS spectrum for an original (no coated layer) composite sample. It contains mainly C, O and S, no Si.

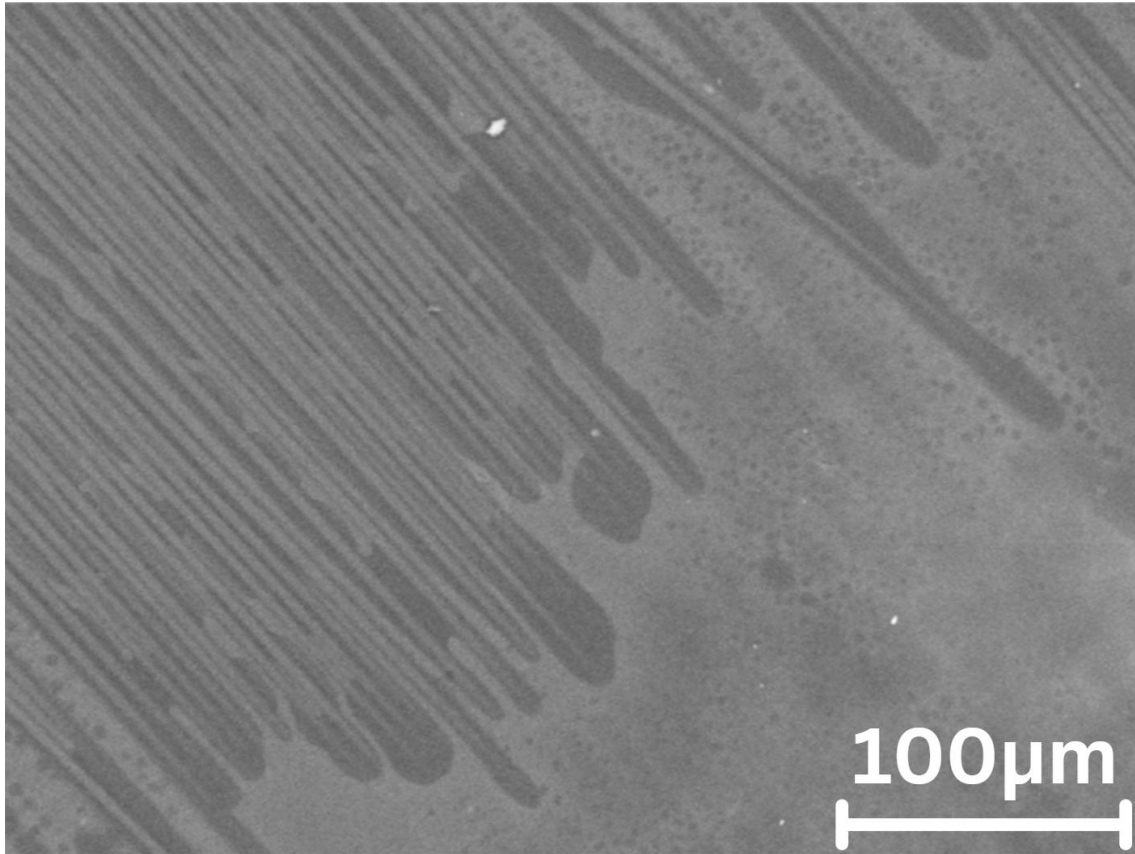


Figure 4-6 An SEM (BSE) image of an original MTM44-1 CFRP sample

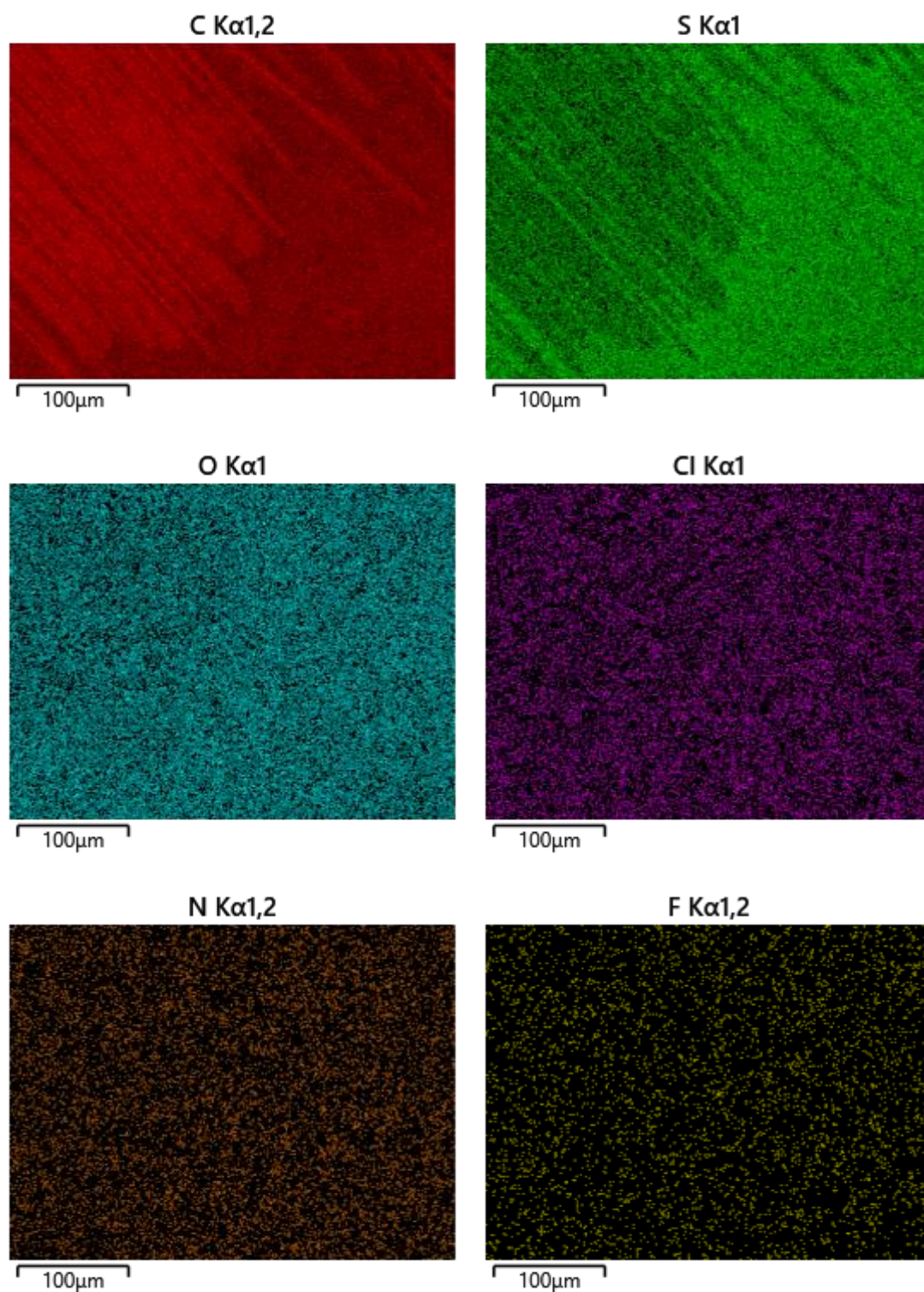


Figure 4-7 area map for a composite sample coated with the Chemlease 41-90 EZ by 6 times. Area maps include Carbon (C); Sulphur (S); Oxygen (O); Chlorine (Cl); Nitrogen(N) and Florine (F).

4.1.1 Coating thickness Estimations

As the Chemlease 41-90 EZ layer is non-electrically conductive, usually very thin, soft and easy to break, it is very difficult to measure its exact thickness. Studies were conducted with both SEM, AFM, CCI as well as through a scratch test method to calculate the thickness. The coating was too small to be detectable via SEM, too soft and uncondusive to be appropriate for both AFM, too translucent to be detectable by CCI or other microscopy and too thin for a scratch test method, the results of which is displayed in Figure 4-8, resulted in scratches of the epoxy.

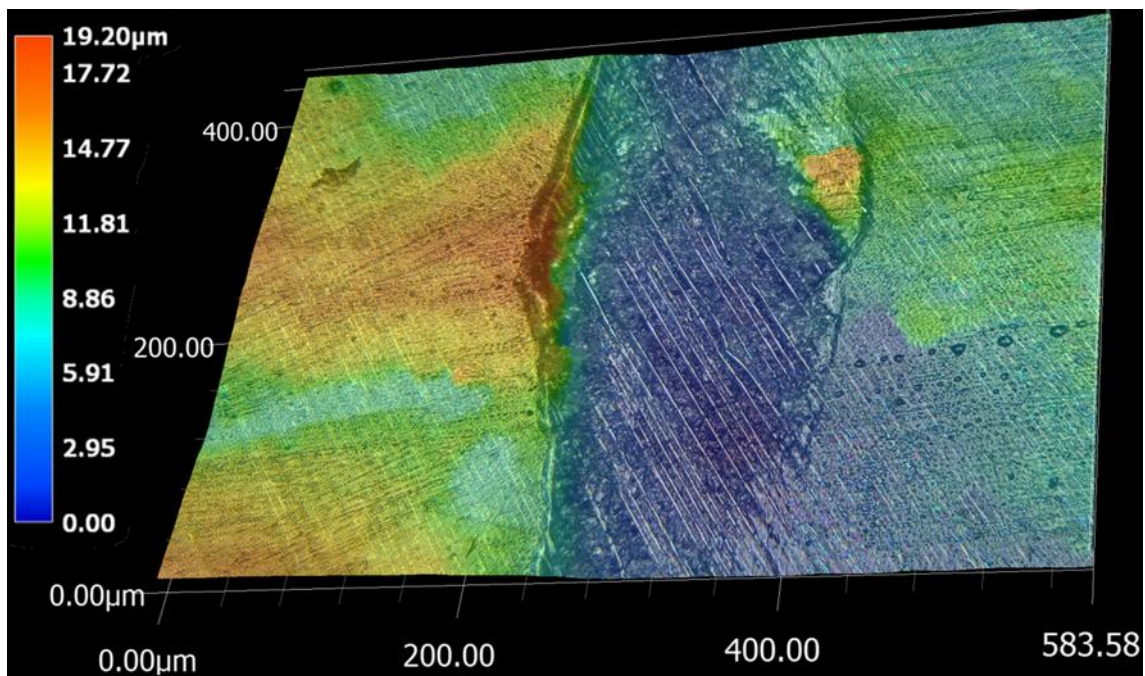


Figure 4-8 displaying the optical microscope image from the scratch test method where the surface layer of epoxy was instead scratched off to reveal the carbon fibre below, rather than scratching off the contamination.

Due the aforementioned difficulties, the EDS results of the coated sample were used to estimate the thickness of the coated Chemlease layer. Figure 4-9 displays the schematic of the EDS analysis of the spin coated (CM2) composite sample. The thickness of the spin coated Chemlease is assumed to be 't' nm thick. A 2 nm gold (Au) layer is deposited for all the samples before SEM/EDX analysis in order to eliminate the charging effect during the SEM investigation.

When a high-energy electron beam interacts with a material, the electrons typically scatter, lose energy, and the beam expands. If the beam energy is sufficiently high and the upper layers are thin, the effect of beam expansion in these layers can be neglected. In such instances, the resulting compositional data can be used to estimate the thickness of one layer, assuming the thickness of the other layer is already known.

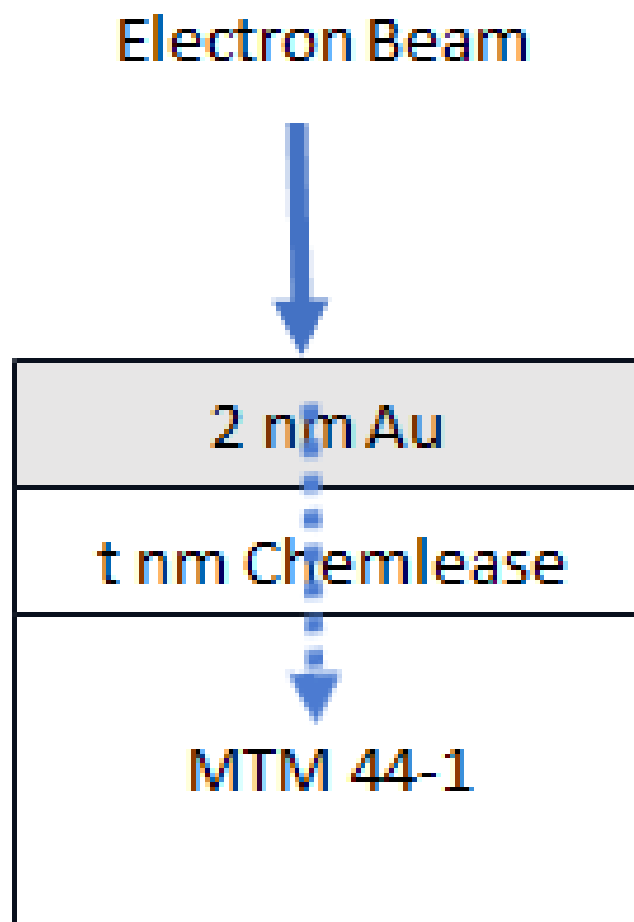


Figure 4-9 Schematic of electron beam path during SEM-EDS investigation for the composite sample coated with a layer of Chemlease. To eliminate charging effect during SEM a 2 nm gold (Au) layer is deposited for all the samples before SEM/EDS analysis.

The Bethe formula (306) describes the mean energy loss per distance travelled by fast charged particles, as they pass through matter, which is also referred to as the stopping power of the material. For electrons, the energy loss mechanism

is slightly different due to their smaller mass, and significant energy loss as they interact with atomic electrons.

A quantitative model of this interaction must account for the rate at which an electron loses energy to its surrounding medium. The stopping power determines both the range of the incident electron and the magnitude and spatial distribution of any emissions, such as secondary electrons or X-rays, that are produced during the process(307).

Joy and Luo (308) suggest a modified form of the Bethe equation (306) where the stopping power ($\frac{dE}{ds}$) represents the average energy loss (dE) per unit distance (ds), with the energy loss in electron volts (eV) per unit path length in centimetres.

Equation 5: A modified form of the Bethe equation (306,308)

$$\frac{dE}{ds} = -7.85 \times 10^{10} * \frac{Z\rho}{AE} * \ln\left(\frac{1.166 E}{J'}\right),$$

In this equation J' is the mean ionisation potential (eV) given by:

$$J' = 1 / (1 + \frac{K * J}{E'}),$$

A = Atomic Mass, Z= atomic number, ρ = material density (g/cm³), K=0.731 + 0.0688 * log(Z) and J = 9.76Z + 58.5Z^{-0.19}.

The beam broadening or beam width can be estimated as:

$$b = a \frac{Z}{E_0} * \left(\frac{\rho}{A}\right)^{0.5} * t^{1.5}$$

Where t= sample thickness t and b= beam broadening (nm). E0 is measured in keV.

a is determined by the fraction of beam intensity used to define the beam diameter. When the beam diameter encompasses 68% of the total intensity, corresponding to the Gaussian distribution variance, $a = 0.11 \text{ nm keV}$.

The electron beam penetration depth R can be expressed by the following equation (309)

$$\rho R = 5.025 \times 10^{12} * A * \frac{E_0^{\frac{5}{3}}}{\lambda_s} * Z^{\frac{8}{9}}.$$

Using these equations, with an incident beam of 20keV, the electron beam energy loss after 2 nm of gold layer is 61 eV and the beam broadening is 0.38 nm. The penetration depth in gold is 857 nm.

The energy loss and beam broadening are very small compared to the beam used for the EDS analysis (20 kV and a large beam size of several nm). As carbon, silicon and oxygen are detected at the surface of the EDS analysis, along with gold, it can be considered that an electron beam with the same energy and beam diameter will pass through the gold and the Chemlease layer. The energy loss and beam broadening will be estimated after the thickness is known. If the Chemlease thickness is not large, the beam broadening and energy loss in the underneath MTM44-1 layer can be considered as negligible, with only the weight ratio of gold/Chemlease being used in the calculation below.

EDS analysis was conducted at 3 sites on a coated sample, so that an average content percentage could be gathered.

Table 4-1 describing the relative percentages of elements at the surface of a Chemlease coated, MTM44-1 CFRP sample.

Site	C	O	Si	S	Cl	Au
1	81.60	14.40	0.14	2.57	0.49	0.75
2	83.08	13.22	0.16	2.38	0.28	0.38
3	80.50	15.03	0.11	3.36	0.20	0.90
Average	81.73	14.22	0.14	2.77	0.32	0.82

The Si weight ratio in Chemlease is 28:74. The Chemlease density is 0.74 g/cm³ and the density of gold is 19.3 g/cm³. The weight ratio of Si to that of Au in the sample should be

$$\frac{0.74t * \frac{28}{74}}{2 * 19.3} = \frac{0.14}{0.82}$$

With this the calculated thickness is worked out to be, t = 22.9 nm.

The calculated energy loss of a 20 keV electron beam pass through a 22.9 nm thickness Chemlease can then be calculated, it is 36 eV, the beam broadening is 0.77 nm. The penetration depth in the Chemlease is 11902 nm, much higher than the calculated thickness. So, the energy loss and beam broadening are still very small after passing through the Chemlease layer. The assumptions that the beam energy loss and beam broadening can be ignored are observed reasonably well.

In practice beam broadening does exist and the average electron beam diameter in the Chemlease layer is larger than that in the gold layer, so the total amount of gold is underestimated and Chemlease is over-estimated. Hence 23 nm (rounded up from 22.9 nm) is a reasonable upper limit of the thickness for the coated layer.

In summary the thickness of the spin coated Chemlease layer in this study is estimated to be 23 nm.

4.1.2 Coating composition analysis by ToF-SIMS

The presence and distribution of silicon containing compounds on the coated surfaces of MTM44-1 was further investigated using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

ToF-SIMS is a highly sensitive surface analysis technique that allows for the detection of both elemental and molecular species at the uppermost layers of a material, making it an ideal tool for investigating coating integrity, and also granting an insight into the chemical components of the Chemlease contaminant itself.

The ToF-SIMS spectra, as detailed in Figure 4-10, indicates the presence of silicon on the coated surfaces in both its elemental form (Si^+) and as part of various silicon-containing polymer groups.

The results of the corresponding peaks to silicon compounds of the coated surface are listed in Table 4-2.

CH_3Si is detected at $m/Q = 43.0$, alongside SiCH_3^+ at $m/Q = 73$, shows the presence of organosilicon compounds, which are common in coatings and adhesives. A peak at $m/Q = 45$ suggests the presence of SiOH^+ and points to the presence of silanol groups on the surface.

The detection of higher mass fragments ($m/Q = 147\text{--}221$) indicates the presence of complex silicon-containing polymeric species on the surface. These fragments, such as $\text{C}_5\text{H}_{16}\text{O}_3\text{Si}_3^+$, $\text{C}_5\text{H}_{17}\text{OSi}_2^+$ and $\text{C}_7\text{H}_{21}\text{O}_2\text{Si}_3^+$ suggest the incorporation of silicon into larger polymer networks.

The presence of silicon in both its pure and polymeric forms on the coated surfaces has significant implications for the material's surface characteristics. Silicon, depending on its chemical form and how it is incorporated into the surface layer, can affect properties such as wettability, chemical resistance, and adhesion. For instance, the presence of silanol groups (SiOH) could enhance surface reactivity, making the surface more amenable to bonding with adhesives or other coatings.

Table 4-2 ToF-SIMS spectra displays the presence of silicon in both its pure form, and as contained within polymer groups on post manufactured samples. References to polymer groups gathered from literature(310,311)

Material	Mass/Charge (m/Q)
Si^+	28.0
SiCH_3^+	43.0
SiOH^+	45.0
SiCH_3^+	73.0
$\text{C}_5\text{H}_{17}\text{OSi}_2^+$	147.0
$\text{C}_5\text{H}_{16}\text{O}_3\text{Si}_3^+$	207.0
$\text{C}_7\text{H}_{21}\text{O}_2\text{Si}_3^+$	221.0

Conversely, the presence of non-polar methylsilyl groups (SiCH_3^+) might impart hydrophobic characteristics, which could be advantageous or detrimental depending on the intended application.

The detection of complex polymeric silicon-containing compounds could suggest that the surface treatment may involve the integration of silicon into the surface polymer matrix.

The findings from the ToF-SIMS analysis align with the observations reported in the literature. According to Keller et al. (310) and Kern, Kern, and Rohnke (311), silicon-containing compounds are commonly found in surface treatments and coatings, particularly in advanced materials used in high-performance applications.

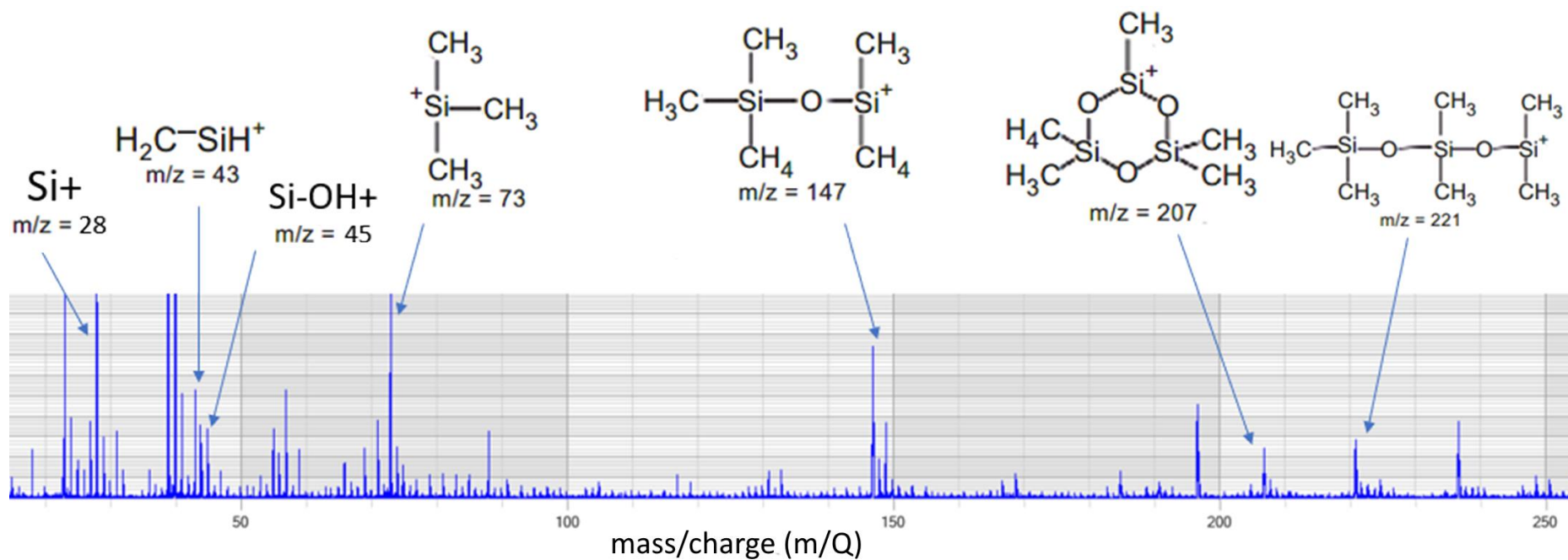


Figure 4-10 ToF-SIMS spectra display of the presence of silicon in both its pure form, and as contained within polymer groups on post manufactured samples. References to polymer groups gathered from literature(310,311)

4.2 The effect of Surface Wave Launched Microwave Plasma (SWL-MP) on the Surface Parameters of Composites

As previously mentioned in Chapter 3, the effect of two separate plasma torches were investigated during initial testing on Microwave plasma systems. These included systems capable of producing plasmas at powers of 200W and 50W respectively.

4.2.1 Initial Process Characterisation using SWL-MP

Initial studies with this torch investigated the effect of Plasma Processing Parameters on the Surface Modification of Carbon Fibre Reinforced Composites by Atmospheric Pressure Plasma Treatment as reported in Frumosu *et al* (30).

Table 4-3 The effect of atmospheric pressure plasma on the Sq of carbon fibre reinforced epoxy.

Forward Power (W)	Flow Rate (L/min)	Z Height (mm)	Surface Roughness (Sq., nm)	
			Before Plasma Treatment	After Plasma Treatment
100	10	2	142	165
		3	81	98
	20	2	68	61
		3	95	101
150	10	2	185	186
		3	125	104
	20	2	83	97
		3	60	156

Two different settings for forward power were set: 150W and 100W with various reflected powers depending on the initial power and flow rate of argon. Flow Rates of 10Lmin and 20Lmin, as well as standoff distances of 2mm and 3mm were explored, resulting in 8 sets of parameter combinations being explored.

Carbon fibre reinforced epoxy laminate samples were cut into 30 x 30 mm squares and ultrasonically cleaned for 30 minutes before processing. The samples were placed directly under the torch, with the centre aligned to that of the quartz tube. Samples were radiated for 180 seconds.

Surface Roughness evaluation was performed using a coherence scanning interferometer (Talysurf CCI 6000, Taylor Hobson Precision). The results, displayed in Table 4-3 found that the Sq decreased after plasma processing in 2/8 parameter sets, with this increasing in 6/8 parameters.

Table 4-4 The effect of atmospheric pressure plasma on the surface energy of carbon fibre reinforced epoxy

Forward Power (W)	Flow Rate (Lmin ⁻¹)	Z Height (mm)	Surface Energy (mJ/m ²)
Before Plasma			34.5
100	10	2	75.6
		3	76.3
	20	2	76.9
		3	78.4
150	10	2	79.0
		3	78.6
	20	2	79.8
		3	78.4

A three-way ANOVA was conducted that examined the effect of flow rate, forward power, and z height on surface roughness. The F-value measures the ratio of the variance between the group means to the variance within the groups. The p-value indicates the probability of observing the data if the null hypothesis is true. In a 3-way ANOVA, the null hypothesis is that none of the factors or interactions have a significant effect on the dependent variable. This is considered the case if the p-value is higher than 0.05.

In this case, at a $F = 0.147$ and $p\text{-value}=0.707$, it indicates that the variability between parameters is very small compared to the variability within each parameter's measured surface roughness value. As such there was not a statistically significant interaction between the effects of flow rate, forward power, and z height on surface roughness.

When looking at surface energy, results displayed in Table 4-4, plasma processing was shown to increase surface energy between 41.1 mJ/m^2 and 45.3 mJ/m^2 depending on the parameters set. The results further indicate that the combination of parameters selected have a negligible difference between surface energy increase.

4.2.2 The effect of hydrophobic recovery on SWL-MP treated samples.

The effect of aging on composite samples was explored further using three sets of parameters. These parameters are detailed in Figure 4-11. 18 hours post plasma processing, the surface energy is highest across all three series, with values above 65 mN/m . Over time, the surface energy decreases for all three series, with the reduction in surface energy is more pronounced within the first 48 hours. After 120 hours and 168 hours (1 week), all three surface series have a similar surface energy range around $35\text{-}45 \text{ mN/m}$, suggesting that the aging effects start to diminish after 5 days. This data shows that the plasma treatment, although effective in increasing surface energy, is a short term solution.

In regard to adhesion, it would be advised, from the results of these studies, to adhere composite surfaces within the first 24 hours post-plasma processing.

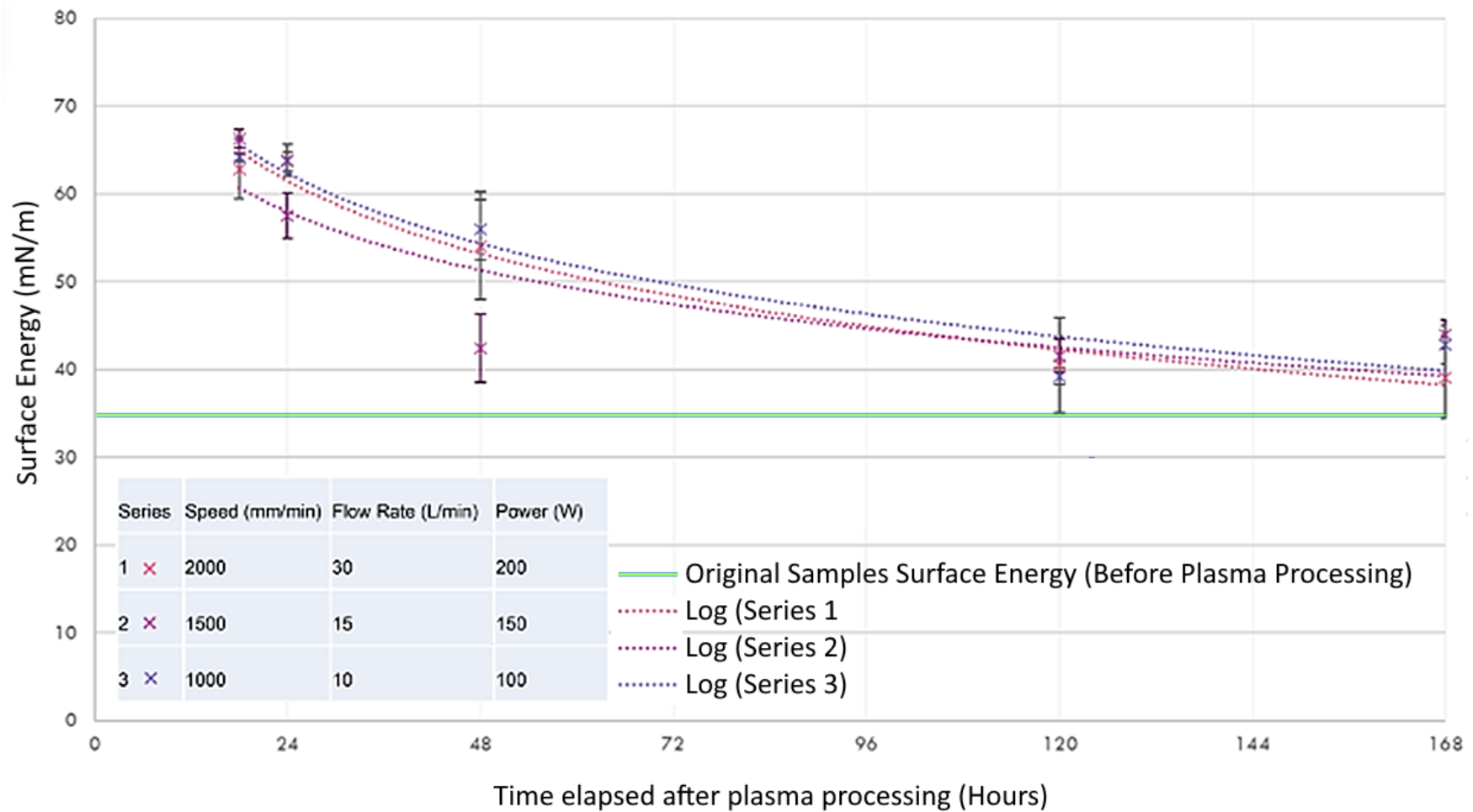


Figure 4-11 Comparison of Plasma Processes detailing the effect of aging on the surface energy of composite samples treated with Surface Wave Launched Microwave Plasma (SWL-MP) under three different sets of parameters.

4.2.3 The use of SWL-MP in contamination removal

The average surface energy of the contaminated samples one hour post processing was found to be extremely low, at $5.52 \pm 0.165 \text{ mNm}^{-1}$. In contrast, the surface energy of the unprocessed samples was much higher at $41.00 \pm 1.6 \text{ mNm}^{-1}$. Samples were left to age for 5 days, before surface energy measurements were taken, displayed in Figure 4-12.

Surface energy results indicate that plasma processing of both original and contaminated samples improves the adhesion properties of the composites. It also indicated that contamination greatly decreases the surface energy.

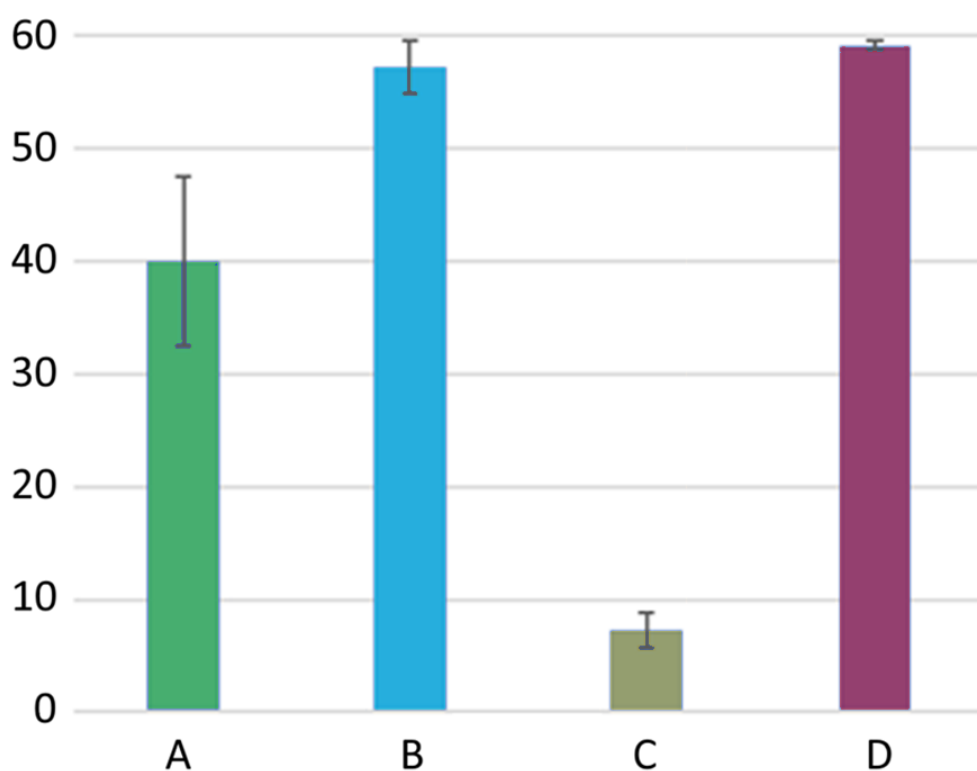


Figure 4-12 Displaying the average surface energies of the 4 categories of samples. The data shows an increase in surface energy among all plasma processed samples, where contamination shows to reduce surface energy compared to the original, untreated samples. A) Untreated Samples. B) Plasma Treated Samples. C) Coated, untreated samples. D) Coated and Plasma Treated samples.

To enhance adhesion on polymer surfaces via plasma treatment, optimising processing parameters is crucial. This involves adjusting surface free energy or wettability of the polymer substrate to improve the adhesion force between the substrate and the coating. However, adhesion doesn't always correlate with the wettability changes due to factors like hydrophobic recovery and the formation of a loosely bonded interlayer composed of low molecular weight fragments (160).

Lap shear strength experimental results, as displayed in Figure 4-13, showed this plasma processing to have a positive effect on the maximum lap shear strength for the clean original samples, but negative effect for samples with contamination. This contrasts with the indicated results from the surface energy calculations, where plasma processing appeared to increase surface energy.

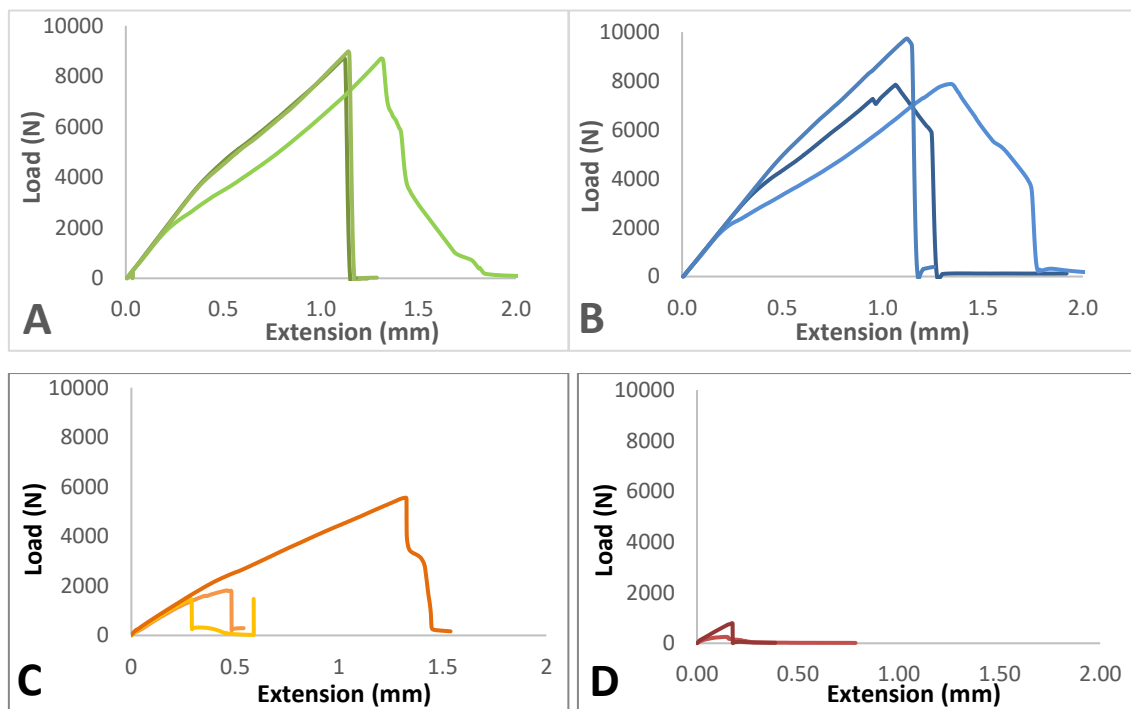


Figure 4-13 A: Displaying Load vs Extension curves in regard to lap shear failure breakage forces at the point of bonding between two adhered composite surfaces. A) Untreated Samples. B) Plasma Treated Samples. C) Contaminated, untreated samples. D) Contaminated and Plasma Treated samples. Each parameter set was conducted 3 times, hence the display of 3 curves.

Although the maximum lap shear strength of the plasma treated original sample of 31.168 Nm^{-2} was higher than the untreated original samples of 28.768 Nm^{-2} , its average value of 27.168 Nm^{-2} (s.d. 2.82) was lower than the average value of the original samples of 28.192 Nm^{-2} (s.d. 0.42), as compared in Figure 4-14. It should be noted that for the clean original and its plasma treated samples the breakages occurred within the composite itself, whereas breakages on contaminated surfaces occurred on the surface-adherent interface. Considering all these factors, we conclude that there is little difference by plasma treatment to the bond strength of the original composite samples.

The fact that the plasma treatment of the coated samples leads to marked reduction of bonding strength indicates that, firstly, the silicon containing contaminant layer was not removed by the plasma treatment.

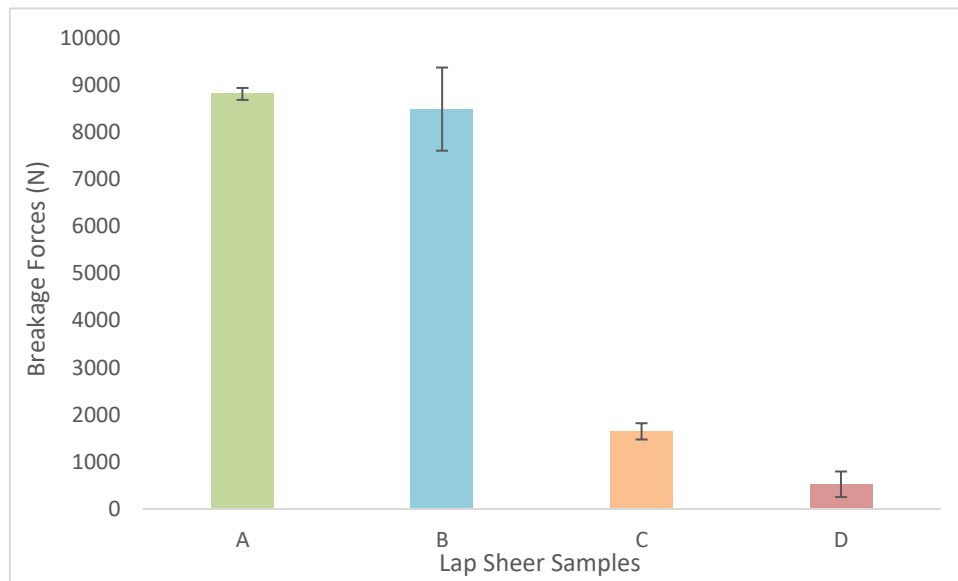


Figure 4-14 Displaying lap shear strength at the point of bonding between two adhered composite surfaces. A) Original Samples. B) Plasma Treated original Samples. C) Contaminated and untreated samples. D) Contaminated and Plasma Treated samples. The existence of surface contamination, including the silicon coated onto the samples, drastically reduced the bonding strength, due to the low surface energy and hydrophobic properties. Large discrepancy for contaminated samples indicates that a non-uniform surface contamination may exist on CM1.

Secondly, plasma treatment may lead to the spread of the contaminants, exacerbating their negative effects on adhesion. When plasma interacts with contaminants such as silicone, instead of completely removing these substances, it may disperse them more broadly across the surface. This spreading effect can lead to more extensive coverage of low-energy contaminants, rather than their concentration in specific areas. As a result, the overall surface area affected by these contaminants increases, further lowering the surface energy and making it even less conducive to effective adhesion.

Plasma treatment can sometimes create micro-etching or surface channels on composite materials. While this can increase surface area and promote adhesion, it may also inadvertently allow contaminants (such as polymer oils or silicone residues) to penetrate deeper into the material. Once embedded within the microstructure, these low-surface-energy contaminants become more difficult to remove or neutralise. Their deeper integration can significantly reduce adhesive performance by interfering with proper bonding. In some cases, the introduction of oxygen- or nitrogen-containing functional groups (e.g. carbonyls, nitrogen oxides), or fluorination (312,313), can further complicate the surface chemistry, especially if contaminants are present.

All these may have contributed to our observed results that the plasma-treated, contaminated samples exhibit worse lap shear breakages compared to untreated samples. The combination of chemical modification, contaminant spreading, and inconsistent surface treatment leads to a more heterogeneous surface with varied adhesion characteristics. Consequently, adhesives may not form uniform, strong bonds across the surface, leading to weaker adhesion and increased susceptibility to failure under shear stress. This contrasts with uncontaminated surfaces, where plasma treatment could enhance adhesion by increasing surface energy and promoting mechanical interlocking, resulting in stronger and more reliable bonds. These results suggest that further study is needed to remove the contamination by APP.

4.2.4 The effect of plasma treatment speed on the surface energy of composite samples

The influence of plasma treatment speed on the surface energy of composite samples was investigated by varying the treatment speed while maintaining a consistent argon flow rate of 15 L/min. The resulting surface energy values for different speeds are presented in Figure 4-15.

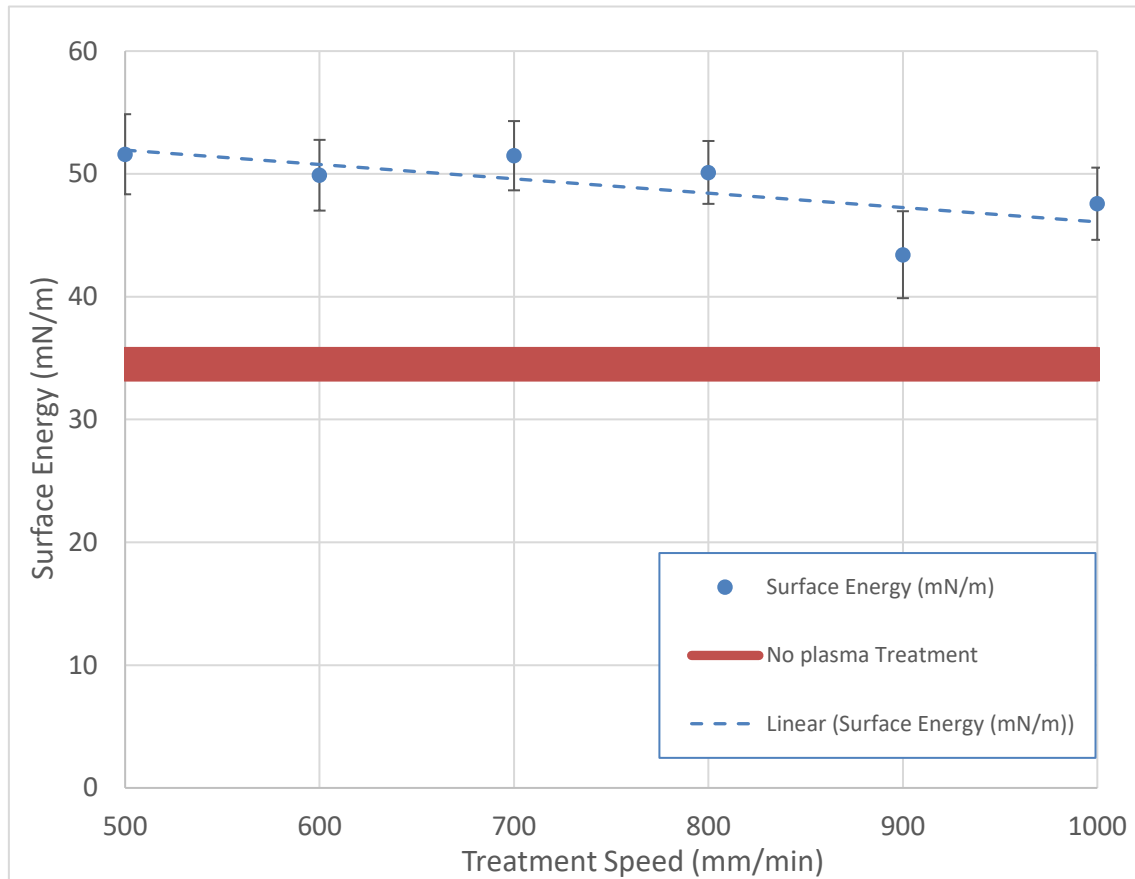


Figure 4-15 The effect of treatment speed on surface energy. Argon plasma had a constant Flow Rate of 15Lmin-1

Plasma treatment significantly enhanced the surface energy of the composite samples compared to the surface energy before treatment (34.5 mN/m).

The maximum surface energy values were observed at treatment speeds below 800 mm/min within the range tested, with the average surface energy being just above 50mN/m. These speeds result in a significant increase in surface energy from the untreated baseline, indicating effective surface modification.

As the treatment speed increases beyond 800 mm/min, there is a noticeable decline in surface energy, with the 900 mm/min and 1m/min averaging 45.5 mN/m). At higher speeds, the exposure time of the surface to the plasma is reduced, leading to less effective treatment.

4.3 The effect of Microwave Induced Power Plasma (MIPP) on the surface properties of MTM44-1

This section explores the use of the MIP plasma torch for surface modification of MTM44-1. This section specifically looks at the effect plasma processing has on the special effects of plasma on the composite surfaces.

4.3.1 Effect of Plasma Pass Spacing on Surface Energy Modification Uniformity

Initial studies into plasma uniformity, as displayed in Appendix B showed clear distinctions between high surface energy regions and low surface energy regions of a polymeric surface after treatment with plasma. Figure 4-16 displays the effect the 50W MW torch has on a composite surface, at a speed of 1m/min.

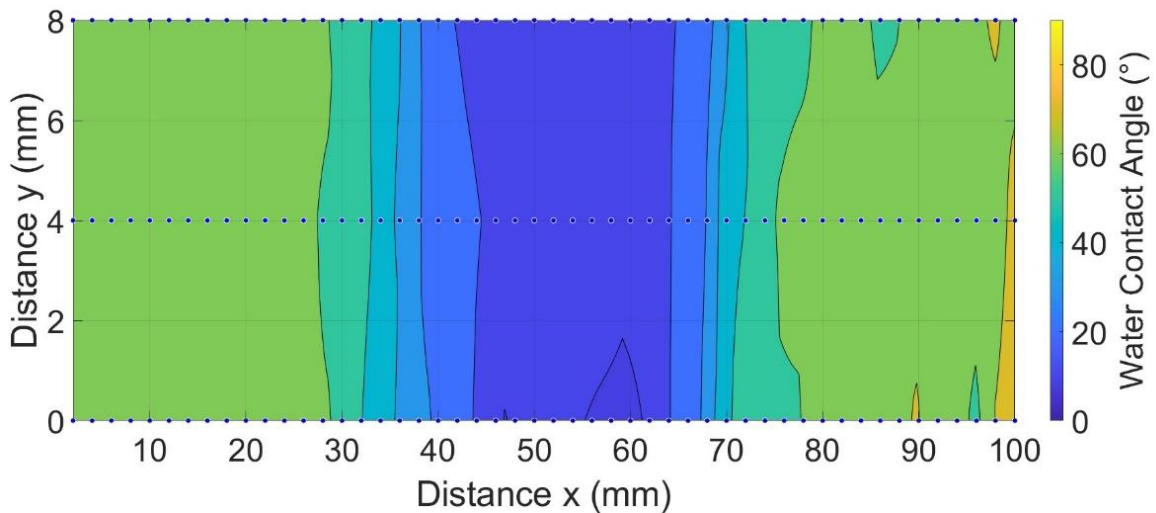


Figure 4-16 Water contact angle map of one pass of argon at 1m/min

This figure provides insight on the special stability of the plasma, in terms of surface energy modification, and more specifically its wettability. It is map of a water contact angles across the middle of the surface of a 100mm x 25mm cut composite sample and the effects of plasma processing on its surface. The x-axis represents the distance (x) in millimetres (mm) along the surface, ranging from 0 to 100 mm, while the y-axis represents the distance (y) in mm across the width of the surface, ranging from 0 to 8 mm.

The colour scale on the right indicates the water contact angle in degrees, ranging from 0° (blue) to 80° (yellow). The distribution of colours on the map suggests the varying surface wettability induced by the plasma processing. Areas of lower water contact angles (blue) indicate increased wettability (higher surface energy), while areas of higher contact angles (yellow to green) indicate reduced wettability.

Figure 4-16 indicates that 1m/min would provide a stable pass of plasma treatment across an 8mm distance, and that this would result in an area of roughly 20mm with high surface energy.

The potential for this study is to understand how the raster effects on the treatment of samples, affects the ability to have a uniform and effective treatment. To compare this effect, first it was measured on a 'clean' solvent wiped surface as shown in Figure 4-17. The solvent sample showed a decent amount of sample WCA variation across it, which indicates that there is heterogeneity at the sample's surface, and that it is still a predominantly hydrophobic surface.

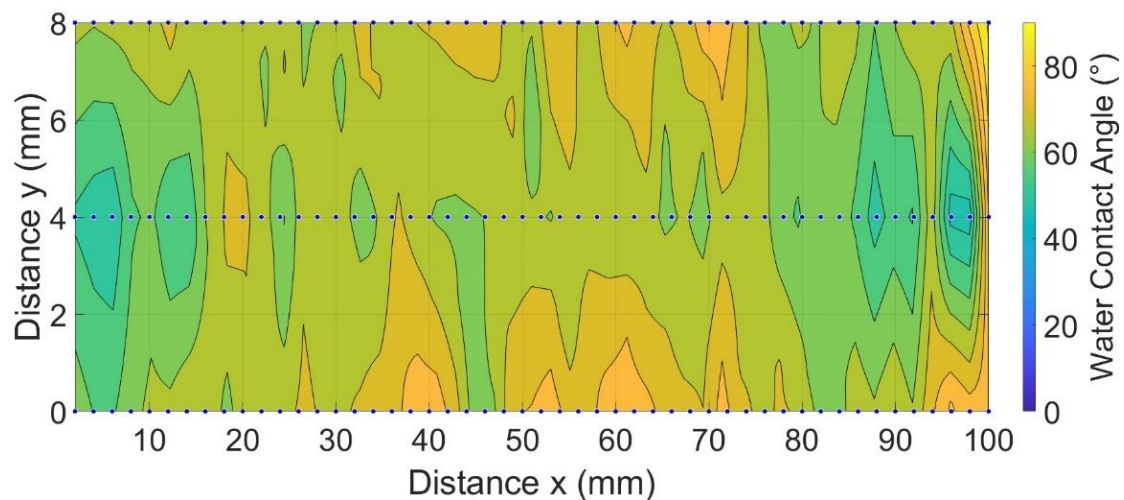


Figure 4-17 WCA map of Solvent Cleaned Sample

To look at how the gap between passes affects the uniformity of samples, passes were conducted at 1m/min, with passes varying in space in between them. Due to the high amount of data collected, some of these results can be found in Appendix 6B.3.

The distance between raster patterns was varied from 17mm to 2mm apart. As a WCA measurement was only taken every 2mm, it was unlikely that variations could be detected at distances of 2mm or less, so these were not measured. The results are displayed in Figure 4-18 with further maps in Appendix 6B.3. Each map corresponds to a different distance between plasma passes. At 17 mm gap, the map shows some regions with higher contact angles (yellow/green areas), indicating less wettability and varying surface energy modification across the sample. While at 13 mm the variation in water contact angles becomes less pronounced, with more blue regions representing increased wettability and relatively uniform surface energy modification.

The map with 6mm distance between passes shows a more uniform distribution of contact angles with predominantly blue areas, suggesting that the plasma treatment has effectively modified the surface energy across the sample. This appears to be the most advantageous spacing, providing a balanced level of surface modification with efficient processing.

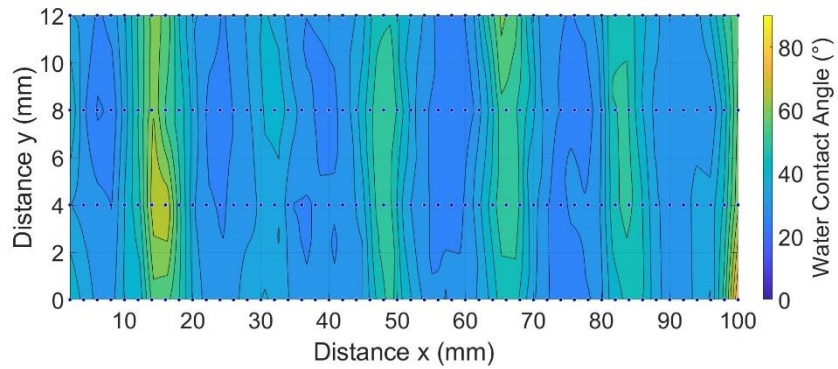
The 4mm, similar to the 6 mm, map also displays a uniform distribution of lower contact angles, but with slight variations. However, the minimal differences suggest diminishing returns on reducing the spacing further.

Overall, the results of this work show that 6mm may be the most advantageous space between passes. 6mm distance apart between plasma passes appears to provide an adequate level of surface energy modification, while keeping the time spent processing the sample low. It may be assumed that 6mm is the effective dimension of the plasma field, in terms of surface energy.

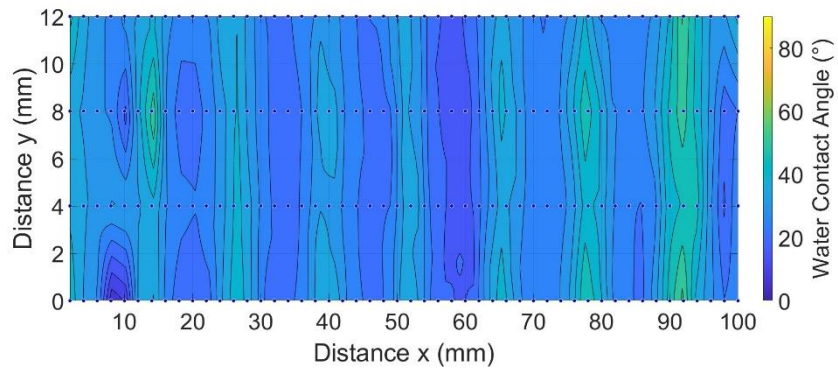
(mm)

Resulting WCA map

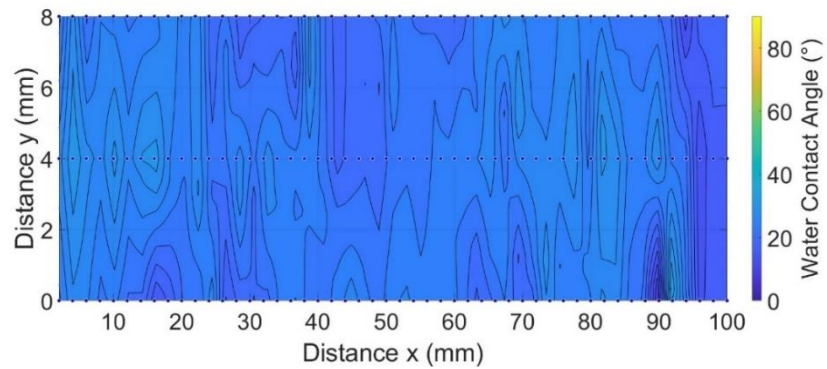
17



13



6



4

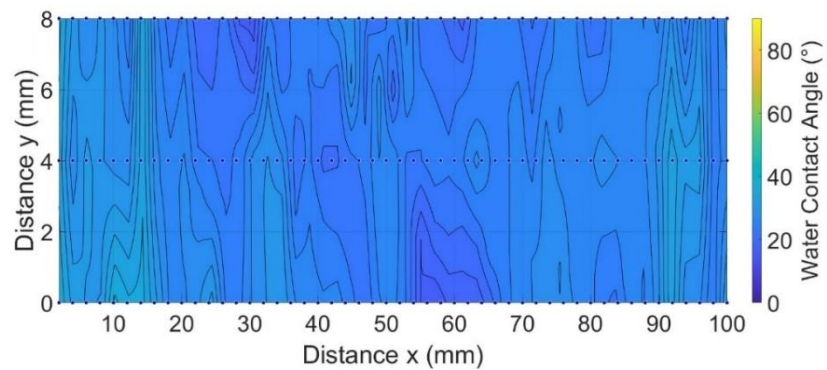


Figure 4-18 displaying maps of WCA across MTM44-1 samples with varying distances in between plasma passes in mm

4.3.2 The relationship between plasma treatment speed and the resulting water contact angle

The relationship between plasma treatment speed and the resulting water contact angle on a treated surface was explored. This is presented in Figure 4-19 which displays an increasing trend in the water contact angle as the treatment speed increases.

At higher plasma treatment speeds (of up to 30 m/min, compared to lower ranges between 0.01 m/min to 1 m/min), the water contact angle increases significantly, reaching a maximum of approximately 57.67° at 30 m/min. This suggests that surfaces treated at higher speeds are more hydrophobic.

In contrast, at lower speeds, the water contact angle remains relatively constant, hovering around 25.33° to 27.67° , indicating a more hydrophilic surface.

The error bars indicate the standard deviation of the measurements at each treatment speed. At higher speeds (25 m/min and 30 m/min), there is slightly more variability (with standard deviations around 1.89° and 1.25° , respectively), compared to lower speeds, where the variability is minimal (around 0.47°).

Generally, plasma treatment decreases the water contact angles. So, higher speeds increase the contact angles. Although the results are plotted to the logarithmic scale, due to more measurements being taken at slower speed, a linear relationship between treatment speed and water contact angle can be noted.

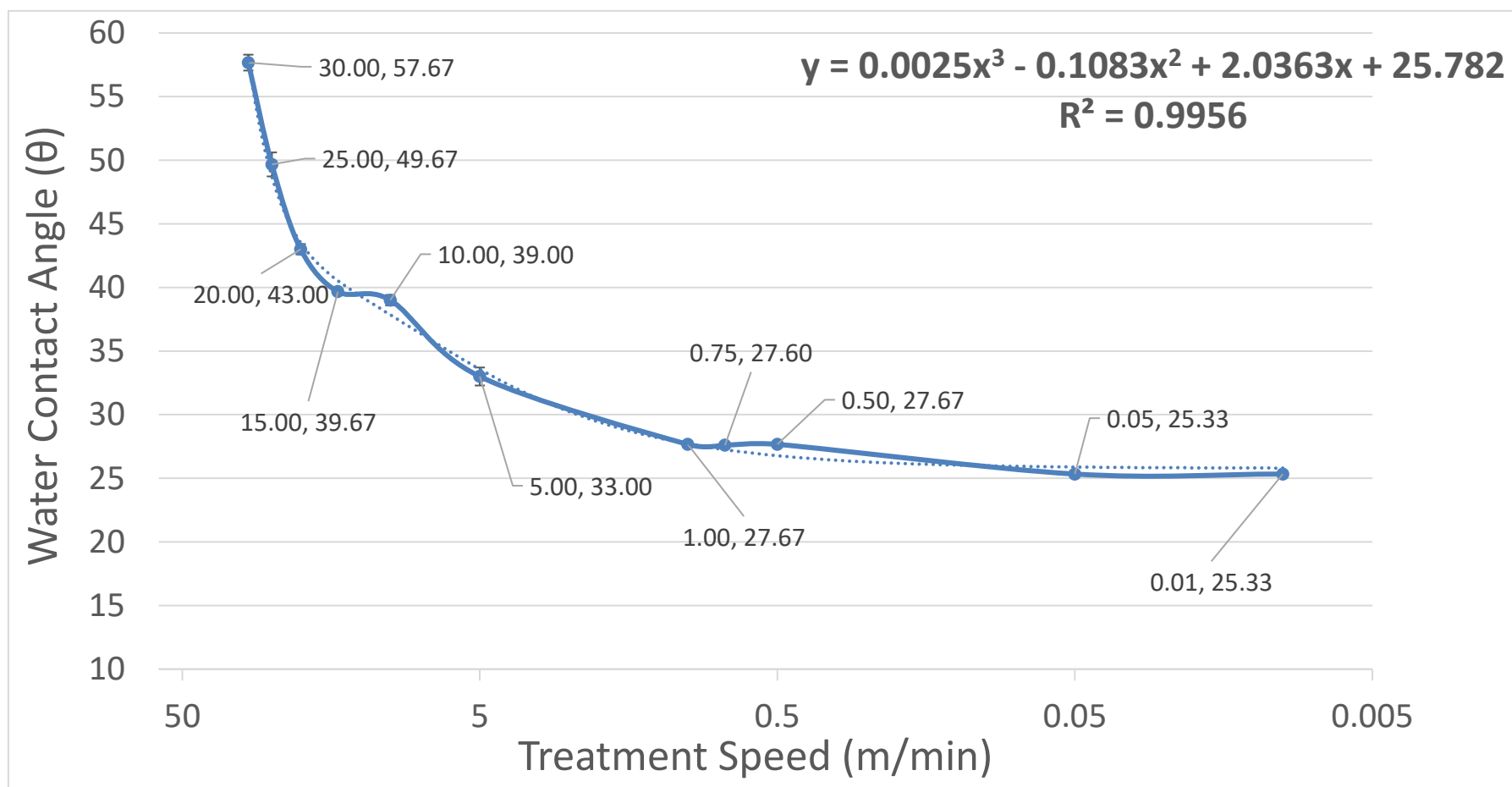


Figure 4-19 The effect of plasma treatment speeds on Water Contact Angle of MTM44-1 samples. Water contact angle follows Square-Cube Law as Treatment Speed increases showcasing the limit from when plasma no longer affects sample and maximum absorption for given sample. Based on 3 measurements taken and averaged to 2 dp.

4.4 The effect of Dielectric Barrier Discharge (DBD) on the surfaces of CFRPs

DBD plasma operates by applying a high voltage across electrodes separated by a dielectric barrier and a gas gap. This setup prevents the formation of arc discharges, thus maintaining a stable, non-thermal plasma at atmospheric pressure. The non-thermal characteristic of DBD plasma is crucial for treating heat-sensitive composite materials, ensuring that their structural integrity is not compromised during treatment.

4.4.1 The effect of Dielectric Barrier Discharge (DBD) Plasma on the surface temperature of CFRPs

To ensure the temperature of the plasma treatment was appropriate for composites, a pyrometer was used to measure the temperature during processing. After 50 seconds of processing, glass temperature reached 28.6°C, which is well below the maximum operating temperature of cured epoxies (314). As glass has a higher thermal conductivity to epoxies (315), it was deemed that this plasma torch will not damage to the composite surface with heat.

The experiment was repeated for a thin carbon fibre epoxy laminate. This test was completed under the same parameters as for the glass except the run time was extended to 3 minutes rather than 50 seconds. Here, 19 measurements were taken, with an average temperature of 34.06°C +/- 0.85°C.

An experiment was then conducted to compare the effect of treatment speed and feed nitrogen gas flow rate on the temperature of the composites recorded (Figure 4-20). In terms of treatment speed, the speed of the motion stage where the composite was placed was changed from moving at a rate of 10 mm/min to 50 mm/min and flow rate of 10L/min. For the flow rate experiments, flow rates of 10L/min to 60L/min were compared with a standard stage speed of 10 mm/min.

At slower speeds (10 mm/min), the temperature of the composite remains relatively high, around 45°C, with a small variation in temperature.

As the processing speed increases from 10 mm/min to 50 mm/min, the recorded temperature decreases slightly, but remains between 40°C and 45°C up to a speed of 30 mm/min.

At 50 mm/min, there is a more noticeable decrease in the composite's surface temperature, dropping closer to 40°C, and the error bars indicate larger variations in temperature.

When the stage moves more slowly, the composite is exposed to the plasma for a longer period of time, allowing more energy to be transferred to the surface. This leads to a higher recorded temperature due to the prolonged plasma-surface interaction.

At Moderate speeds, the composite experiences a reduced amount of plasma exposure per unit time, leading to a slight but not significant decrease in temperature. The plasma energy has less time to accumulate on the surface, resulting in more stable temperature readings with smaller error margins.

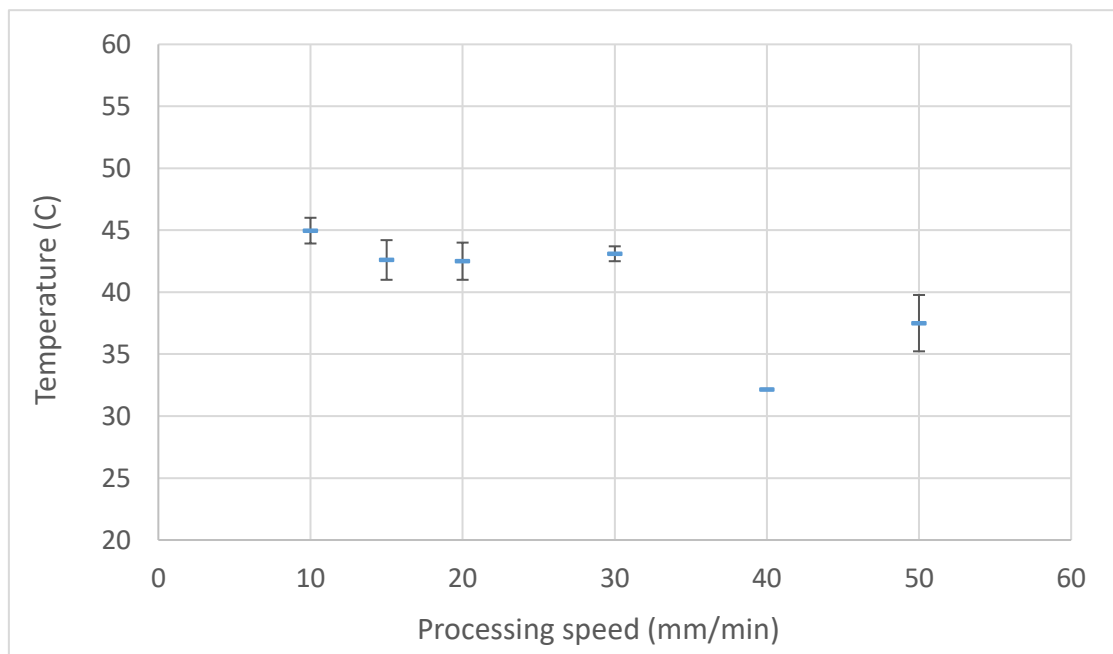


Figure 4-20: Measured surface temperature of a thin carbon fibre epoxy laminate as a function of sample moving speed relative to the fixed plasma torch.

As the stage speed increases to 50 mm/min, the composite moves through the plasma more quickly, reducing the exposure time. This leads to a more noticeable drop in temperature, likely because the surface does not have sufficient time to absorb as much energy from the plasma. The larger error bars at this speed suggest some variability in the heat transfer or in the plasma uniformity at higher speeds.

This demonstrates that processing speed has a clear influence on the temperature of the composite during nitrogen plasma treatment. Lower speeds result in higher surface temperatures due to longer exposure times, while higher speeds reduce the temperature as the surface is exposed to the plasma for shorter periods.

The relationship between nitrogen gas flow rate and the surface temperature of the composite sample during DBD nitrogen plasma treatment was also explored and displayed in Figure 4-21. The graph presents the measured surface temperature as a function of varying nitrogen flow rates, ranging from 10 L/min to 60 L/min, while maintaining a constant stage speed of 10 mm/min.

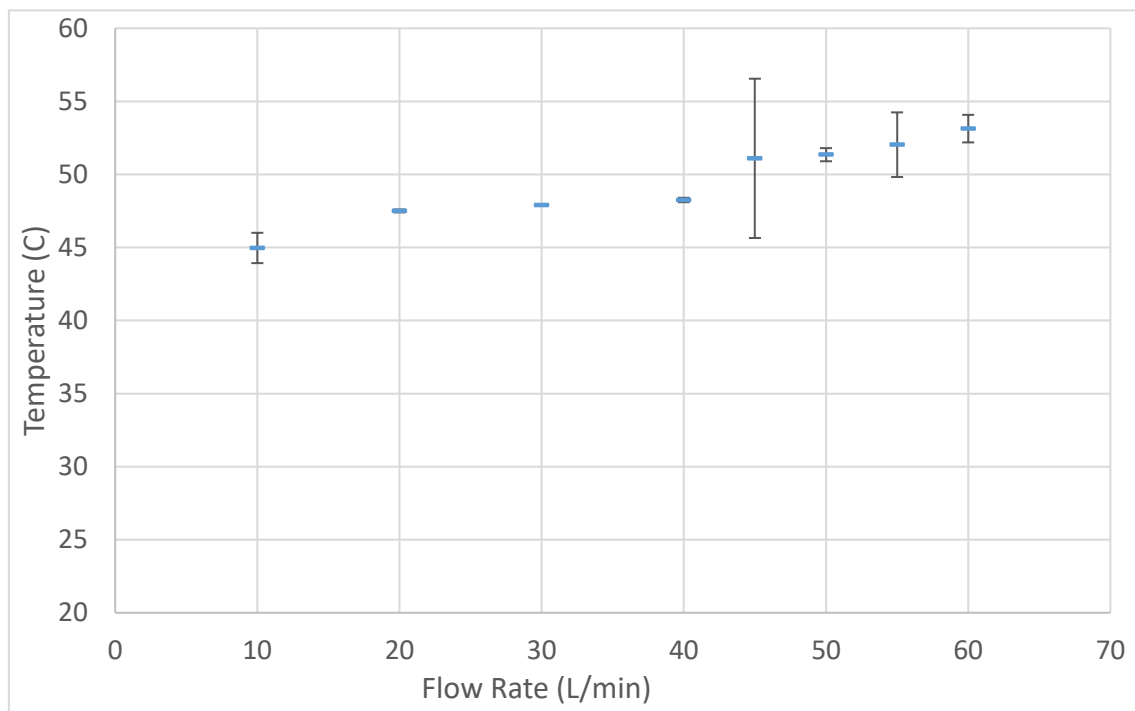


Figure 4-21: Measured surface temperature of the composite sample as a function of gas flow rate.

At lower flow rates the surface temperature remains relatively stable, with values between around 44°C and 48.5°C. The small variation and steady trend suggest that, at these flow rates, the plasma energy input remains consistent, and the flow rate has little impact on the surface temperature.

From 45 L/min onward, the surface temperature begins to rise, with a larger spread in the data (indicated by larger error bars), suggesting increased variability in heat transfer or plasma uniformity at higher flow rates.

The overall temperature did not vary beyond 15°C and as such would be appropriate for most experiments with CFRP.

To really test the heat transfer from the plasma to the sample, a continuous measurement across 8 minutes was taken, where the measured samples area was under constant processing, as shown in Figure 4-22.

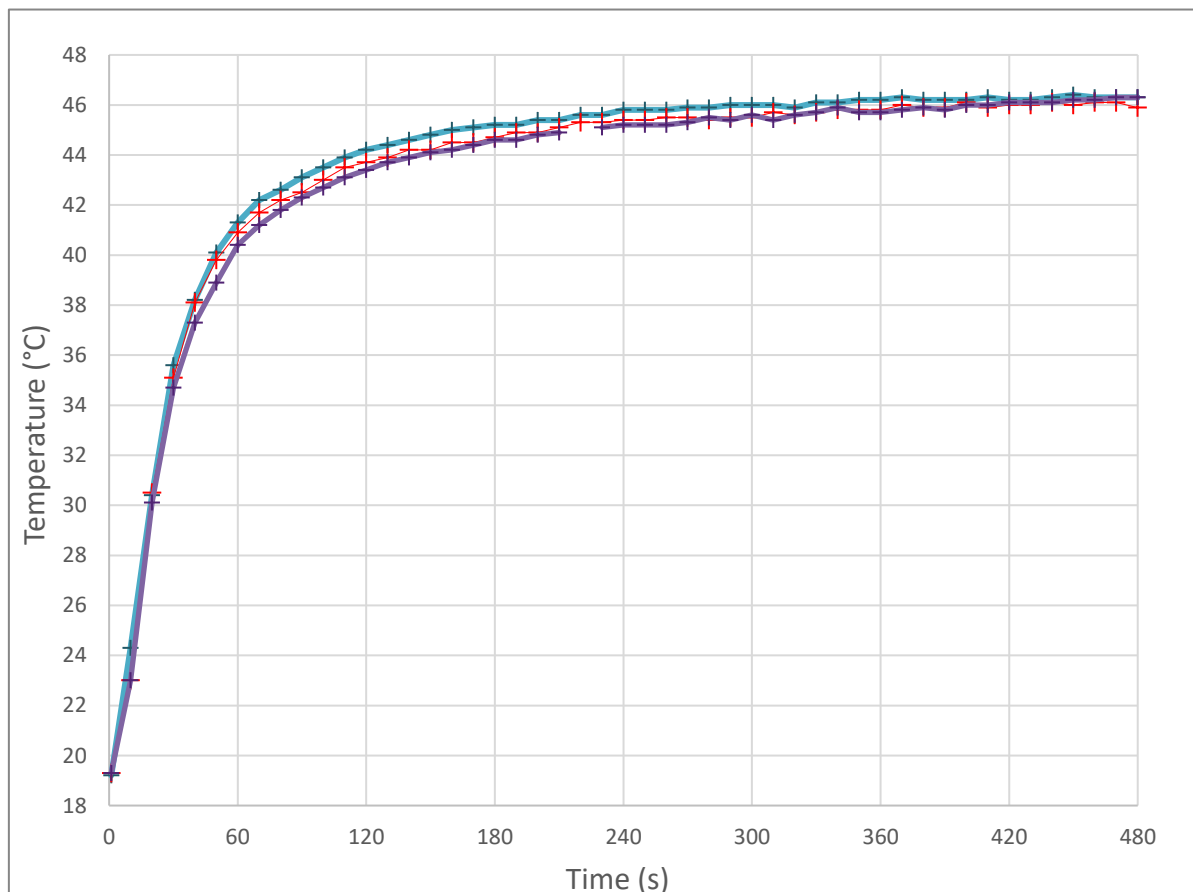


Figure 4-22 Measured surface temperature of the composite sample as a function of time under plasma beam.

During the first 60 seconds of plasma exposure, the surface temperature rises quickly from room temperature (around 20°C) to between 40°C and 42°C. This steep increase indicates significant heat transfer from the plasma to the sample during the initial phase of treatment.

After the initial rapid increase, the rate of temperature rise slows down considerably. The temperature gradually increases from around 42°C to approximately 46°C over the next 6-7 minutes, indicating that the sample is approaching a thermal equilibrium where heat input from the plasma is balanced by heat dissipation from the surface.

After 5 minutes, the surface temperature starts to stabilise around 46°C, showing minimal further increase over time. This suggests that the system has reached a steady-state thermal condition, where the plasma continues to apply heat, but the temperature no longer increases significantly as the sample dissipates heat at an equivalent rate.

The result demonstrates how heat transfer occurs between the plasma and the composite surface during prolonged exposure. In the initial phase, the plasma rapidly heats the sample, as shown by the sharp rise in temperature. However, as the sample heats up, the rate of heat dissipation from the surface to the surroundings increases, slowing the temperature rise. Eventually, the sample reaches a thermal balance where the heat added by the plasma equals the heat lost to the environment, leading to a plateau in the temperature.

The gradual increase in temperature beyond the initial 60 seconds suggests that the plasma maintains a relatively uniform energy input over time, but the surface reaches its maximum temperature threshold. The slight fluctuations observed after the plateau might be due to small variations in the plasma discharge or in the heat dissipation characteristics of the sample.

The continuous monitoring of the sample's temperature over an 8-minute period under constant plasma processing reveals how the plasma initially transfers a large amount of energy to the sample, resulting in rapid heating, followed by a stabilisation phase where the surface temperature approaches equilibrium. This

insight into heat transfer dynamics is critical for understanding how prolonged plasma treatments can affect the thermal properties and overall performance of composite materials, particularly in applications requiring controlled surface modification without excessive thermal damage.

4.4.2 DBD as a method for modifying surface energy of MTM44-1

As shown in Figure 4-22 the surface energy before plasma processing is an average of 30mN/m (± 0.88), as shown by the peach line on the graph. The surface energy of samples treated with nitrogen plasma were measured 1 hour post treatment, showing that nitrogen plasma treatment had doubled the surface energy of the composite samples. The surface energy of the samples was measured over time to show how the effect of plasma processing diminishes on processed samples over time. After just 1 week, there's a significant drop in surface energy which seems to maintain until the 12-week mark. After this time, there appears to be an even more significant drop in surface energy, resulting in samples with surface energy below 40 mN/m at 20- and 28-weeks post treatment.

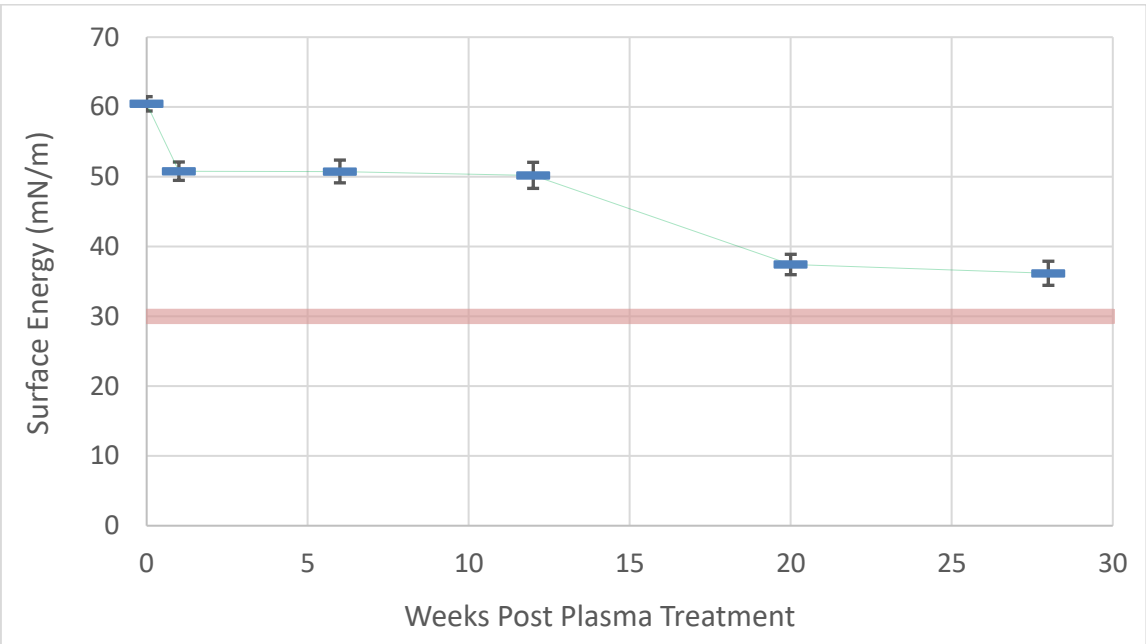


Figure 4-23 Measured Surface Energy on MTM44-1 post nitrogen plasma processing.

4.4.3 XPS analysis of DBD Nitrogen Plasma for silicon contamination removal of the surfaces of MTM44-1

The effect of DBD nitrogen plasma on CFRP samples was explored using X-ray Photoelectron Spectroscopy (XPS) to evaluate changes in surface composition. Four samples were analysed: clean and coated samples, both before and after nitrogen plasma treatment. The elemental composition of carbon (C), oxygen (O), nitrogen (N), and silicon (Si) was assessed, with the results displayed in Figure 4-24.

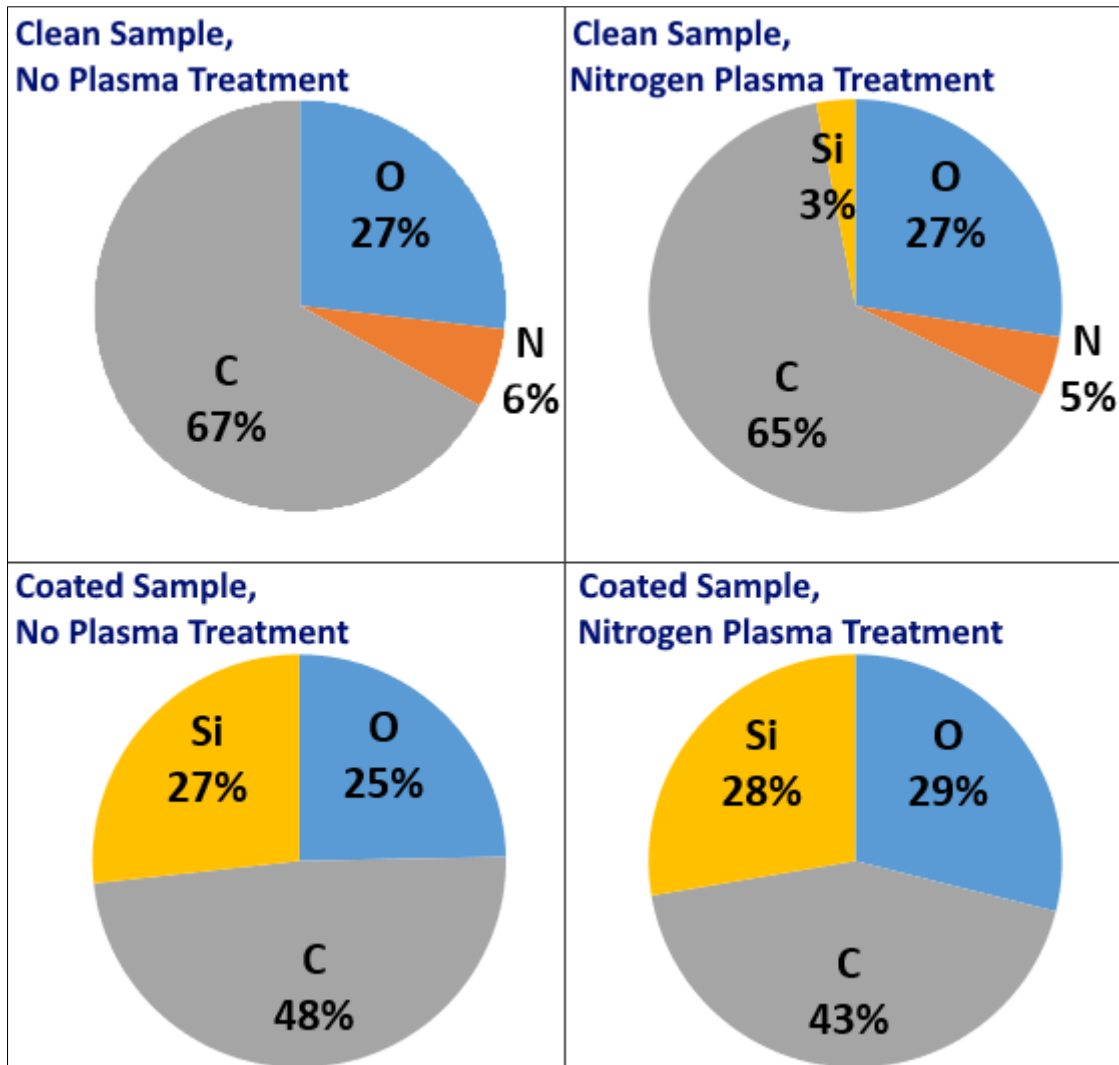


Figure 4-24 XPS analysis of MTM44-1 DBD plasma treated samples, including samples that had not been coated, and samples that were coated with CM1.

In the clean, untreated sample, the surface was predominantly composed of carbon (67%), with oxygen comprising 27%, and nitrogen present at 6%.

Following nitrogen plasma treatment of the clean sample, the surface exhibited a slight decrease in percentage carbon content to 65%, while oxygen remained unchanged at 27%. Additionally, a small amount of silicon (3%) appeared on the surface, and the nitrogen content decreased marginally to 5%.

This indicates that the plasma treatment removed some surface carbon and exposed a subsurface layer containing silicon, likely originating from the underlying composite structure or contaminants.

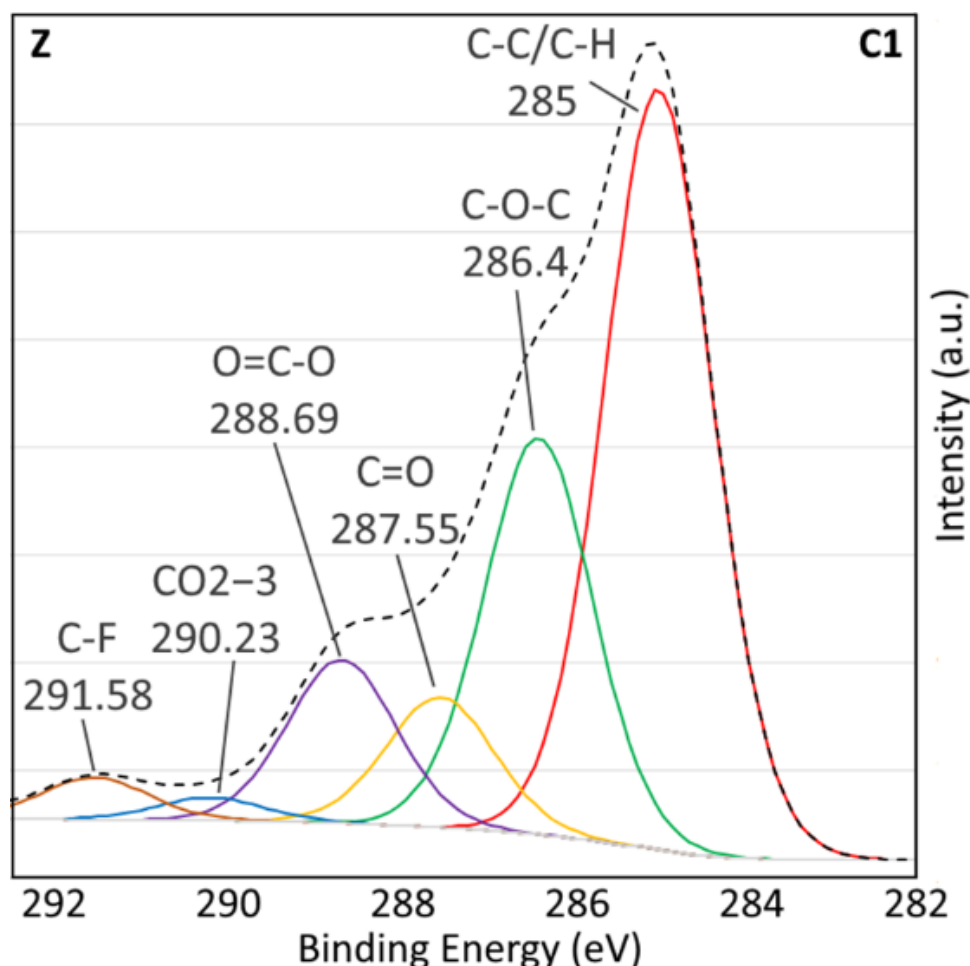


Figure 4-25: XPS spectrum (dashed curve) and its deconvoluted C_{1s} core level spectrum of clean MTM44-1 Composite. This highlights 6 different species which were analysed to determine percentage concentrations.

For the coated sample without plasma treatment, the presence of release agent significantly altered the surface composition. Silicon accounted for 27% of the surface, with oxygen at 25% and carbon reduced to 48%. The absence of nitrogen suggests that the release agent masks any nitrogen present on the surface of MTM44-1. This is consistent with previous findings from section 4.1.

After nitrogen plasma treatment of the coated sample, the surface composition shifted further. Silicon percentages again increased to 28% and oxygen to 29%, while the carbon content decreased to 43%. Nitrogen remained absent, which indicates that nitrogen plasma is unlikely to have an effect on the nitrogen content at the surface of the samples. The increase in both silicon and oxygen suggests enhanced exposure of the silicon containing elements after plasma treatment, possibly through carbon etching. It also shows that DBD plasma processing in this case was ineffective in removing silicon release agent contamination.

In-depth scans of specific binding regions related to single elements, as displayed in Figure 4-25 with the C1s binding region, were conducted to determine the peak shift and bonding types.

There are 6 key bonding environments identified for this region.

- C-C/C-H/C-Si: These bonds represent the typical carbon-carbon, carbon-hydrogen, and carbon-silicon environments found in organic and silicon-containing compounds.
- C-O/C-N: These bonds indicate the presence of carbon-oxygen and carbon-nitrogen single bonds, common in alcohols, ethers, amines, and related functional groups.
- C=O: This bond signifies carbon-oxygen double bonds, found in carbonyl groups like aldehydes, ketones, and carboxyls.
- O=C-O / O=C-R: These are complex carbon-oxygen environments, often found in esters, anhydrides, and other oxygen-rich functional groups.
- O=CO₂: Indicates carbon-oxygen environments typical of carbonates
- C-F: Indicates the presence of carbon-fluorine bonds, found in fluorinated compounds.

The C1s core-level spectra was examined to assess the relative percentages of different carbon bonding states on the surface of MTM44-1 before and after plasma treatment. Table 4-5 summarises the distribution of carbon states in both clean and coated samples, before and after nitrogen plasma treatment, providing further insight into the chemical modifications induced by the plasma treatment.

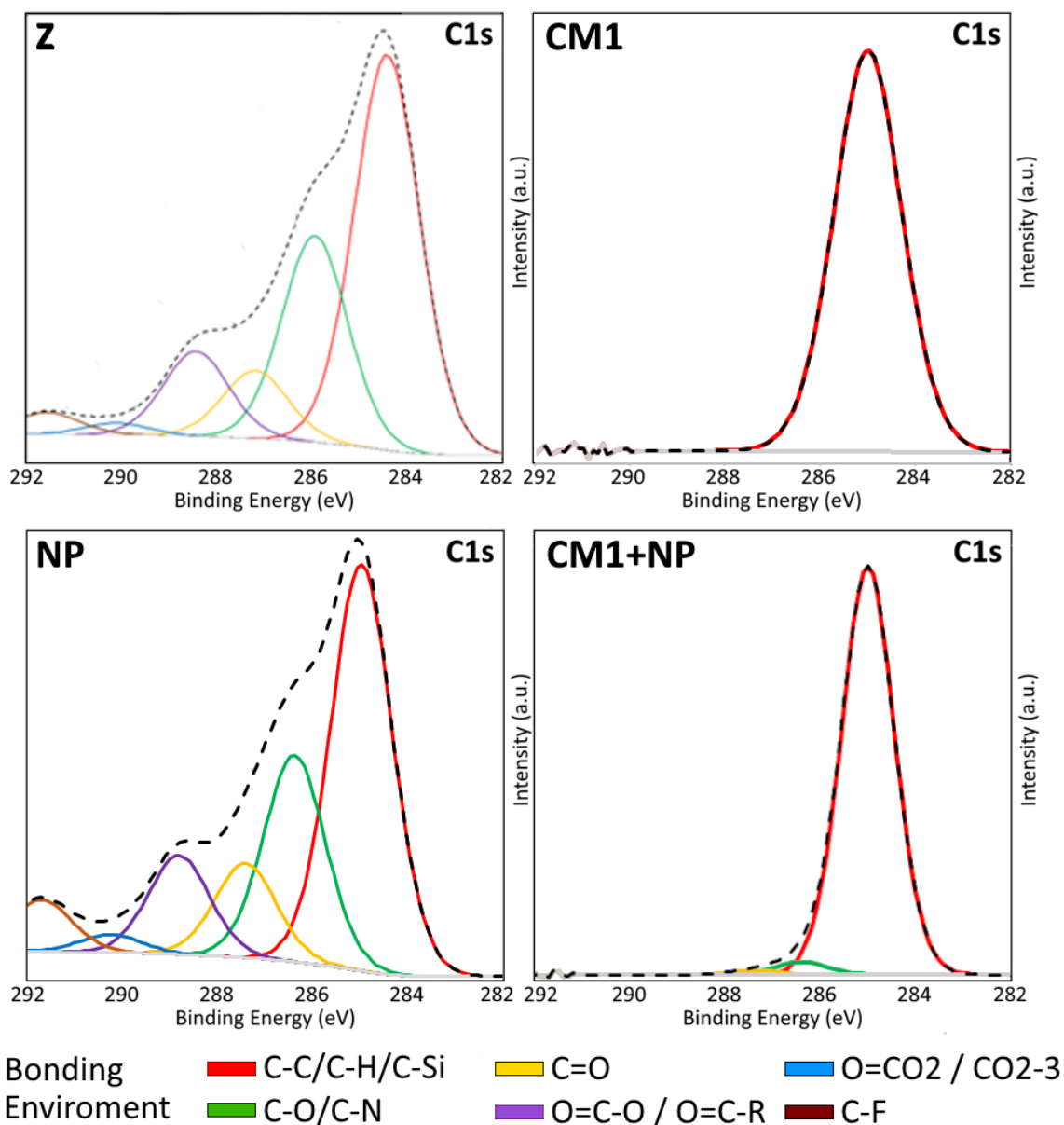


Figure 4-26 Deconvoluted Peaks of Carbon states at the surface of MTM44-1 where samples are; Untreated (z), Coated (CM1), DBD plasma treated (NP) and both coated and then nitrogen plasma treated (CM1+NP)

Table 4-5 Relative Percentages of Carbon states at the surface of MTM44-1 under various surface conditions, where samples are; Untreated (Original), Coated with CM1, DBD plasma treated (N2 Plasma) and both coated and then nitrogen plasma treated (Coated- N2 plasma)

Bonding environment	Percentage (%) of region			
	Original	Original – N2 Plasma	Coated	Coated – N2 Plasma
C-C/C-H/C-Si	50.0	46.1	100.0	95.8
C-O/C-N	26.2	23.6	-	3.1
C=O	8.6	10.8	-	1.2
O=C-O / O=C-R	10.8	11.3	-	-
O=CO ₂	1.6	2.2	-	-
C-F	2.9	6.0	-	-

For the original, untreated sample, the C1s spectrum reveals a diverse range of carbon bonding environments. The dominant carbon state is C-C/C-H/C-Si, comprising half of the surface carbon, indicating a high proportion of hydrocarbon species, typical for CFRP materials. The presence of oxygen- and nitrogen-containing functional groups is evident, with C-O/C-N bonds accounting for 26.2%, while carbonyl groups (C=O) contribute 8.6%. Additionally, 10.8% of the surface carbon is in the form of carboxyl or ester-like species (O=C-O / O=C-R), and smaller amounts of O=CO₂ (1.6%) and C-F (2.9%) are detected.

Following nitrogen plasma treatment of the original sample, there is a reduction in the C-C/C-H/C-Si component to 46.1%. The C-O/C-N and C=O bonds show slight increases to 23.6% and 10.8%, respectively, suggesting an oxidation or effect induced by the plasma. The proportion of O=C-O / O=C-R remains relatively stable, increasing only slightly to 11.3%, while the presence of O=CO₂

bonds also increases to 2.2%. Notably, the C-F content doubles to 6.00%, indicating further support that the plasma treatment may be etching a carbon rich surface layer of the epoxy, revealing existing elements below.

In contrast, the coated sample without plasma treatment exhibits a completely different carbon bonding environment, with the C-C/C-H/C-Si dominating the surface (100%), indicating that the silicon-containing release agent completely masks any oxygen- or nitrogen-containing functional groups within MTM44-1. No C-O/C-N, C=O, O=C-O / O=C-R, or O=CO₂ bonding environments are detected, consistent with a surface fully coated by the release agent.

After nitrogen plasma treatment of the coated sample, the C-C/C-H/C-Si component remains high at 95.8%, although trace amounts of oxygen-containing groups can be observed. The C-O/C-N bonding state accounts for 3.1%, and a minor proportion of C=O (1.2%) is detected, indicating that the plasma treatment has introduced or exposed oxygenated carbon species on the previously inert surface. No O=C-O / O=C-R or O=CO₂ species are observed after treatment.

In summary, the C1s analysis indicates that nitrogen plasma treatment leads to the removal of hydrocarbons and the introduction of oxygen- containing functional groups on the surface of the original, untreated CFRP sample. The coated sample, which initially showed no oxygenated carbon species due to the silicon-containing release agent, begins to exhibit minor amounts of oxygen functional groups after plasma treatment, suggesting that the plasma modifies portions of the coating.

The N1s core-level spectra were also examined, displayed in Figure 4-27, to assess the nitrogen bonding environments on the surface of the samples, both before and after nitrogen plasma treatment, as summarised in Table 4.6.

For the original untreated sample, the dominant nitrogen species present on the surface is CNH₂, accounting for 94.8% of the nitrogen detected. This bonding environment likely corresponds to amine groups or nitrogen incorporated into carbon-nitrogen chains, which is common in CFRP materials such as MTM44-1 due to the presence of curing agents or additives in the resin matrix. A smaller

proportion of NH^+ species, indicative of protonated amines, were detected, making up 5.2% of the nitrogen content.

After nitrogen plasma treatment, there is only a slight shift in the nitrogen bonding environments. The proportion of CNH_2 remains high at 93.2%, while the proportion of NH^+ species increases to 6.8%. The presence of NH^+ is likely to be a direct result of nitrogen plasma treatment. Nitrogen radicals and ions can interact with the surface amine groups, leading to bond cleavage or changes in the bonding structure. When CNH_2 groups on the surface are exposed to the plasma, some of the nitrogen radicals can abstract hydrogen atoms from the CNH_2 groups, leading to the formation of positively charged NH^+ species. This process is often accompanied by surface oxidation, as plasma treatments can introduce functional groups like hydroxyl or carboxyl, providing additional protons to convert CNH_2 into NH^+ (316).

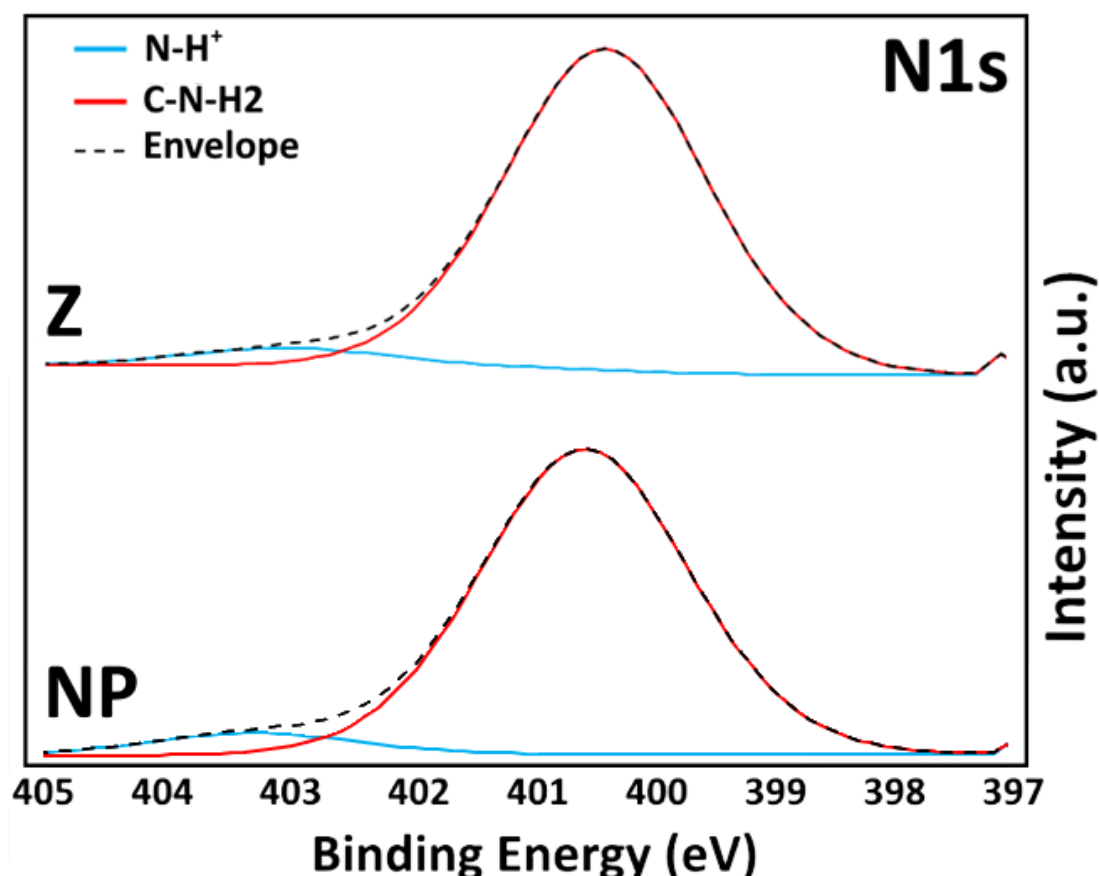


Figure 4-27 Sample N1s deconvoluted peak at the surface of MTM44-1 where samples are; Untreated (z) and DBD plasma treated (NP)

Table 4-6 Relative Percentages of N1s Nitrogen states at the surface of MTM44-1 samples, before and after both coating and/or DBD nitrogen plasma treatment.

Bonding environment	Percentage (%) of region	
	Original	Original & Nitrogen Plasma
CNH ₂	94.8	93.2
NH ⁺	5.2	6.8

Nitrogen plasma treatment can also modify the surface charge environment. The introduction of charged species (e.g., NH⁺) might be due to an increase in the local electric field or charge build-up on the surface during the plasma process. This modification can facilitate the protonation of amine groups, converting CNH₂ into NH⁺ (317).

In the contaminated sample, no nitrogen species were detected on the surface, indicating that the contamination, likely from the release agent, has completely masked the underlying nitrogen species. This result is consistent with the C1s analysis, where the coated sample also showed no nitrogen-related bonding environments prior to plasma treatment.

Following nitrogen plasma treatment of the contaminated sample, nitrogen species remain undetected, indicating that the plasma treatment was either insufficient to remove the contamination fully or that the nitrogen species are still not exposed on the surface. This aligns with the C1s results, where only minor oxygen functional groups were observed after plasma treatment of the coated sample, suggesting that the release agent still partially covers the surface.

Overall, the N1s analysis shows that nitrogen plasma treatment has a minor impact on the nitrogen bonding environments in the original sample, with a slight increase in NH⁺ species. However, in the contaminated samples, nitrogen species remain undetected both before and after plasma treatment, suggesting that the surface contamination prevents exposure of nitrogen-containing species.

Table 4-7 Relative Percentages of O1s oxygen states at the surface of MTM44-1 under various surface conditions, where samples are; Untreated (Original), Coated with CM1, DBD plasma treated (N2 Plasma) and both coated and then nitrogen plasma treated (Coated- N2 plasma)

Bonding environment	Percentage (%) of region			
	No Plasma	Nitrogen Plasma Treated Sample	Contaminated Sample	Contaminated & Nitrogen Plasma
C=O/ Si-O	35.7	48.5	100.0	91.5
C-O/ SiO ₂	45.6	44.2	-	8.5
H-O-H	18.7	7.3	-	-

These findings complement the C1s and XPS elemental analyses, further highlighting the challenges of removing surface contamination and revealing nitrogen species in coated samples.

The O1s core-level spectra were analysed to examine the relative percentages of different oxygen bonding states at the surface, as displayed in Table 4-7.

For the no plasma treatment sample, the dominant oxygen bonding environments are C-O (45.6%) and C=O (35.7%), indicating a significant presence of carbon-oxygen species at the surface. Additionally, H-O-H (hydroxyl groups or water) is present at 18.7%, reflecting either some surface moisture or hydroxyl functional groups.

After nitrogen plasma treatment, there is a notable shift in the distribution of oxygen bonding environments. The proportion of C=O increases significantly to 48.5%, suggesting an enhancement of carbonyl bonds, likely due to surface oxidation. The C-O content remains relatively stable at 44.2%, while the H-O-H component decreases to 7.3%, indicating a reduction in surface-bound water or hydroxyl groups as a result of plasma treatment. This reduction in moisture could be due to the slight heating effect from the plasma, causing water at the surface to evaporate.

Table 4-8 Relative Percentages of different elements within the Si2p binding region, at the surface of MTM44-1 under various surface conditions, where samples are; Untreated (Original), Coated with CM1, DBD plasma treated (N2 Plasma) and both coated and then nitrogen plasma treated (Coated- N2 plasma)

Bonding environment	Percentage (%) of region			
	No Plasma	Nitrogen Plasma Treated Sample	Contaminated Sample	Contaminated & Nitrogen Plasma
Si-O (Silicone)	-	47.2	100.0	91.1
SiO ₂	-	52.8	-	8.9

In the contaminated sample, the surface is completely dominated by Si-O bonds, accounting for 100% of the oxygen bonding environment. The absence of C-O/SiO₂ and H-O-H bonds supports that the contamination has fully masked the surface. Following nitrogen plasma treatment of the contaminated sample, there is a slight decrease in the Si-O proportion to 91.5%, while a small amount of C-O/SiO₂ bonding reappears at 8.5%.

The Si 2p region was analysed to assess the relative percentages of silicon bonding states, as displayed in Figure 4-28. Table 4-8 summarises the results, identifying the presence of silicon in different oxidation states (Silicone and SiO₂).

For the no plasma treatment sample, no silicon bonding states are detected, indicating that either the silicon-containing regions are not exposed at the surface or are completely masked by carbon and oxygen species, as suggested by previous results.

After nitrogen plasma treatment, Si 2p peak shows a significant regional percentage of silicon, with the region accounting for 47.2%, making up nearly half of the detected silicon. The other 52.8 of the region falls under the, SiO₂ bonding environment.

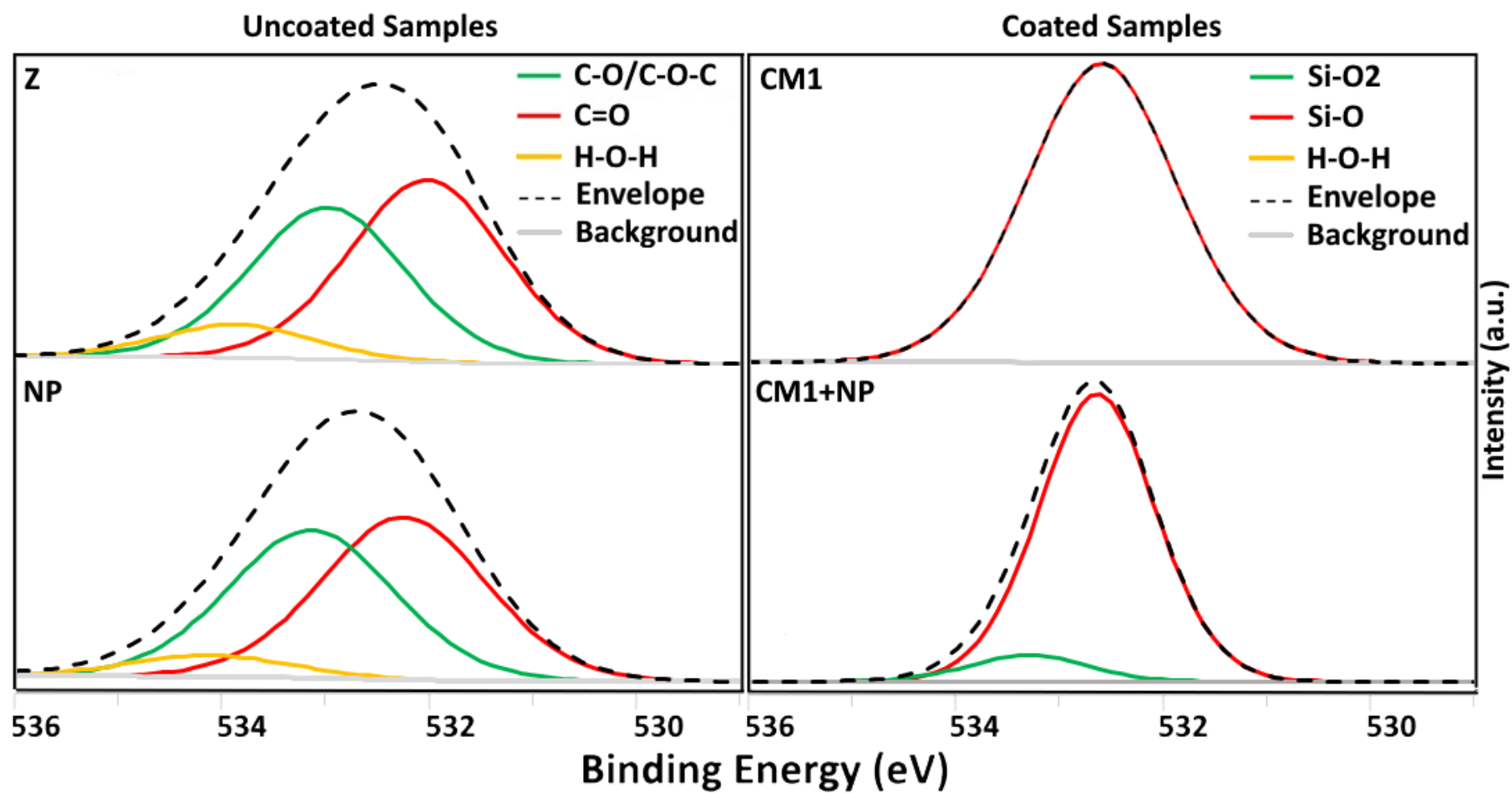


Figure 4-28 Oxygen O1s region for the original sample (top left) and after it has then undergone nitrogen plasma treatment (bottom left), contaminated sample (top right) and a contaminated sample that has undergone nitrogen plasma treatment (bottom right).

In the contaminated sample, the silicon surface is dominated by Si-O bonds, leaving no trace of SiO₂ bonds. This suggests that the silicone-based release agent entirely coats the surface. The dominance of Si-O bonds is consistent with the O1s results, which showed 100% of the oxygen bonding to be in the Si-O state in the contaminated sample.

Following nitrogen plasma treatment of the contaminated sample, the proportions of Si-O bonds decrease slightly to 91.1%, SiO₂ accounts for 8.9%. This further supports DBD plasma having an oxygenising effect on the surface.

It's also likely to see a higher percentage of SiO₂ on the surface, as there is less silicon on the surface overall, meaning there was less silicon on the surface to begin with, to interact with oxygen.

It is also likely that there's little to no C=O in the sample because 8.86% of sample is SiO₂ in the Si2p bonding region, which is a similar percentage value of either SiO₂ or C-O at the O1s bonding region (8.52%). This is supported by the results of the C1s binding region which shows a predominant C-C/C-H/C-Si binding region.

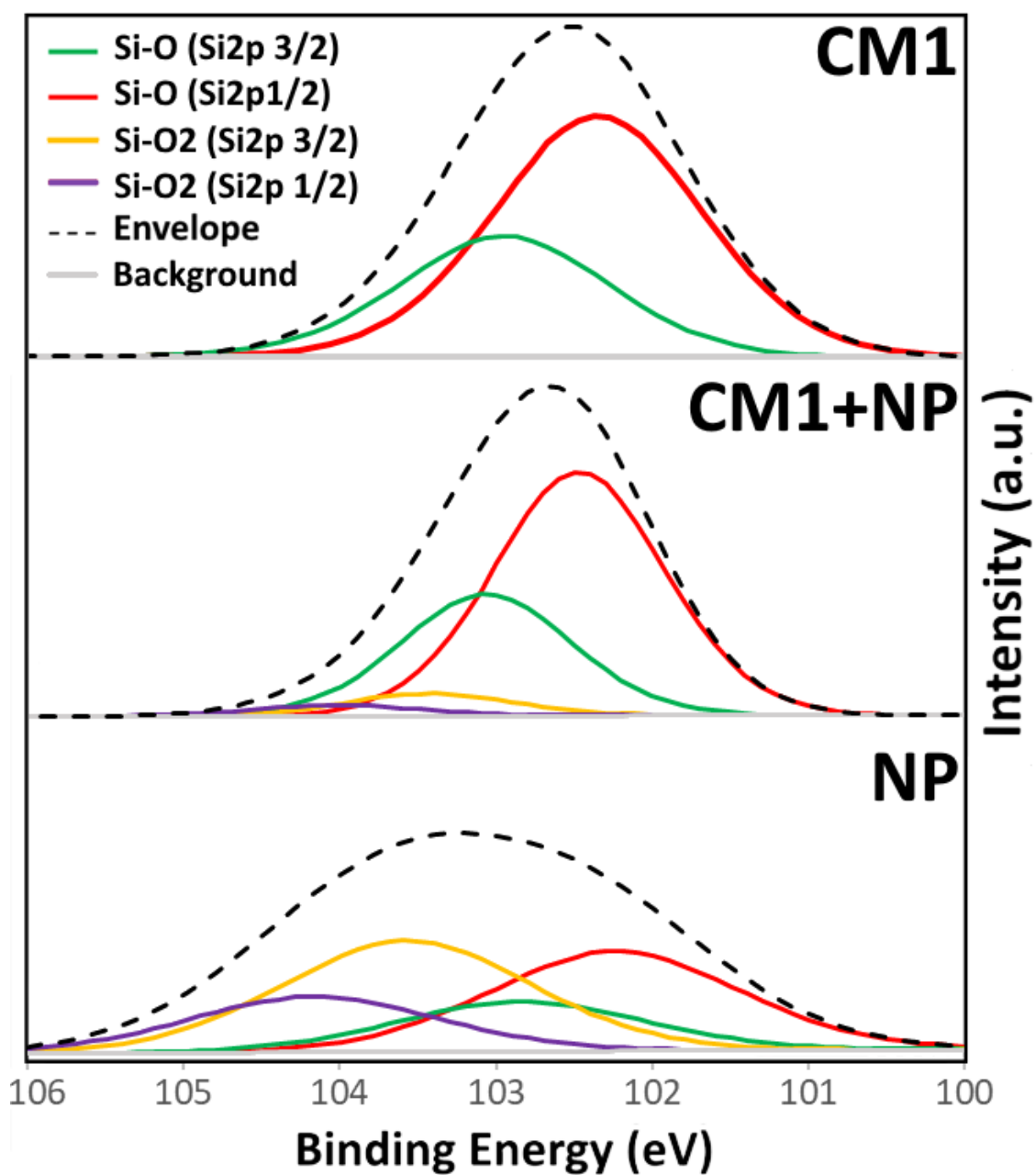


Figure 4-29 Sample Si 2p deconvoluted peak at the surface of MTM44-1 where samples are; Coated (CM1), DBD plasma treated (NP) and both coated and then nitrogen plasma treated (CM1+NP)

4.4.3.1 Contamination Focused Study

A second study of XPS was conducted, this time at the Leeds test facility, where there was a focus on contamination removal. Samples were spin coated by CM2 and then plasma treated with 10 or 20 passes. Figure 4-30 displays the relative percentages of carbon, oxygen and silicon at the surface of these samples, alongside samples that were coated with CM2 but did not undergo plasma treatment.

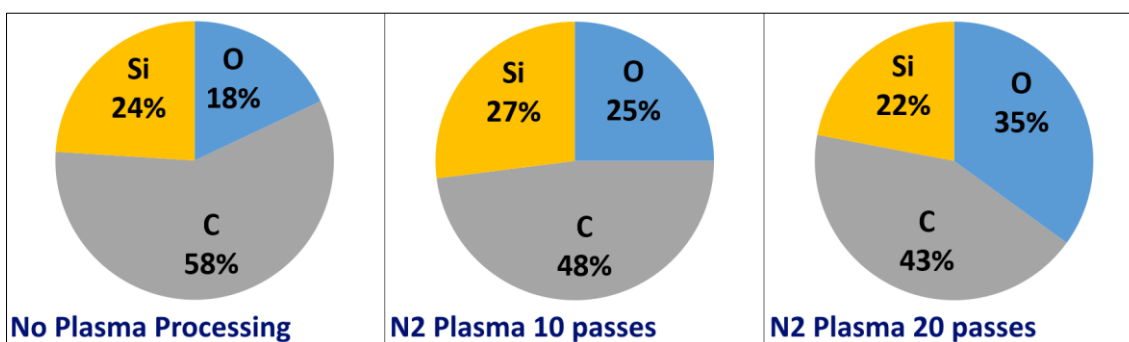


Figure 4-30 Spin Coated Samples which were then processed with no, 10 and 20 plasma passes respectively.

In the untreated (no plasma processed) sample, the surface is dominated by carbon (58%), with significant amounts of silicon (24%) and oxygen (18%). This is consistent with the presence of the silicone-based release agent coating the surface, where the carbon content comes from the organic nature of the silicone compound and the release agent, and the silicon and oxygen are likely due to the Si-O bonding in the silicone.

After 10 plasma passes, there is a noticeable reduction in the carbon content to 48%, with a corresponding increase in both silicon (27%) and oxygen (25%). The reduction in carbon suggests that the plasma treatment has begun selectively etching carbon from the surface. The increase in oxygen indicates the formation of more oxygenated species, such as SiO_2 , as observed in previous XPS results.

After 20 plasma passes, the oxygen content increases significantly to 35%, while the carbon content further decreases to 43%. The silicon percentage decreases slightly to 22%. The large increase in oxygen indicates significant surface oxidation, a trend also observed in the previous MTM44-1 samples, which may

indicate increasing the presence of SiO_2 . The continued reduction in carbon reflects the progressive removal or oxidation of the silicone-based release agent.

Across the three conditions, the carbon content decreases progressively with increasing plasma passes. This reduction in carbon is indicative of the breakdown and removal of the silicone-based release agent, which is rich in carbon, although not the silicon atoms itself.

The silicon content shows a slight increase after 10 plasma passes and further decreases after 20 passes. Initially, the plasma treatment exposes more of the silicon content from the silicone-based coating, but with extended plasma exposure, silicon becomes slightly less prominent as oxygen-rich species like SiO_2 become dominant, replacing some of the Si-O bonds, with a possibility for release agent etching taking effect after several passes.

The oxygen content increases steadily as the number of plasma passes increases. This rise in oxygen indicates surface oxidation, likely due to the formation of oxygen-rich species such as C=O, C-O, and SiO_2 . The significant increase in oxygen after 20 plasma passes reflects the strong oxidising effect of the nitrogen plasma, leading to a more reactive, oxygenated surface.

4.4.3.2 Summary

In the sample without plasma treatment, the absence of detected silicon states suggests that the surface is dominated by carbon and oxygen, preventing any exposure of silicon-containing regions. This is corroborated by the C1s results, which indicated a high proportion of C-C/C-H/C-Si bonds and oxygen states like C-O/SiO₂. Nitrogen plasma treatment, however, exposes and oxidises silicon at the surface, as evidenced by the appearance of both silicone and SiO₂ states. The increase in oxygenated species (from the O1s analysis) is consistent with the formation of SiO₂.

In the contaminated sample, the results are dominated by silicon reflecting the silicone-based release agent coating the surface. This masking effect is seen across all bonding environments, including C1s and O1s, where only silicon-related bonding environments are present. After nitrogen plasma treatment of the contaminated sample, there is partial removal of the surface contamination, leading to the reappearance of SiO₂ bonding environments and a slight decrease in Si-O (silicone) bonds. This trend is consistent with the O1s results, where C-O/SiO₂ bonding reappears after plasma treatment of the contaminated sample.

The XPS analysis of the MTM44-1 samples, both with and without contamination, demonstrates that nitrogen plasma treatment significantly alters the surface chemistry. In the clean samples, plasma treatment primarily oxidises the surface, increasing the proportions of carbonyl, hydroxyl, and silicon oxide bonds.

Overall, the XPS results suggest that DBD nitrogen plasma is a powerful tool for modifying the surface chemistry of MTM44-1 samples by increasing surface oxidation and altering functional groups. However, the effectiveness of plasma treatment is reduced in the presence of surface contamination, which may require Radio Frequency Plasma Treatment for removal of Silicon Contamination and improved surface Adhesion of Composites

4.5 The effect of RF-ICP on the surfaces of MTM44-1

For the final section of this study, the use of thermal radio frequency plasma is explored.

As the contaminants of interest in this study is mainly silicon based, the use of reactive atom plasma (RAP) was considered to be a variable avenue to pursue to etch contaminated samples chemically.

The temperature for this material removal method needs to be carefully considered as high heat can result in the burning/melting of polymer composites.

As a result, high processing speeds and an adapted raster pattern are required to reduce the heat effects on the substrate.

To ensure adequate silicon removal through this process, XPS was explored. This technique was used to observe the effect the use of both argon RF plasma and RAP has on the surface chemistry of both coated and uncoated samples.

Finally with consideration to the adhesive properties of the composites after RF plasma processing, the surface energies of the composites were explored, and lap shear testing was conducted.

4.5.1 X-Ray photoelectric spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy (XPS) was conducted on both drop-coated and spin-coated samples to analyse the chemical composition and states of the elements present on the surface of the composites.

4.5.1.1 Conventional Raster Patterned samples

Drop Coated samples were plasma processed with RF plasma processing every 6mm. XPS was used to understand the relative percentages of elements at the surface of the composite.

Figure 4-31 presents the XPS analysis of MTM44-1 samples, both with and without a silicon contamination coating, following different plasma treatments.

The untreated original samples primarily consist of carbon (C) at 66%, oxygen (O) at 27%, a minor amount of fluorine (F) at 6% and a trace of sulphur (S) at 1%. These levels of Carbon and Oxygen are due to the composition of the MTM44-1 surface epoxy and potentially surface oxidation, while the small percentage of sulphur and fluorine are likely to have originated from the manufacturing process or environmental exposure.

After Argon plasma treatment (PT1), the carbon content decreases to 61%, while oxygen increases to 34%, indicating that the plasma treatment introduces more oxygen-containing functional groups to the surface, enhancing the surface reactivity. Silicon (Si) is detectable at 2%, which is likely present due to release agent usage in its manufacturing process, which cannot be fully removed in the cleaning step- hence the need for plasma cleaning. Fluorine decreases to 2%, which suggests some surface cleaning or modification of the fluorine containing compounds during the plasma treatment.

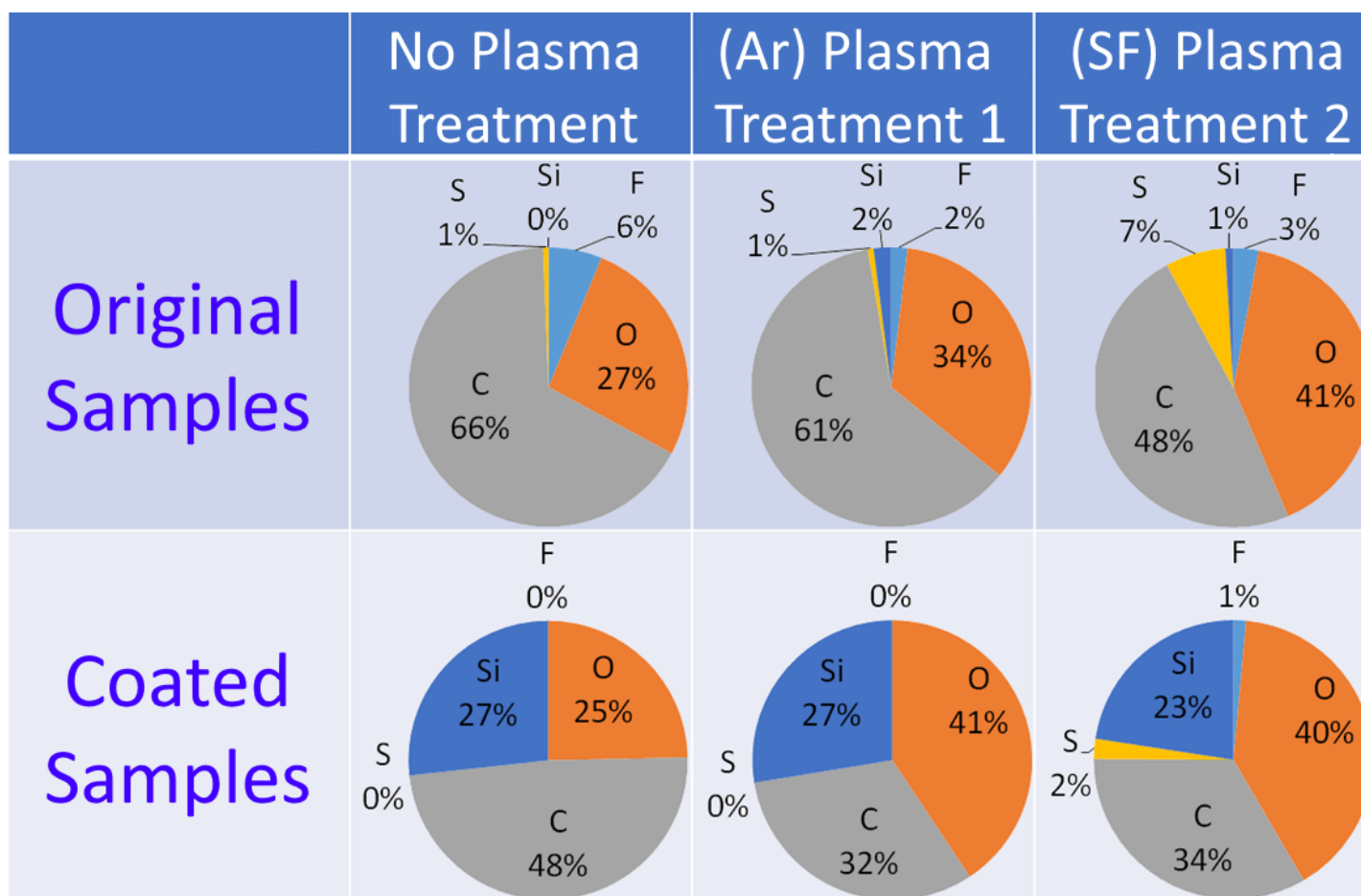


Figure 4-31 XPS analysis of MTM44-1 samples with and without silicone contamination coating. Samples were subjected to i) No plasma treatment, ii) Argon Plasma Treatment iii) Fluorinated Plasma treatment Plasma treatment was conducted with a raster of 6mm inbetween passes

There's a possibility that the conventional sample cleaning steps are only capable of cleaning surface level of contamination, with silicon contamination being seeped into the sub-surface through diffusion. Argon plasma treatment could then have an etching effect on the surface level of carbon, revealing a more contaminated layer.

With SF₆ reactive atmospheric plasma (RAP) treatment (PT2), the carbon content further decreases to 48%, while oxygen content increases to 41%, suggesting even more significant surface oxidation compared to Argon plasma treatment. Silicon content decreases to 1%, with sulphur at 7% and fluorine at 3%, indicating that this treatment strongly alters the surface composition, likely through the introduction of oxygenated groups and the incorporation of Sulphur-based segments.

The coated samples without plasma treatment have a significantly different composition from the original samples. The silicon content is 27%, while carbon decreases to 48% and oxygen to 25%. The silicon contamination is evident from the high Si percentage. The absence of sulphur and fluorine suggests that these elements are masked by the silicone coating.

PT1 of the coated samples shows this had little effect on the prevalence of silicon which remained at 27%. Significant oxidation of the surface has occurred with the oxygen increasing from 25% to 41%. This suggests there may have been some carbon etching with carbon content decreasing to 32%. The RAP treatment of coated samples also shows signs of oxidation and carbon etching, with carbon reduced to 34% and oxygen increased to 40%. There is an indication that PT2 may be effective in etching silicone as Si content at the surface was reduced to 23% from its original value of 27%.

The introduction of sulphur at 2% and fluorine at 1% suggests two possibilities; 1) that the RAP treatment partially etch the coating to expose the underlying original materials containing these elements or

2) the sulphur and fluorine components in the plasma may be left on the surface after processing. In regards for sulphur, it is more likely due to the presence of

sulphur in the plasma, rather than the presence of sulphur in the underlying composite, as this increase in sulphur on the surface of original surfaces was also observed. This is also supported by the high remaining percentage of silicon on the surface, suggesting the coating was predominant on the surface.

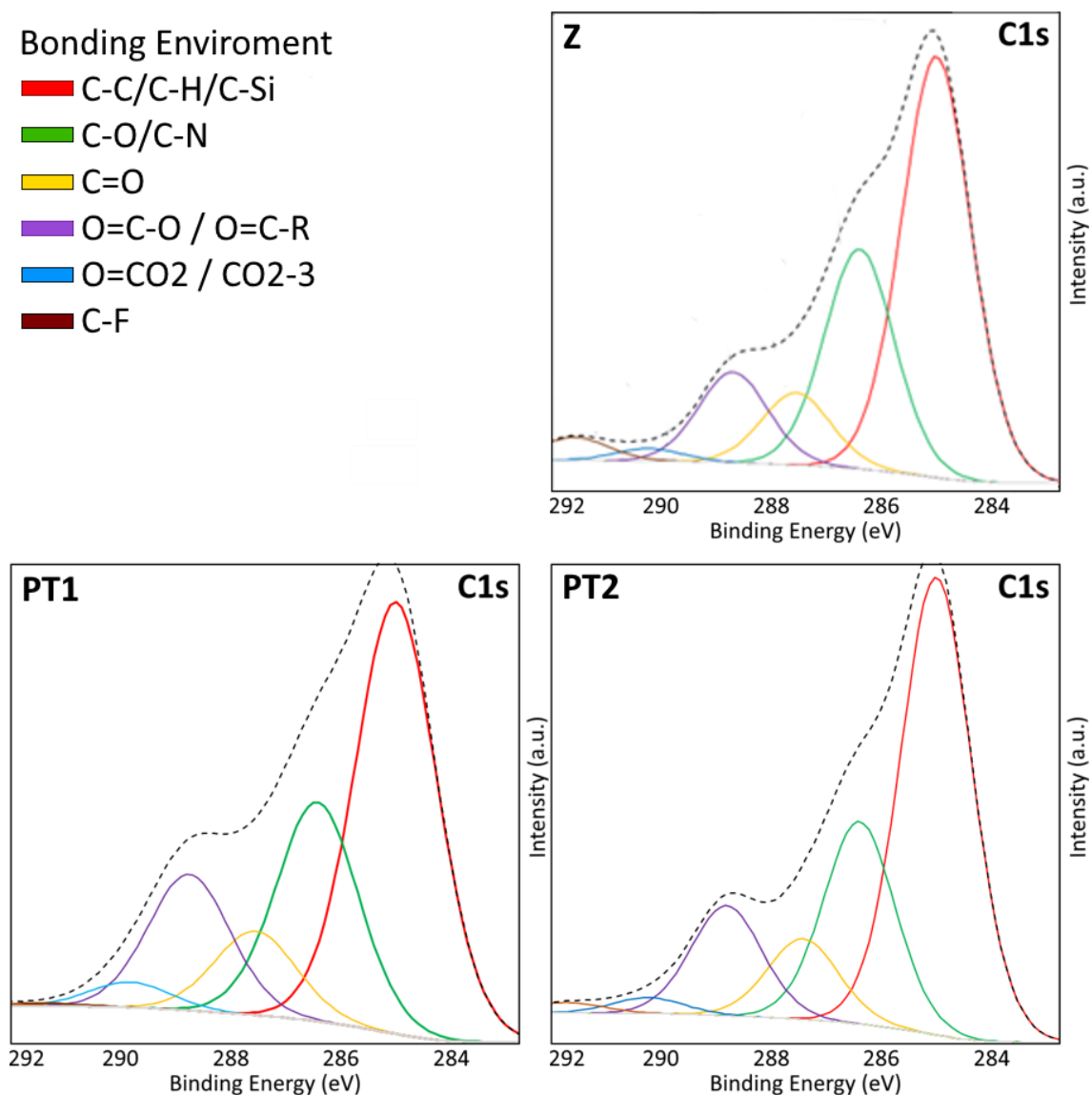


Figure 4-32 displaying deconvoluted XPS C 1s core level spectrums of clean MTM44-1 Composites. This includes samples that were uncontaminated (Z) and those that underwent further plasma treatment either with just argon treatment (PT1) or fluorinated argon treatment (PT2).

Although the removal of silicon in this study was small, the observable reduction shows promise and suggests a more intensive plasma treatment could reduce the silicon content considerably.

The core-level spectra of essential elements in both clean and contaminated XPS samples were analysed, as illustrated in the previous section, in Figure 4-25. This analysis involved examining the characteristic energy levels of specific elements, providing insights into the chemical states and composition of the samples. By comparing the spectra from the clean and contaminated samples, differences in peak positions, intensities, and shapes reveal information about surface contamination, elemental composition, and possible chemical shifts.

The C1s peak spectra was deconvoluted, as displayed in Figure 4-32, to understand the carbon states at the surface of uncontaminated samples. This data has been presented in Table 4-9.

Table 4-9 Relative Percentages of Carbon states at the surface of uncontaminated samples

Bonding environment	Percentage (%) of region		
	No Plasma	Argon Plasma (PT1)	Fluorinated Plasma (PT2)
C-C	50.0	47.8	51.7
C-O/C-N	26.2	24.3	23.0
C=O	8.6	9.4	9.3
O=C-O / O=C-R	10.8	15.2	12.6
O=CO ₂	1.6	2.9	2.0
C-F	2.9	0.4	1.4

Looking at the effect of argon plasma treatment when compared to untreated samples, Argon plasma treatment shows a slight decrease in C-C bonds (from 50% to 47.8%) and C-O/C-N bonds (from 26% to 24.3%), with an increase in O=C-O/O=C-R (10.8% to 15.2%) and O=CO₂ bonds (1.6% to 2.9%), indicating oxidation or etching effects. There is also a significant reduction in fluorinated components (2.9% to 0.4%).

Fluorinated plasma treatment results in a slight increase in C-C/C-H/C-Si bonds, possibly due to surface reorganisation or the introduction of new C-C bonds, increasing C-C bonds while reducing oxygen groups as well as possible conversion of simple C-O bonds to C=O bonds. Interestingly there's a slight decrease in C-F bonds, despite the extra SF₆ within the plasma.

Table 4-10 Relative Percentages of N1s Nitrogen states at the surface of uncontaminated samples.

Bonding environment	Percentage (%) of region		
	No Plasma	Argon Plasma (PT1)	Fluorinated Plasma (PT2)
CNH ₂	94.8	93.3	46.3
NO/NH ⁺	5.2	6.8	53.7

As Nitrogen is heavily present in the atmosphere, there may be nitrogen interaction with the sample surface, when undergoing treatment with atmospheric pressure plasma. A review of relevant literature identified three states where this region could fall into; N⁺H⁺ (318) N⁻O (319) and NH₂. (320) Further information was also sourced from Beamson and Briggs (321).

N1s regions were also explored, with the data displayed in Table 4-10 and Figure 4-33. Argon plasma slightly reduces CNH₂ and this indicates that argon plasma causes oxidation, as supported by literature (35,322)., converting NH⁺ to NO.

Fluorinated plasma by contrast drastically reduces CNH₂ and significantly increases NO, indicating strong fluorination and oxidation effects. This is supported by similar findings from literature (35,322).

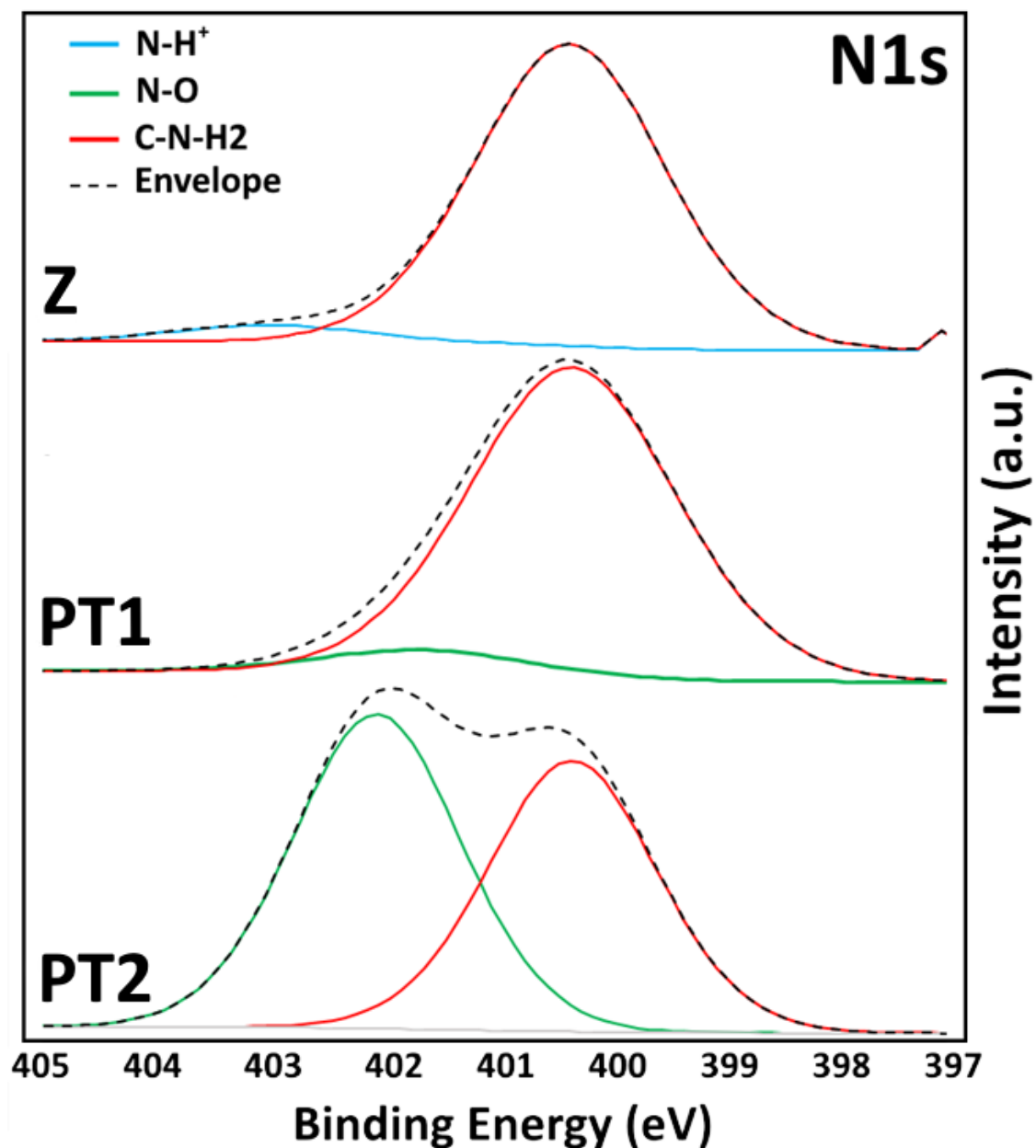


Figure 4-33 displaying deconvoluted XPS N 1s core level spectra of clean MTM44-1 Composites. This includes samples that were uncontaminated (Z) and those that underwent further plasma treatment either with just argon treatment (PT1) or fluorinated argon treatment (PT2).

Table 4-11 Relative Percentages of O1s Oxygen states at the surface of uncontaminated samples.

Bonding environment	Percentage (%) of region		
	No Plasma	Argon Plasma (PT1)	Fluorinated Plasma (PT2)
C=O/C=O-N	35.7	34.3	57.9
C-O/C-O-C	45.6	47.0	29.8
H-O-H	18.7	18.7	12.3

Table 4-11 and Figure 4-34 display data from the O1s Oxygen states at the surface of uncontaminated samples. This shows that argon plasma treatment has a slight effect in reducing C=O/C=O-N bonds and increases C-O/C-O-C bonds, indicating partial oxidation with an increase in oxygen-carbon single bonds.

Fluorinated plasma significantly increases C=O/C=O-N bonds, reduces C-O/C-O-C, and decreases H-O-H, indicating strong oxidation and fluorination effects. A second fluorinated plasma exposure intensifies the increase in C=O/C=O-N bonds and further reduces C-O/C-O-C and H-O-H, reflecting intense surface modification and oxidation.

Plasma treatments dynamically modify oxygen states on surfaces. Argon plasma causes initial oxidation and reconfiguration, while fluorinated plasma significantly increases carbonyl groups, indicating intense oxidation and fluorination.

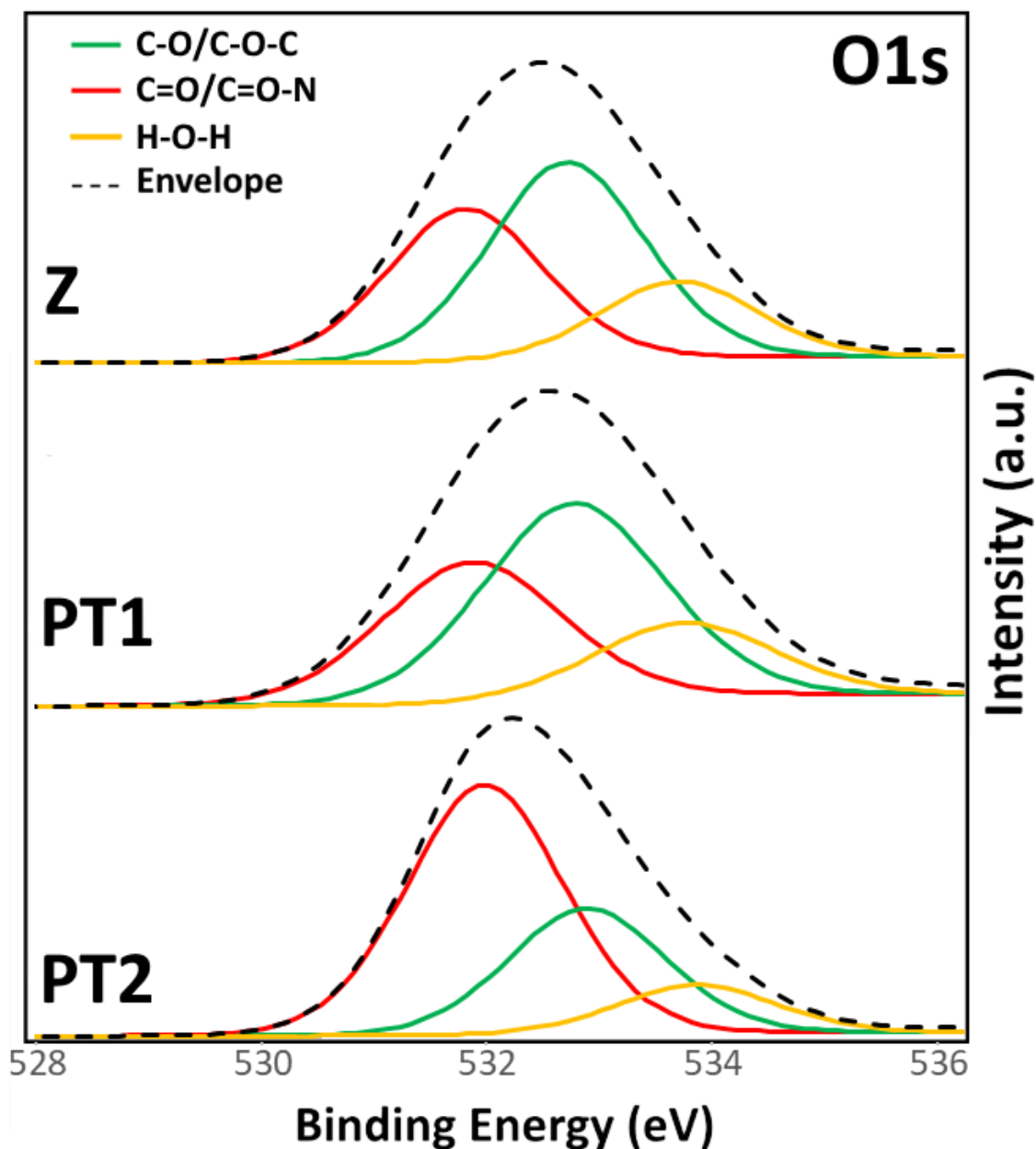


Figure 4-34 displaying deconvoluted XPS O 1s core level spectrums of clean MTM44-1 Composites. This includes samples that were uncontaminated (a) and those that underwent further plasma treatment either with just argon treatment (PT1) or fluorinated argon treatment (PT2).

Summary and Discussion

This section focused on the effects of argon and fluorinated plasma treatments on the surface chemistry of the original and contaminated MTM44-1 samples. XPS was employed to analyse the surface chemistry of samples subjected to different plasma treatments. The relative percentages of various bonding environments were measured to understand the changes induced by argon and fluorinated plasma.

In the original samples, the surface is dominated by carbon and oxygen, with minor contributions from other elements. The introduction of Argon and RAP plasma treatments reduces the carbon content while increasing oxygen, indicating surface oxidation which is a key factor in enhancing surface reactivity and potential bonding strength.

For silicone-contaminated samples, the high initial silicon content is dramatically altered by plasma treatments. Both Argon and RAP plasma treatments are effective in increasing percentage oxygen and decreasing carbon, suggesting that these treatments clean or modify the surface to remove or redistribute the carbon and oxygen contents. The RAP plasma treatment appears to be particularly effective, as evidenced by the significant reduction in carbon percentage.

These changes in surface composition are crucial for improving adhesion properties, as increased oxygen content and the removal of contaminants like silicon and fluorine enhance the chemical reactivity and bonding potential of the surface. This suggests that RAP plasma treatment may offer superior advantages for surface preparation, especially in cases where silicon contamination is present.

Plasma treatments, such as those involving argon and fluorinated gases, introduce polar functional groups (e.g., hydroxyl, carbonyl, and carboxyl groups) on the epoxy surface. These functional groups enhance the surface energy and wettability of the epoxy material, improving its adhesive properties. For instance, the increase in C=O/C=O-N and O=C-O/O=C-R groups observed in the XPS data

after plasma treatment indicates a higher concentration of oxygen-containing polar groups, which aligns with findings from Ayaz *et al* (323)

Argon plasma treatment leads to oxidation and etching of the surface, breaking down some of the original bonds (such as C-C/C-H/C-Si) and introducing new oxygen functionalities. This process sees an increase in oxygen-containing groups such as O=C-O and O=CO₂.

4.5.1.2 Chemical Shift in Contaminated Samples

Supplementary visualisations for this section (pie charts) can be found in Appendix C

Table 4-12 alongside Figure 4-35 shows a reduction in C-C/C-H/C-Si bonds from 100% to 87%, indicating etching of the silicone layer. New peaks for C-O/C-N, C=O, and O=C-O/C=R appear, indicating oxidation but less effective compared to clean surfaces. Argon plasma introduces 8% of C-O/C-N bonds, and 3% C=O bonds.

With fluorinated plasma the C-C/C-H/C-Si bond percentage drops further to 81%, indicating extensive modification. Strong oxidative effects can be seen from the increase in carbonyl groups.

Table 4-12 Relative Percentages of Carbon states at the surface of contaminated samples

Bonding environment	Percentage (%) of region		
	No Plasma	Argon Plasma	Fluorinated Plasma
C-C/C-H/C-Si	100.00	86.85	80.59
C-O/C-N		8.13	8.80
C=O		3.00	8.30
O=C-O / O=C-R		2.00	2.40

Table 4-13 and Figure 4-36 presents the relative percentages of various oxygen bonding environments on the surface of contaminated samples under three conditions: no plasma treatment, Argon plasma treatment, and fluorinated plasma treatment. In untreated samples, 100% of the oxygen is present in the C=O/Si-O state. Following Argon and fluorinated plasma treatments, the proportion of this state decreases to approximately 72% and 69%, respectively. Simultaneously, a new oxygen state, C-O/Si-O₂, emerges, accounting for 27% after Argon plasma and 29% after fluorinated plasma. Additionally, a small

proportion of the H-O-H state is observed, increasing slightly from 1.5% after Argon plasma to 2.3% after fluorinated plasma.

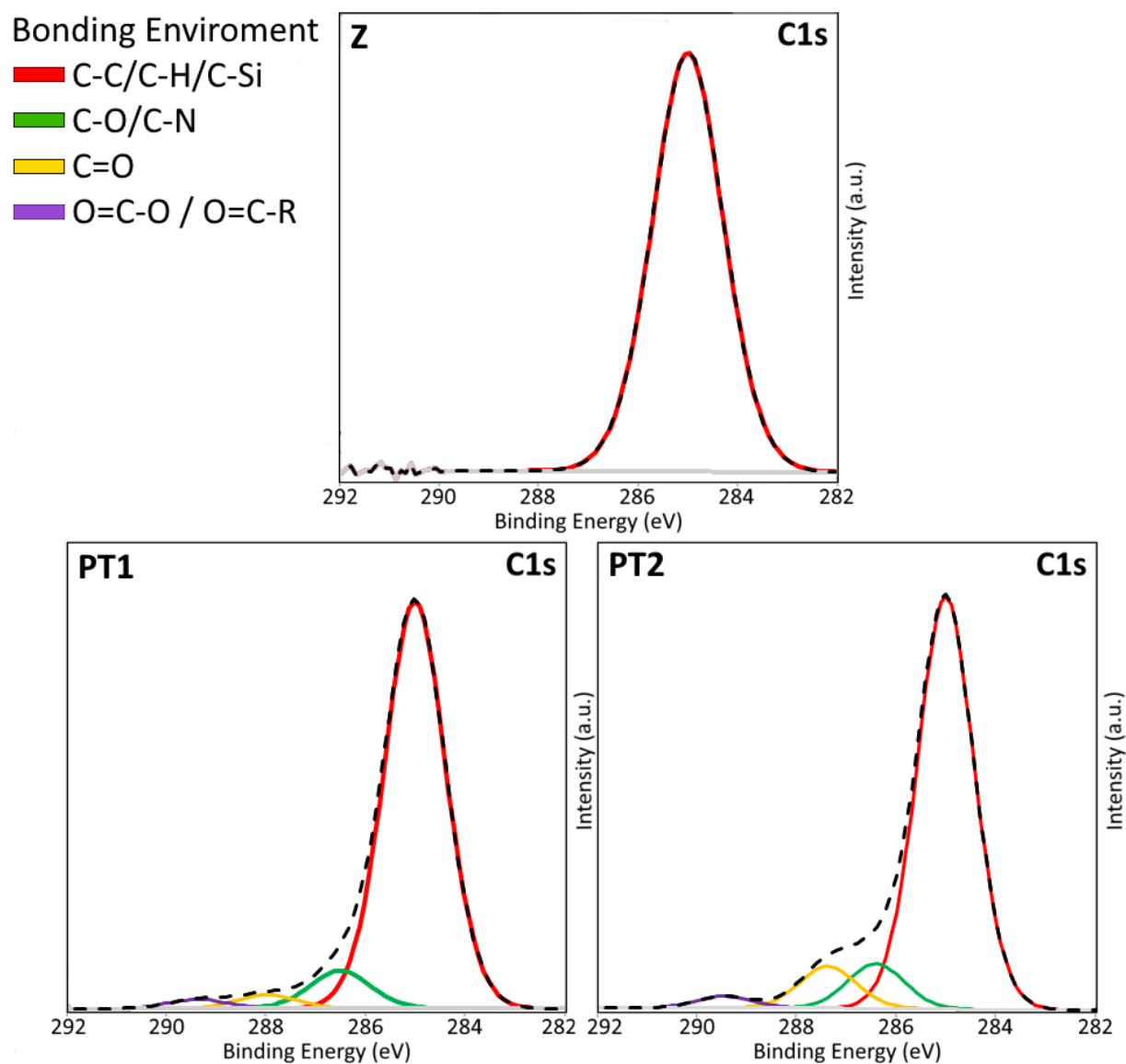


Figure 4-35 Carbon C1s peaks of coated samples.

Table 4-13 Relative Percentages of O1s Oxygen states at the surface of contaminated samples.

Bonding environment	Percentage (%) of region		
	No Plasma (Z)	Argon Plasma (PT1)	Fluorinated Plasma (PT1)
C=O/Si-O	100	71.6	68.6
C-O/Si-O ₂		27.0	29.2
H-O-H		1.5	2.3

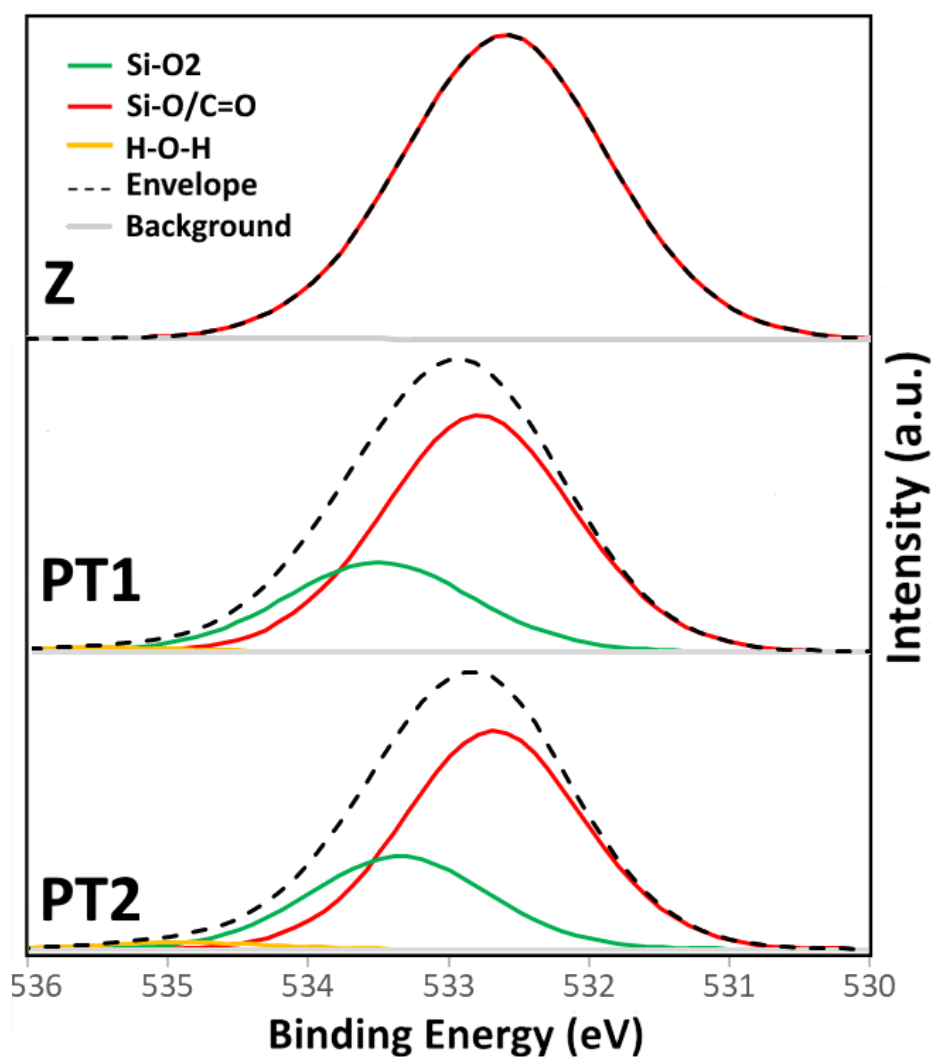


Figure 4-36 O1s Oxygen states at the surface of contaminated samples.

Comparing the oxygen states there is a major decrease in C=O/Si-O from 100% in untreated samples to lower percentages after plasma treatments.

Argon plasma shows a stable introduction of C-O/Si-O₂ bonds, and a slight introduction of hydroxyl groups across all treatments, although slightly more pronounced with fluorinated plasma, likely due to the oxidising effect of APP.

Table 4-14 displays a reduction in silicon-related bonds after plasma treatments, particularly with fluorinated plasma, indicates effective etching and modification of the silicone layer. Figure 4-37 displays two primary silicon bonding environments: SiO (Silicone) and silicon dioxide (SiO₂). The introduction of SiO₂ indicates oxidation of the silicone contamination. Argon plasma shows stable oxidation, while fluorinated plasma shows dynamic changes, reflecting complex oxidation and reconfiguration.

Without plasma treatment the silicon on the sample surface is entirely in the silicone (Si-O) state, accounting for 100% of the detected silicon. After Argon Plasma treatment, there is a significant change in the silicon bonding environment. The percentage of SiO bonds decreases to 57.1%, indicating a reduction in silicon at the surface. The SiO₂ environment, emerges, making up 43% of the silicon detected. This suggests that the Argon plasma treatment alters the chemical structure of the surface, leading to the formation of oxygen-bridged silicon atoms.

With Fluorinated Plasma treatment, the SiO bonds slightly increase to 62%, but they do not return to the levels seen in the untreated sample. The SiO₂ bonds remain present, constituting 38% of the silicon detected. This indicates that the fluorinated plasma treatment also alters the surface chemistry, maintaining a significant proportion of the SiO₂ bonding environment.

Overall, both Argon and fluorinated plasma treatments reduce the dominance of Si-O bonds, and introduce SiO₂ bonds, highlighting changes in the surface chemistry that could influence the material's properties and behaviour.

Table 4-14 Relative Percentages of Silicon Si2p states at the surface of contaminated samples

Bonding environment	Percentage (%) of region		
	No Plasma	Argon Plasma	Fluorinated Plasma
Si-O	100	57.1	62
O-Si-O		43	38

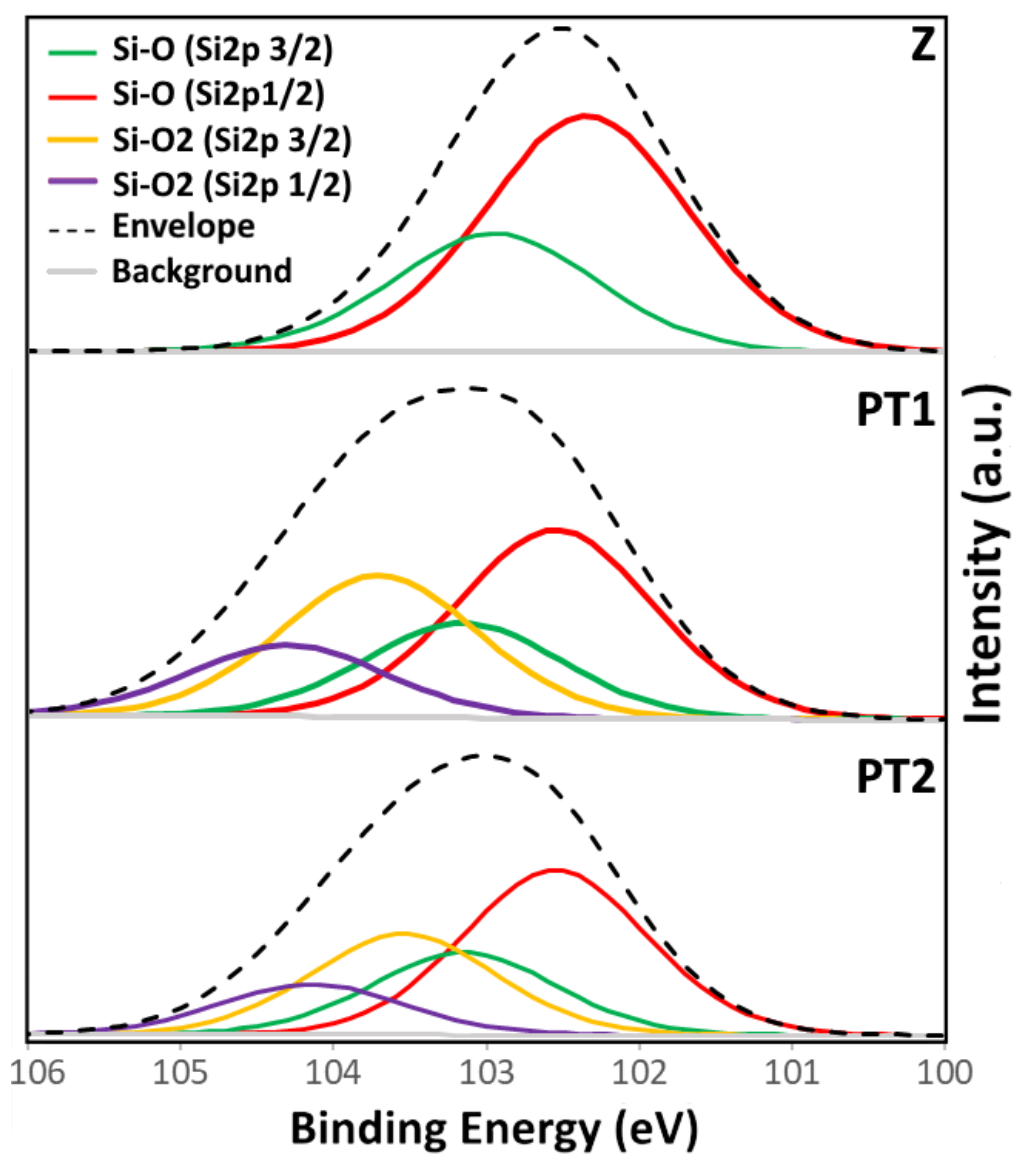


Figure 4-37 Si2p silicon peaks with contaminated samples coated using CM1.

Argon plasma primarily engages in a physical etching process. Argon ions bombard the silicone surface, physically dislodging contaminants and breaking predominantly C-Si chemical bonds. This physical interaction is evidenced by the significant reduction in these bonds from 100% to 86.9%.

Although Argon plasma is primarily a physical process, some oxidation occurs due to the presence of reactive oxygen species formed during plasma generation. New bonds such as C-O/C-N (8.1%) and C=O (3%) are observed.

Fluorinated plasma introduces highly reactive fluorine radicals, which are more aggressive than Argon ions. These radicals break down the C-C/C-H/C-Si bonds more extensively (reduced to 80.6%), facilitating the formation of new oxidised species.

The presence of fluorine enhances the oxidation process, leading to higher percentages of C-O/C-N (8.8%) and C=O (8.3%) bonds. This indicates that fluorinated plasma not only etches but also significantly oxidises the silicone surface.

Both plasma treatments reduce the proportion of C=O/Si-O bonds. Argon plasma reduces these bonds to 71.55%, while fluorinated plasma shows a reduction to 68.58%. This reduction suggests the formation of new surface oxides and hydroxides.

The data indicate that Argon plasma treatment results in higher C-O/Si-O₂ bonds 27% compared to fluorinated plasma 29.2%. This difference highlights the varying oxidation mechanisms between the two treatments, with Argon plasma favouring the formation of single-bonded oxygen species.

The significant reduction in SiO bonds in the Si2p after plasma treatments indicates effective etching. Increased SiO₂ bonds (to around 22-23%) in plasma-treated samples suggest the oxidation of the silicon surface, forming a silicon dioxide layer. Fluorinated plasma appears to form slightly less SiO₂ compared to Argon plasma, potentially due to the formation of other fluorine-containing silicon compounds.

Both Argon and fluorinated plasma treatments effectively modify and clean Chemlease-contaminated surfaces by reducing original carbon and silicon bonds and introducing new oxidised species. However, fluorinated plasma treatment is more effective in achieving extensive surface modification and oxidation, making it more suitable for contaminated surfaces.

Argon plasma shows a stable introduction of C-O/Si-O₂ bonds, and a slight introduction of hydroxyl groups across all treatments, although slightly more pronounced with fluorinated plasma, likely due to the oxidising effect of APP.

4.5.1.2.1 Further analysis of O1s binding region

Looking again at the oxygen O1s region from Figure 4-36 and Table 4-13, there is a lack of clarity over whether a region is Carbon and Oxygen bonded or silicon oxygen bonded due to binding energy overlap.

The data in Table 4-15 was calculated using the combined data from Table 4-12, Table 4-13 and Table 4-14 to cross calculate in order to estimate values from overall silicon and carbon content.

The oxygen bonding environment is expected to be predominantly SiO, followed by SiO₂. In the carbon bonding environment for fluorinated samples (Table 4-12), the C=O and C-O bonding environments were found to be nearly equal. Comparing the oxygen states, however as displayed in Table 4-13, there is a major decrease in C=O/Si-O from 100% in untreated samples to lower percentages after plasma treatments (71.6% and 68.6%, respectively)

This means that approximately 40% of this O1s bonding environment cannot be attributed to the C=O/SiO binding region, which implies that about two-thirds of the oxygen binding region for C=O/SiO must consist primarily of Si-O.

This estimate assumes that all of the C-O/SiO₂ region is C-O; if it is a combination of both, then the proportion of the C=O/SiO region that is SiO will be significantly higher.

Table 4-15 Relative Percentages of Bonding Environments in O1s spectrum under Different Plasma Treatments.

Bonding environment	Percentage (%) of region		
	No Plasma	Argon Plasma	Fluorinated Plasma
Si-O	100	67.4	57.4
Si-O₂		22.1	20.6
C=O		4.4	11.2
C-O		4.6	8.6
H-O-H		1.5	2.3

The ratio of SiO to SiO₂ is approximately 6:4, which means it is not feasible for around 60% of the C=O/Si-O region to be Si-O without the SiO₂ region comprising 40%.

Therefore, a formula needs to be developed to accurately determine this proportion.

Through calculating the total amounts of oxygen, silicon, and carbon from the survey, a percentage of bonds corresponding to the amount of carbon-oxygen and silicon-oxygen bonds was calculated, with Table 4-15 now displaying the full O1s content, separating the oxygen and silicon bonds for better analysis.

Calculating the untreated sample was relatively straightforward. The carbon peak indicated no carbon and oxygen bonding, implying all O₂ and Si would be bonded together. Si2p peak displayed only SiO bonds, and as such this would fit being in the SiO/C=O category but only being dominated by SiO bonds. For the plasma treated samples, the data analysis would need to be assessed and calculated.

The significance of each bond was determined by analysing the amount present in the survey scan and other spectrum analyses. This approach was used to estimate the likely contributions from both the carbon-oxygen bonded regions and the silicon-oxygen bonded regions. By assigning significance to each bonding

environment, it was possible to calculate the relative amounts of these bonds, helping to differentiate between the areas where carbon-oxygen and silicon-oxygen interactions occur on the surface of the samples. This method ensures a more accurate representation of the surface chemistry of the O₂ binding region, reflecting the changes induced by different plasma treatments.

Initially, in the untreated sample (No Plasma), the surface is entirely dominated by SiO bonds, constituting 100% of the bonding environment. However, this composition changes significantly with the application of plasma treatments.

After Argon plasma treatment, the proportion of Si-O bonds decreases to 67.4%, while new bonding environments such as SiO₂ (22.1%), C=O (4.4%), C-O (4.6%), and H₂O (1.5%) emerge. This indicates that Argon plasma treatment introduces oxygen-rich species and carbon-oxygen bonds at the surface, altering the surface chemistry. The fluorinated plasma treatment further reduces the SiO bond proportion to 57.4%, while increasing the presence of C=O bonds to 11.2% and C-O bonds to 8.6%. This treatment also maintains the presence of SiO₂ (20.6%) and slightly increases H-O-H bonds to 2.3%.

Overall, both plasma treatments significantly modify the surface composition, with fluorinated plasma having a more pronounced effect on the formation of carbon-oxygen bonds, likely due to the etching effect on silicon.

4.5.1.2.2 Summary

The XPS analysis of coated samples reveals that Argon plasma treatment leads to partial oxidation of the silicone layer, reducing the C-C/C-H/C-Si bonds and introducing new oxygenated species such as C-O/C-N and C=O bonds. The reduction in these bonds indicates that Argon plasma primarily engages in physical etching, with limited oxidation. In contrast, fluorinated plasma treatment results in more extensive chemical modification, as evidenced by a greater reduction in C-C/C-H/C-Si bonds and a significant increase in oxidised species. The formation of SiO₂ bonds, particularly under fluorinated plasma treatment, suggests the effective oxidation of the silicone surface, leading to improved surface properties.

Silicon contaminants, particularly groups such as Si-O and Si-CH₃, significantly affect the surface properties by forming a hydrophobic layer that diminishes the effectiveness of plasma treatment. The presence of these contaminants alters the plasma's ability to modify the surface, impacting the material's wettability, adhesion, and overall chemical characteristics. Even trace amounts of silicon can significantly interfere with surface treatments and bonding processes, emphasising the need for effective removal techniques to ensure reliable adhesion and surface modification(49)

Both argon and fluorinated plasma treatments are effective at etching and modifying contaminated surfaces. This is evidenced by the reduction of original carbon and silicon bonds and the introduction of new oxidised species. However, fluorinated plasma tends to be more aggressive in its etching behaviour. A study by (324) compared different fluorocarbon plasmas and their effects on etching kinetics, noting that fluorine atoms act as the primary agents for silicon etching, significantly enhancing the removal of silicon-based contaminants.

4.5.1.3 Contamination Removal Focused Study

Spin Coated samples (CM2) were plasma processed with RF plasma processing every 1mm. XPS was used to understand the relative percentages of elements at the surface of the composite.

XPS analysis on samples treated with RF argon plasma alone, showed a negligible effect of plasma surface treatment in terms of percentage Silicon reduction. Oxygen containing species at the surface did appear to increase after plasma treatment in all 3 cases. For the fluorinated plasma processed samples, there was a significant reduction in silicon found at the surface, when compared to the untreated samples. Sulphur was also found at the surface of these samples. This could be due to the presence of sulphur in the reactive gas, or due to the presence of sulphur found in the epoxy of uncoated samples as shown in Figure 4-38.

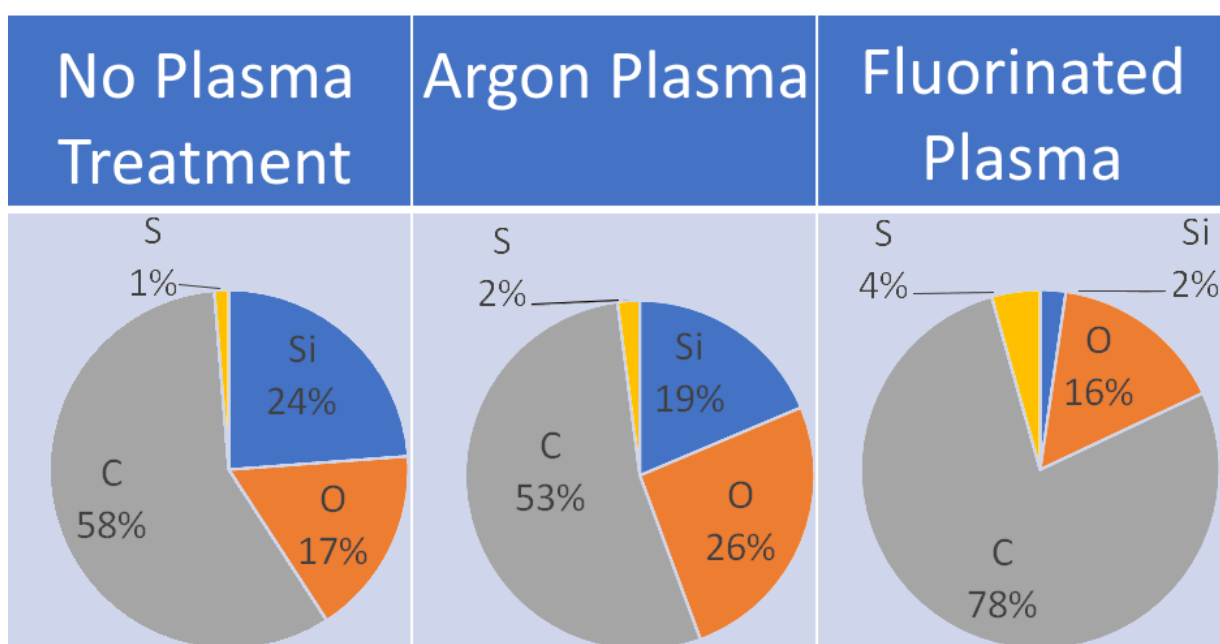


Figure 4-38 XPS compositional analysis of samples which have been spin coated. The affect of argon plasma treatment with fluorinated argon plasma treatment was compared with completely untreated samples. Plasma treatment was conducted with a raster of 1mm in between passes.

Table 4-16 Atomic Percentages of Each Element

Treatment	C (%)	S (%)	Si (%)	O (%)
No Plasma Treatment	58	1	23	17
Argon Plasma Treatment	53	2	19	26
Fluorinated Plasma Treatment	78	4	2	16

The contaminated samples, as displayed in Table 4-16 and Figure 4-38, show a significant presence of carbon (58%) and silicon (23%), with lower amounts of oxygen (17%) and sulphur (1%). This indicates that the contamination consists predominantly of organic material and silicon-based compounds.

With Argon Plasma treatment there is a reduction in carbon content (53%) and silicon content (19%), with an increase in oxygen content (26%) and sulphur content (2%). This suggests that Argon plasma treatment effectively etches the surface, removing some of the organic contamination and partially oxidising the surface.

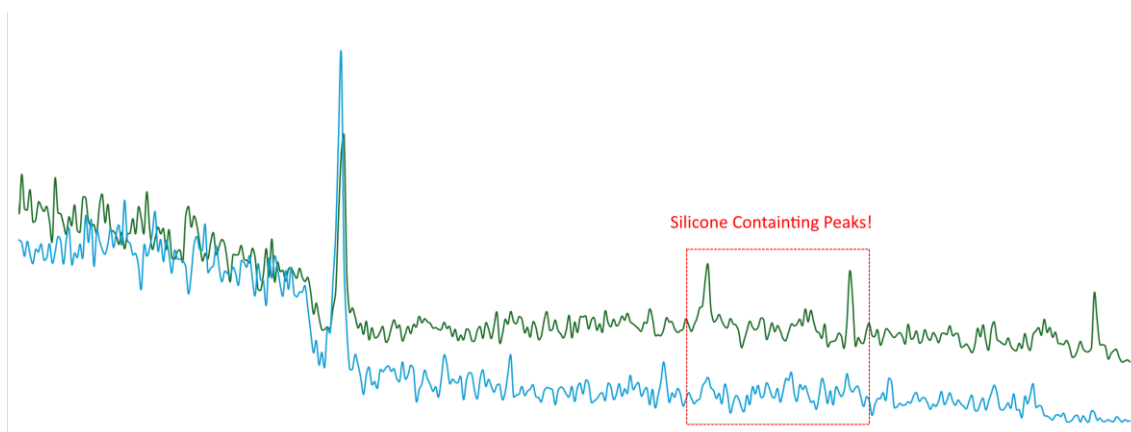


Figure 4-39 XPS Line Scan of an Untreated Sample (Green) and Sample treated with Fluorinated plasma (blue). The green line scan shows two peaks; Si2s (left) and Si2p (right). The blue scan does not show presence of Silicon due to the low resolution nature of the line scan and the low concentration of Si on the sample surface after treatment.

Table 4-17 Displaying the average (taken from 3 separate curves) Silicon Regions of Contaminated and plasma treatment samples.

Percentage (%) of region	Bonding Environment		
	Si	R ₂ SiO	SiO ₂
No Plasma Treatment	2.2 (+/- 3.1)	78.3 (+/- 6)	19.5 (+/- 7.4)
Argon Plasma Treatment		66.1 (+/- 0.8)	33.9 (+/- 0.8)
Fluorinated Treatment	1.8 (+/- 2.5)	98.2 (+/- 2.5)	

The data in the Argon plasma treatment region results in a consistent composition across samples, with approximately 66.1% R₂SiO and 33.9% SiO₂, with elemental silicon undetected. 'R' in this instance represents an organic group such as CH₃ which is commonly found in silicones. This indicates effective etching and oxidation, converting a portion of the silicon surface into silicon dioxide, and possibly contributing to removal of Si contamination and other contaminants. Figure 4-40 shows the distribution of silicon bonding states varies significantly, indicating uneven contamination and different levels of oxidation. Argon plasma treatment results in a consistent composition across samples, with approximately 66.1% R₂SiO and 33.9% SiO₂, with elemental silicon undetected. This indicates effective etching and oxidation, converting a portion of the silicon surface into silicon dioxide, and possibly contributing to removal of Si contamination and other contaminants(325–327).

Fluorinated Plasma Treatment indicates that there may be some variation, with sample 1 having a predominantly R₂SiO (94.62%) region alongside minimal elemental silicon (5.38%) and no SiO₂. Samples 2 and 3 exhibit complete conversion to R₂SiO (100%), with no detectable elemental silicon or SiO₂. This indicates a highly effective oxidation process, converting nearly all the surface to the R₂SiO state, alongside physical etching leading to minimal residual contamination. Accompanying this with data from Table 4-16, the minimal presence of silicon (2%) and high carbon content (78%) suggest the formation of

a fluorocarbon layer, which significantly alters the surface composition (324,326,327,330).

Lim et al (324) compare the effects of different fluorocarbon-based plasmas (CF_4 , CHF_3 , and C_4F_8 mixed with Ar/O_2) on silicon etching, highlighting how variations in gas composition influence plasma parameters and etching mechanisms. It finds that fluorine atoms primarily drive the chemical etching pathway, with each gas mixture showing distinct behaviours in polymer film formation and etching selectivity. variations in surface oxidation and polymer film formation, consistent with the described outcomes of fluorinated plasma treatment converting surfaces to R_2SiO and forming fluorocarbon layers.

Table 4-17 Displaying the average (taken from 3 separate curves) Silicon Regions of Contaminated and plasma treatment samples. provides insights into the changes in silicon bonding environments after plasma treatment on contaminated silicone surfaces. When comparing samples with no Plasma treatment, the bonding state is predominantly R_2SiO with variable levels of Si and SiO_2 .

Without plasma treatment, surfaces tend to have uneven contamination and different levels of oxidation, leading to variability in the silicon bonding states such as Si, SiO_2 , and various suboxides like R_2SiO .

This is because plasma treatments typically enhance the hydrophilicity and uniformity of the surface. Plasma treatments are known to remove organic contaminants, and such would likely result in less Silicon-Carbon chains, a higher concentration of silicon overall and the formation of silicon oxides on the surface (328,329).

Figure 4-40 shows the distribution of silicon bonding states varies significantly, indicating uneven contamination and different levels of oxidation. Argon plasma treatment results in a consistent composition across samples, with approximately 66.1% R_2SiO and 33.9% SiO_2 , with elemental silicone undetected. This indicates effective etching and oxidation, converting a portion of the silicon surface into

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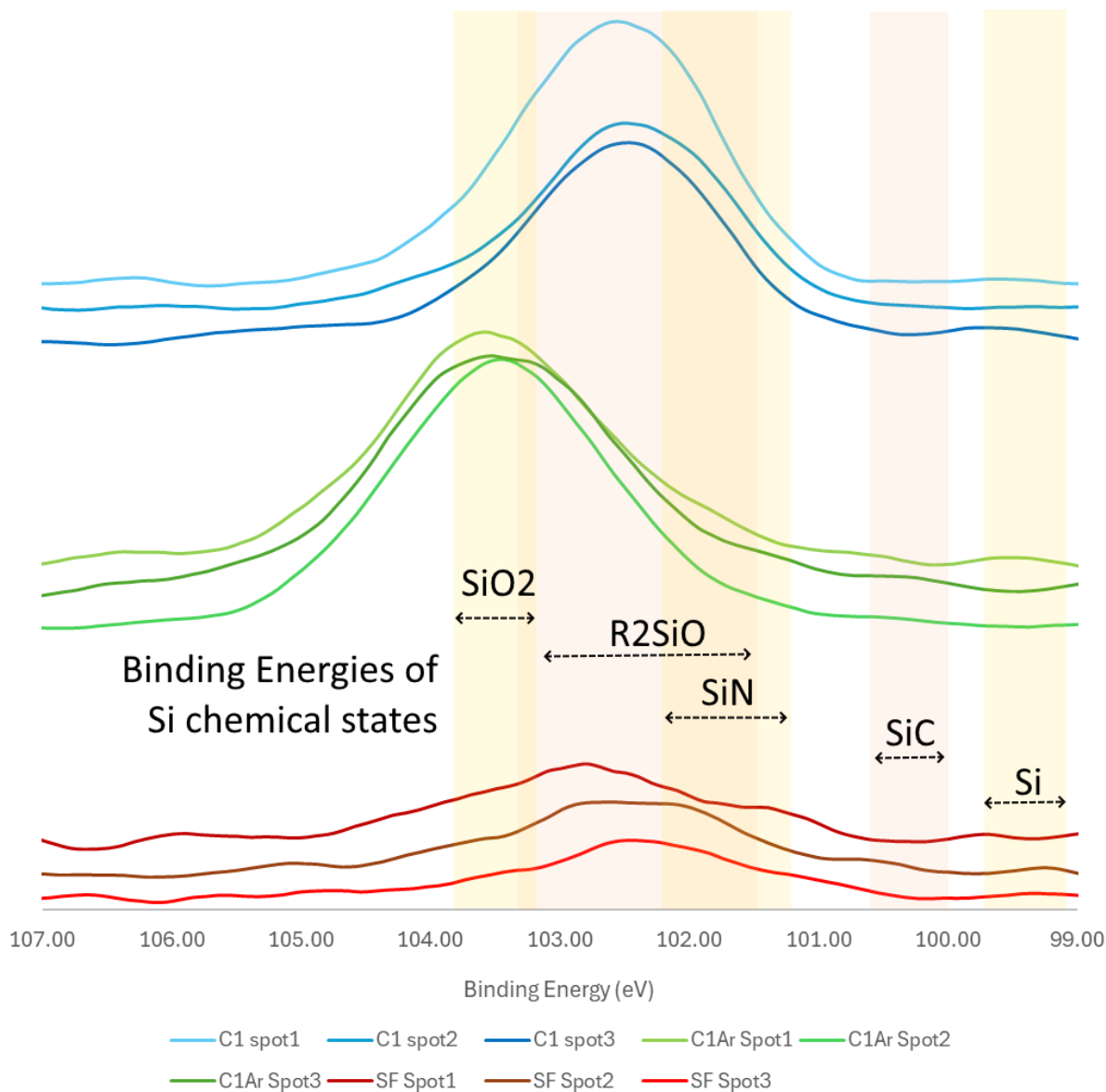


Figure 4-40 Displaying the Si_{2p} binding energy profiles of untreated (blue), argon treated (green) and fluorinated plasma (red) treated samples. Data was collected from 3 random data points across each sample. The data shows the distribution of silicon bonding states varies significantly, indicating uneven contamination and different levels of oxidation (315–317).

When considering argon treatment, by contrast, Lim et al (324) suggests that pure argon etching results in low physical sputtering rates (<5nm/min). They further emphasise the minimal contribution of pure argon to the etching process compared to reactive ion etching involving fluorocarbon gases.

The increase in oxygen content under argon treatment is consistent with the formation of new oxygen-containing functional groups, as seen in the increase of SiO₂ in Argon plasma treatment results in a consistent composition across samples, with approximately 66.1% R₂SiO and 33.9% SiO₂, with elemental silicon undetected. This indicates effective etching and oxidation, converting a portion of the silicon surface into silicon dioxide, and possibly contributing to removal of Si contamination and other contaminants and the increase of oxygen containing carbon species in Figure 4-40 shows the distribution of silicon bonding states varies significantly, indicating uneven contamination and different levels of oxidation. Argon plasma treatment results in a consistent composition across samples, with approximately 66.1% R₂SiO and 33.9% SiO₂, with elemental silicon undetected. This indicates effective etching and oxidation, converting a portion of the silicon surface into silicon dioxide, and possibly contributing to removal of Si contamination and other contaminants(325–327).

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with the described outcomes of fluorinated plasma treatment converting surfaces to R_2SiO and forming fluorocarbon layers.

When looking at the C1s part of the samples' spectrum, as displayed in Figure 4-41 and detailed in

Table 4-18 the majority of carbon atoms are found in the C-C bonding environment, accounting for $81.2\% \pm 2.2\%$ of the total carbon of untreated samples. The C-O bond comprises $14.2\% \pm 2.2\%$, while the C=O bond makes up $3.9\% \pm 1.2\%$. The presence of O=C-O / O=C-R groups is barely detectable and inconsistent, representing only $0.7\% \pm 0.7\%$ of the carbon bonds, with no detectable O=CO₂ or C-F groups.

Under Argon treatment, there is a noticeable shift in the carbon bonding environment. The proportion of C-C bonds increases slightly to $85.3\% \pm 6.4\%$, suggesting that Argon plasma treatment enhances the retention of C-C bonds or reduces the formation of oxygenated carbon species. The percentage of C-O bonds decreases significantly to $5.3\% \pm 3.7\%$, indicating a reduction in oxygen-containing functional groups. Interestingly, the C=O bonds increase slightly to $5.3\% \pm 3.6\%$, with O=C-O / O=C-R also increasing, which account for $2.6\% \pm 1.9\%$. A new bonding environments emerges, O=CO₂, although its significance is negligible as it makes up only $1.5\% \pm 1.5\%$.

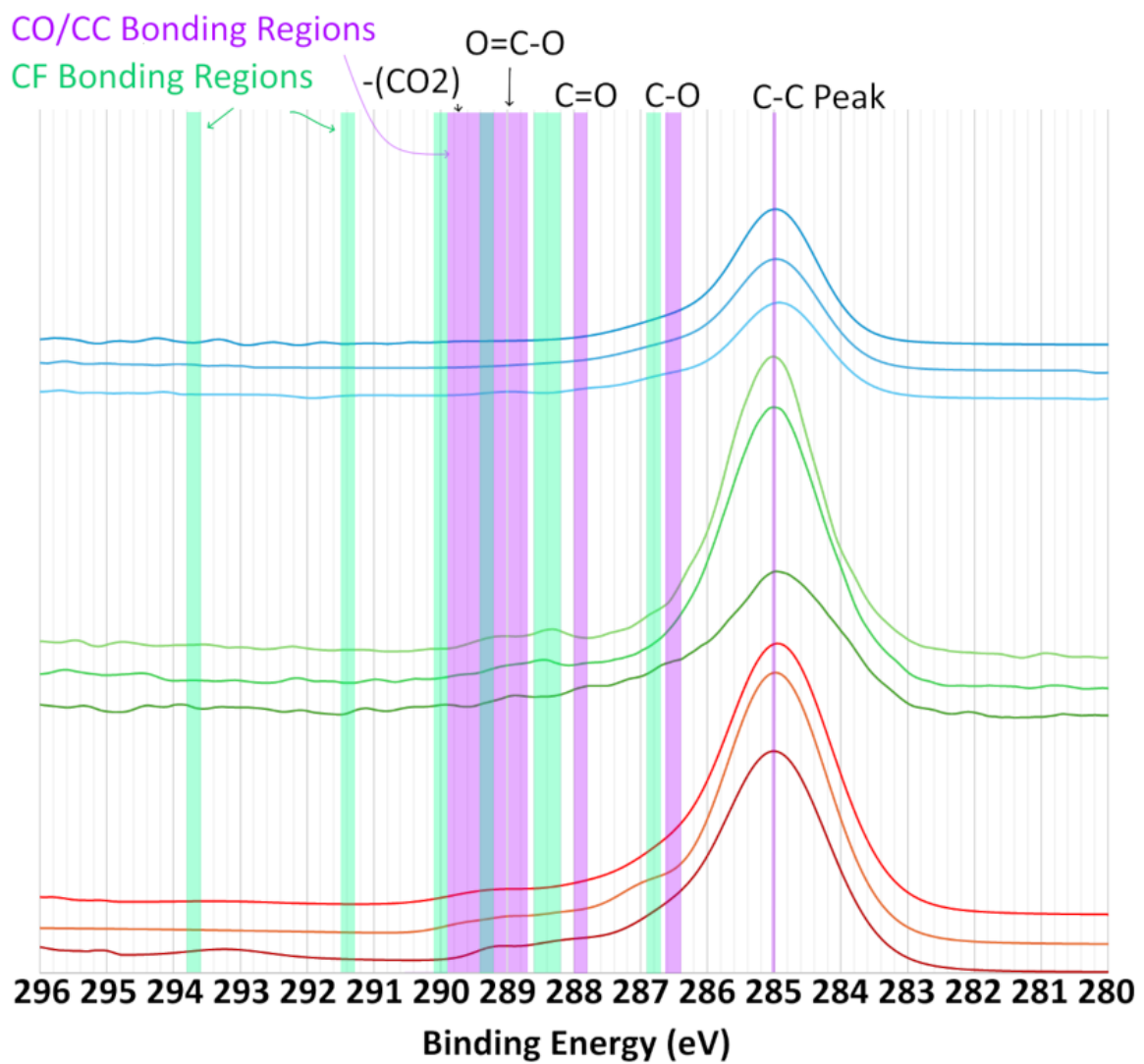


Figure 4-41 Displaying the C1s binding energy profiles of untreated (blue), argon treated (green) and fluorinated plasma (red) treated samples. Data was collected from 3 random data points across each sample.

Table 4-18 Describing the average (taken from 3 separate curves) percentage of carbon C1s binding regions under different plasma conditions.

<i>Bonding environment</i>	Percentage of region (%)					
	C-C	C-O	C=O	O=C-O / O=C-R	O=CO ₂	C-F
No Plasma Treatment	81.2 (+/- 2.2)	14.2 (+/- 2.2)	3.9 (+/- 1.2)	0.7 (+/- 0.7)		
Argon Treatment	85.3 (+/- 6.4)	5.3 (+/- 3.7)	5.3 (+/- 3.6)	2.6 (+/- 1.9)	1.5 (+/- 1.5)	
Fluorinated Treatment	83.4 (+/- 1.4)	7.4 (+/- 1.5)	5.7 (+/- 0.6)	1.5 (+/- 1.8)	1.4 (+/- 0.5)	0.6 (+/- 0.6)

Fluorinated plasma further modifies the carbon bonding landscape. The C-C bonds account for 83.4% $\pm$ 1.4%, dominating the environment just as with samples processed with argon plasma or no plasma at all. The C-O bond percentage increases to 7.4% $\pm$ 1.5%, suggesting retention of oxygenated groups under fluorinated plasma processing. The percentage of C=O bonds continue to remain relatively the same as argon treatment at 5.7% $\pm$ 0.6%. The O=C-O / O=C-R groups are present at 1.5% $\pm$ 1.8%, while O=CO₂ bonds account for 1.4% $\pm$ 0.5%. Additionally, the fluorinated treatment introduces C-F bonds, which, although minor, are detected at 0.6% $\pm$ 0.6%, indicating some incorporation of fluorine into the carbon structure.

To understand the effects of various treatments on the chemical composition of the material, particularly the bonding of oxygen to carbon, the percentage of total oxygen associated with carbon species was analysed, as presented in Table 4-19.

Table 4-19 Showing average (taken from 3 separate curves) Percentage Total Oxygen from Carbon Species

	No Plasma Treatment	Argon Treatment	Fluorinated Treatment
Amount of Carbon from Survey	80.1 (+/- 1.4)	66.6 (+/- 9.7)	82.6 (+/- 0.7)
Amount of Oxygen from Survey	19.9 (+/- 1.4)	33.4 (+/- 9.7)	17.4 (+/- 0.7)
Atomic Percent (portion of Oxygen Amount from Survey)	11.7 (+/- 1.1)	10.9 (+/- 3.5)	14.6 (+/- 1.2)
Remaining Oxygen Amount from Survey	8.3 (+/- 0.7)	22.4 (+/- 6.3)	2.8 (+/- 1.2)
Percentage of Total Oxygen from Carbon Species	58.4 (+/- 2.6)	32.6 (+/- 2.0)	83.8 (+/- 6.5)

The amount of carbon from the survey, which represents the atomic percentage of carbon within the sample, needs to be identified. In the untreated sample, the carbon content was measured at 80.1% $\pm$ 1.4%. Following Argon plasma treatment, this value decreased to 66.6% $\pm$ 9.7%, while it increased to 82.6% $\pm$ 0.7% after the fluorinated plasma treatment.

Subsequently, the Amount of Oxygen from the Survey was assessed to determine the total percentage of oxygen present in the sample. For the untreated sample, oxygen constituted 19.9% $\pm$ 1.4% of the composition. After Argon treatment, the oxygen content increased to 33.4% $\pm$ 9.7%, but decreased to 17.4% $\pm$ 0.7% following fluorinated treatment.

In order to determine how much of this oxygen is specifically bonded to carbon atoms, the Atomic Percent (portion of Oxygen Amount from the Survey) was calculated. This metric quantifies the percentage of total oxygen that is bonded to carbon. The untreated sample showed an atomic percent of 11.7% $\pm$ 1.1%, which slightly decreased to 10.9% $\pm$ 3.5% after Argon treatment, and increased

to $14.6\% \pm 1.2\%$ following fluorinated treatment. This analysis provides insight into the extent of oxygen-carbon bonding within the sample under different treatment conditions.

To gain further insight, the Remaining Oxygen Amount from the Survey was evaluated. This parameter, representing the oxygen not associated with carbon, was calculated by subtracting the oxygen bonded to carbon from the total oxygen content. The untreated samples exhibited a remaining oxygen amount of $8.3\% \pm 0.7\%$. This value increased significantly to $22.4\% \pm 6.3\%$ after Argon treatment but decreased to $2.8\% \pm 1.2\%$ following fluorinated treatment. The remaining oxygen helps to clarify the portion of oxygen that is either free or bonded to elements other than carbon.

Finally, the Percentage of Total Oxygen from Carbon Species was determined. This key metric indicates the percentage of total oxygen in the sample that is specifically bonded to carbon atoms. In the untreated sample, $58.4\% \pm 2.6\%$ of the oxygen was associated with carbon. After Argon treatment, this percentage decreased to $32.6\% \pm 2.0\%$, but it increased markedly to $83.8\% \pm 6.5\%$ following fluorinated treatment. This increase may slightly influence the increase in the percentage amount of carbon and a slight decrease in the percentage of oxygen, skewing to show that more of the oxygen that is present, is attached to the carbon, as oxygen is more abundant.

Table 4-19 shows a reduction in Percentage of Total Oxygen from Carbon Species even though data from

Table 4-18 would suggest otherwise. The data from these two tables, combined with the data from Table 4-16 shows that although argon plasma may increase the percentage of oxygenated carbon species, it is likely that the increase in oxygen is in the form of either atomic oxygen, or oxygenation of other species such as silicon.

After fluorinated Plasma Treatment there is a significant increase in carbon content (78%) and sulphur content (4%), with a drastic reduction in silicon content (2%) and a slight decrease in oxygen content (16%).

Table 4-19 Showing average (taken from 3 separate curves) Percentage Total Oxygen from Carbon Species indicates that argon plasma increases percentages of oxygen at the surface of samples, however these are not bonded to carbon, where fluorinated plasma results in a higher percentage of oxygen-carbon bonds. When comparing this to the data observed in Table 4-16 and Table 4-17 it makes sense that this would be the case, with argon plasma increasing the percentage of oxygen at the surface, although this may result in more carbon-oxygen bonds, the higher amounts of oxygen has also resulted in more oxygen bonds with silicon, converting Si-O to Si-O₂. Fluorinated plasma not only shows predominantly more Si-O bonds to Si-O₂ bonds, but it also demonstrates a decrease in overall silicon from about a quarter of the content to roughly 2%. As a result, the carbon content is the predominant content for the oxygen content to form bonds with.

4.5.1.4 Summary

All the data supports that fluorinated plasma treatment was successful in removing surface contamination. Although a trace amount of surface contamination remains, there is a significant reduction regardless for how many times the surface had been spin coated. This trace amount could also be due to trace amount sulphur.

For these results comparing argon plasma treatment alone, to Fluorinated argon plasma treatment, argon would appear to be suitable for applications where moderate cleaning and oxidation are sufficient, where treatment results in significant etching and partial oxidation, the treatment converts a substantial portion of the surface to SiO₂.

Fluorinated plasma, in contrast, appears to provide a more extensive surface modification. The highly reactive fluorine radicals oxidise the silicon surface more thoroughly, converting it predominantly to R₂SiO. This treatment is more effective for achieving comprehensive surface oxidation, even on lightly contaminated surfaces.

This suggests that fluorinated plasma treatment introduces a substantial amount of carbon-fluorine bonds on the surface, as also observed in the work of Lim et al (324).

Reactive fluorine radicals in fluorinated plasma treatments effectively etch and oxidise the silicon surface, leading to the formation of various silicon-fluorine compounds. Fluorine atoms generated in plasma etching processes, such as those involving CF₄/O₂, SF₆, or NF₃, react with silicon to form silicon-fluorine compounds. This reaction is well-documented and results in the formation of volatile SiF₄ as a primary product. Additionally, these treatments result in the deposition of a fluorocarbon layer on the surface, which can obscure the underlying silicon in XPS analysis due to signal attenuation (34,324,331–333)

4.5.2 Surface Energy & Adhesion

Understanding the surface energy and adhesion properties of MTM44-1 composites is crucial for their application in high-performance aerospace and industrial sectors. This section examines the key metrics of water contact angle, surface energy, and lap shear strength to evaluate pre and post plasma processing bonding and adhesion characteristics.

Up to 4 surface treatment regimes, alongside untreated samples, were compared on both coated and uncoated samples. These regimes are detailed in Table 3-1 detailing the shorthand names for various treatment methods.

4.5.2.1 Water Contact Angle

Water contact angle measurements assess the wettability of a material's surface by evaluating the angle formed between a water droplet and the surface. A low contact angle indicates high wettability and hydrophilicity, suggesting strong adhesive potential. Conversely, a high contact angle indicates hydrophobicity, which may impede adhesion.

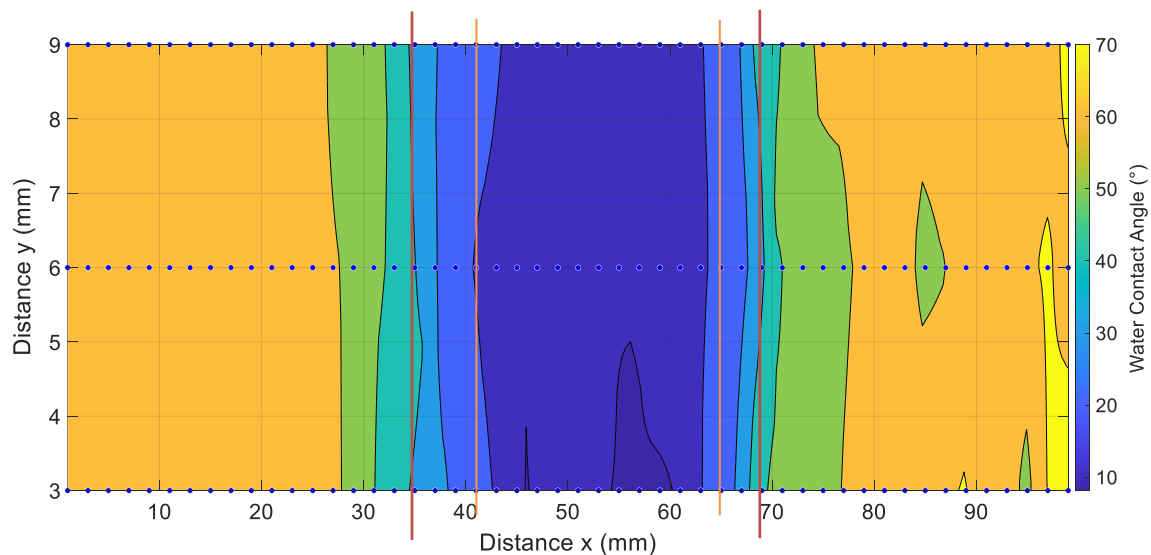


Figure 4-42 A map displaying the WCAs across a sample that was treated by 1 pass of radio frequency plasma.

RF plasma was used to treat a clean 100mmx25mm sample at 1m/min. This is to give a clear understanding of how a single plasma pass can improve the

wettability across a sample, as visualised in Figure 4-42. The water contact angle was measured across the sample every 2mm. Three measurements in total were made every 3mm. MATLAB was used to visualise the water contact angle change across the sample to understand where the saturated region of each pass lies. The RF torch has an inner diameter of 17mm, although the saturated region is between 19-24mm across, with a 34mm effective treatment width.

4.5.2.2 Surface Energy

Surface energy measurements are essential for evaluating the adhesive potential and interfacial compatibility of MTM44-1 composites. Quantifying surface energy provides insights into the work of adhesion and the interaction between the composite and other materials.

Figure 4-43 illustrates the surface energy (mN/m) of samples subjected to various plasma treatments, with a comparison between uncontaminated samples (represented by blue bars) and contaminated samples (represented by orange bars). The treatments evaluated include PT-2, PT-3, PT-4 (as described in Table 3-1) with comparison to samples without plasma treatment.

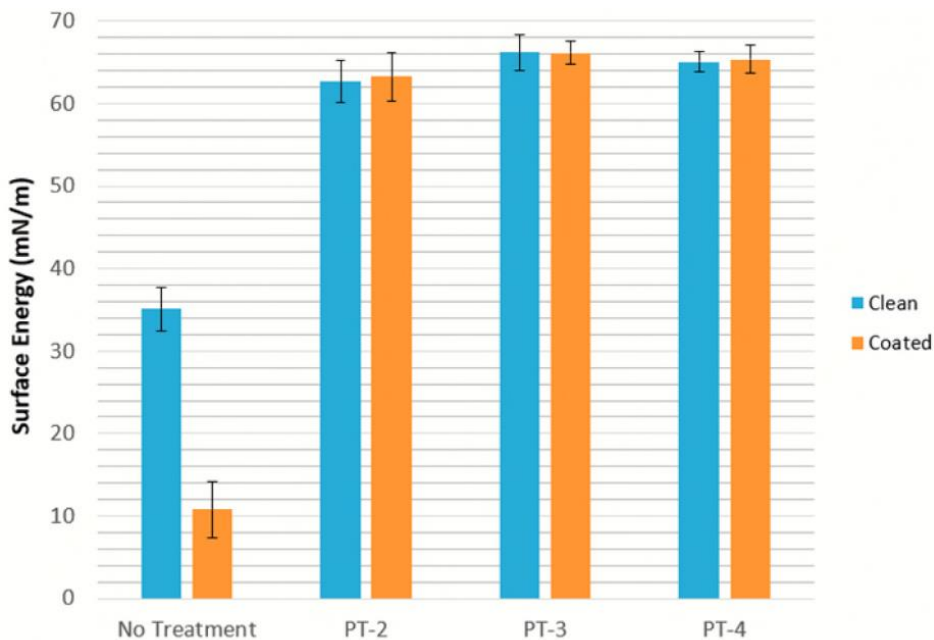


Figure 4-43 Surface energy of original (blue) and coated (orange) and uncontaminated (blue bars) samples subjected to different plasma treatments.

The untreated samples show a significant disparity in surface energy between uncontaminated and contaminated conditions. Plasma treatments PT-2, PT-3, and PT-4 substantially increase surface energy for both uncontaminated and contaminated samples, with minimal differences between the two conditions, indicating the treatments' effectiveness in mitigating the impact of contamination.

The surface energy for uncontaminated samples that received no treatment is an average of 35mN/m. The surface energy for contaminated samples without treatment is significantly lower, around 11mN/m. This demonstrates the adverse effect of contamination on surface energy when no treatment is applied.

After treatment with PT-2, the surface energy of original (uncontaminated) samples increases substantially to an average of just shy of 63mN/m. This shows a significant enhancement in surface energy due to the plasma treatment. Coated (contaminated) samples treated with PT-2 also experience a significant increase in surface energy, reaching to similar surface energies to the original samples.

This indicates that PT-2 is effective in mitigating the negative effects of contamination coating.

The surface energy of both original and coated samples treated with PT-3 is approximately 66mN/m, which is marginally the highest among all the treatments, indicating a robust enhancement in surface properties. This suggests that PT-3 maintains high surface energy even in the presence of contamination.

The surface energy of both original and coated samples treated with PT-4 is around 65mN/m, slightly lower than PT-3 but still very high, demonstrating significant surface energy improvement. With both coated and original samples having similar results, PT-4 was also effective in counteracting the effects of contamination on surface energy.

The effect of hydrophobic recovery over time was assessed in PT2 samples and displayed in Figure 4-44. The data captures the impact of plasma treatment on both clean and coated surfaces at two different time intervals: immediately after treatment (<1 hour) and after 1 week (168 hours).

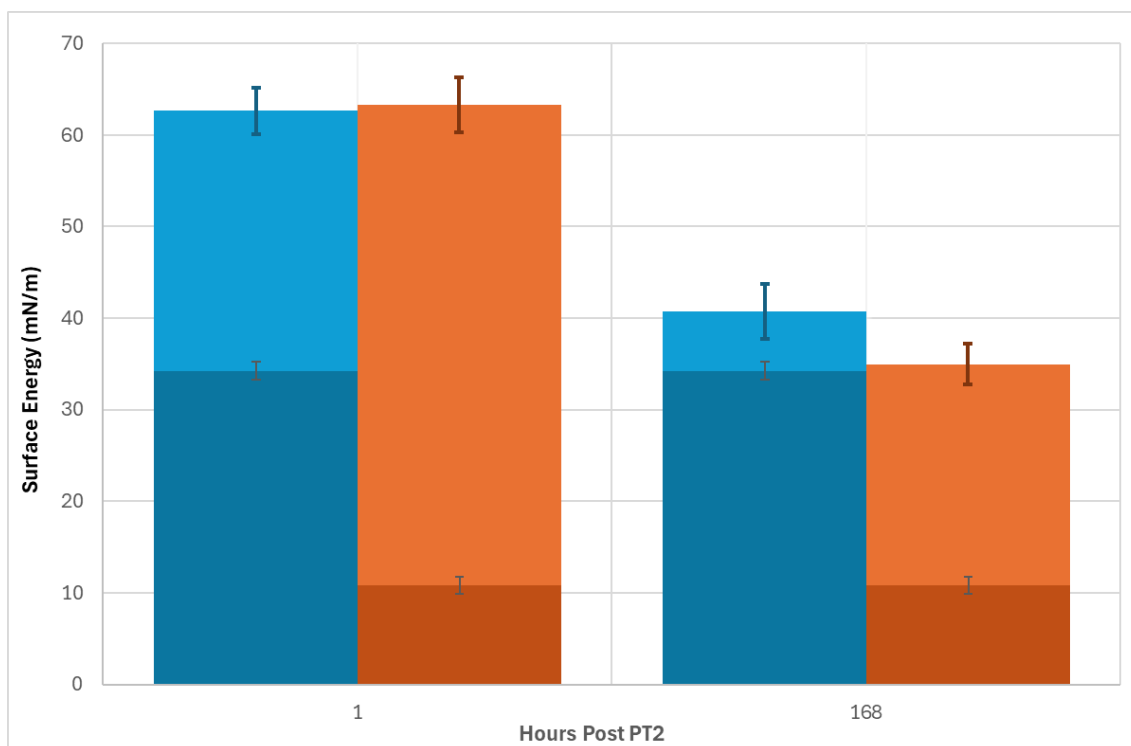


Figure 4-44 Surface energy of clean (blue) and coated (red) samples 1 hour and 168 hours after argon plasma treatment. The dark blue and dark red regions of the stacked bars represent the pre-plasma surface energies of the clean and coated samples, respectively. The light blue and light red regions show the increase in surface energy due to plasma treatment.

For uncoated samples, those that underwent plasma treatment exhibited a significantly higher surface energy (62.6 mN/m) compared to the non-treated samples, which had a surface energy of 34.26 mN/m. This indicates that the plasma treatment substantially enhances the surface energy of clean surfaces. Similarly, the plasma-treated coated samples showed an increase in surface energy (52.5 mN/m) compared to the non-treated coated samples which had a much lower surface energy of 10.8 mN/m.

After 168 hours, the surface energy of the plasma-treated clean samples decreased from 62.6 mN/m to 40.7 mN/m, showing a reduction over time but remaining significantly higher than the non-treated samples, with a surface energy of 34.26 mN/m. The surface energy of the plasma-treated coated samples also declined, from 52.5 mN/m to 24.2 mN/m. In contrast, the non-treated coated samples had a considerably lower surface energy of just 10.8 mN/m.

The argon plasma treatment significantly enhances the surface energy of both clean and coated samples initially. Over time, the surface energy of the plasma-treated samples decreases, indicating some loss of the initial surface modification effects. However, even after 168 hours, the plasma-treated surfaces still maintain higher surface energy than their non-treated counterparts.

The surface energy of clean and coated samples subjected to fluorinated plasma treatment (PT3) was measured over time, with comparisons made to samples that were not treated with plasma as displayed in Figure 4-44 respectively. The surface energy was recorded at three different time intervals: immediately after treatment (1 hour), after 24 hours, and after 48 hours.

The clean samples treated with fluorinated plasma exhibited a high surface energy of 66.5 mN/m, which is significantly higher than the non-treated clean samples, which had a surface energy of 34.26 mN/m. This indicates a substantial increase in surface energy due to the plasma treatment.

The coated samples also showed a high surface energy of 66.2 mN/m immediately after plasma treatment, a stark contrast to the much lower surface energy of 10.8 mN/m observed in the non-treated coated samples.

After 24 hours, the surface energy of the plasma-treated clean samples decreased slightly to 64.6 mN/m and further declined to 60.1 mN/m after 48 hours. Although there is a reduction in surface energy over time, the treated clean samples still maintained significantly higher surface energy compared to the non-treated samples.

The surface energy of the plasma-treated coated samples remained relatively stable over time, with only a minor decrease from 66.2 mN/m at 1 hour to 65.5 mN/m at 24 hours and 48 hours. This suggests that the fluorinated plasma treatment provides a lasting surface energy enhancement on coated surfaces.

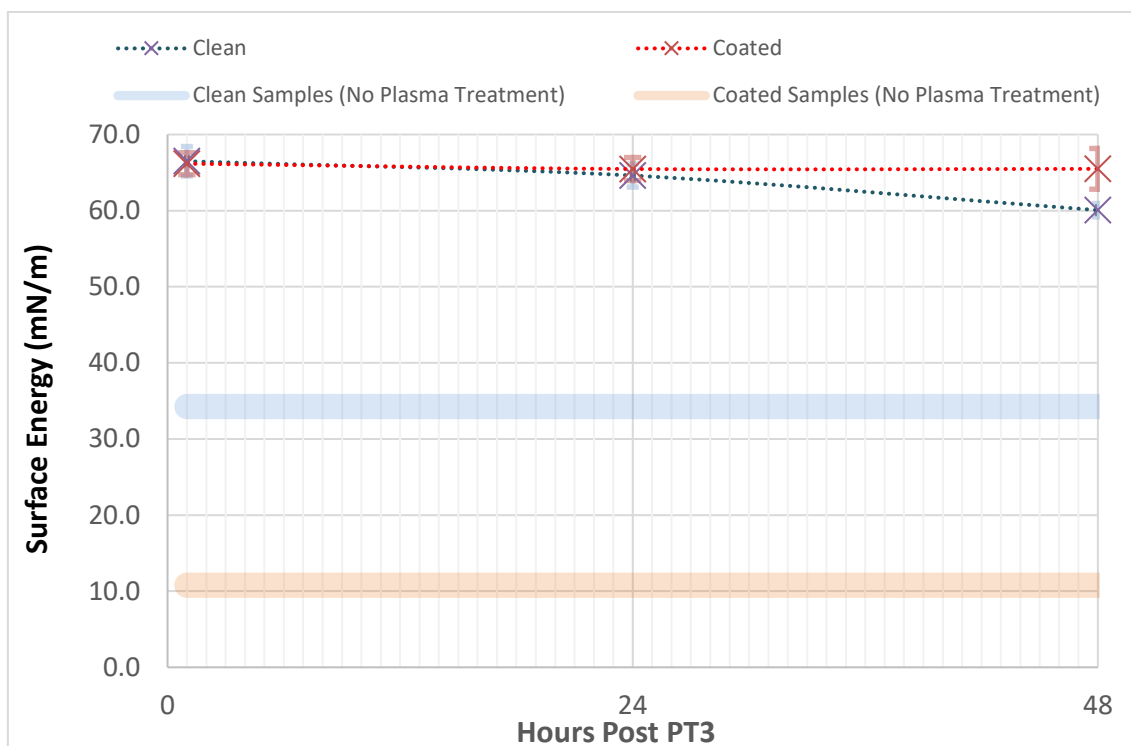


Figure 4-45 Surface energy of coated and non-coated samples measured at 1, 24, and 48 hours post fluorinated RF plasma treatment using an adapted raster pattern (PT3). Blue markers represent clean (non-coated) samples, while red markers indicate coated samples. The light blue and orange lines represents the pre-plasma surface energy of the original, and coated samples respectively.

PT3 significantly enhances the surface energy of both clean and coated samples, with the initial surface energy values being much higher than those of the non-treated samples. Over time, the surface energy of the plasma-treated clean samples decreases slightly, indicating some reduction in the plasma-induced surface modification. However, the surface energy remains significantly higher than that of non-treated samples, even after 48 hours. The coated samples treated with plasma exhibit excellent stability, with minimal changes in surface energy over the 3-day period.

In order to further examine the longer-term effect of the surface energy of uncoated fluorinated plasma treatment (PT3) was measured over a prolonged post-treatment period. The surface energy was measured at five different time intervals: immediately after treatment (1 hour), 24 hours, 48 hours, 168 hours (7 days), and 336 hours (14 days) as displayed in Figure 4-46.

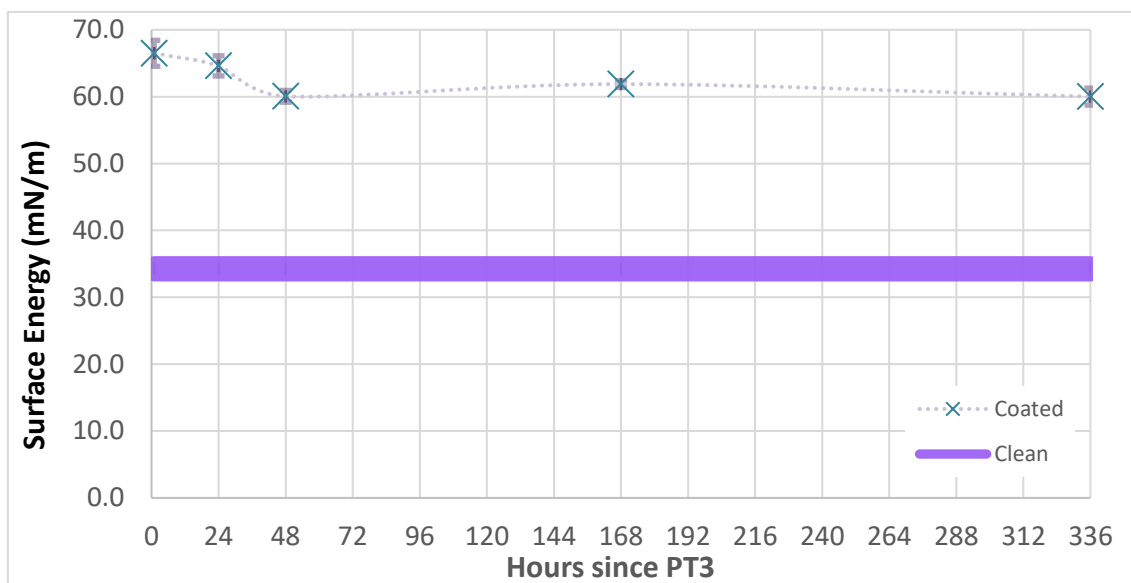


Figure 4-46 Surface energy of clean samples treated with fluorinated plasma (PT3) measured over two weeks. Blue markers represent the surface energy post-plasma treatment at each time interval, showing an initial decrease from 66.5 mN/m at 1 hour to 60.0 mN/m at 336 hours. The purple region represents the pre-plasma surface energy.

The clean samples treated with fluorinated plasma initially displayed a high surface energy of 66.5 mN/m, indicating a significant enhancement due to the plasma treatment. After 24 hours, the surface energy slightly decreased to 64.6 mN/m. At the 14-day mark, the surface energy slightly decreased again to 60.0 mN/m, indicating that while the surface energy remains relatively stable after the initial drop, there is a slight downward trend over this time. However, from observation it appears that the surface energy is still relatively stable, post 48 hours.

The surface energy stabilises around 60.0 mN/m after 14 days, which is still considerably higher than the initial surface energy of untreated samples. This suggests that while some loss of surface energy enhancement occurs, the treatment remains effective in maintaining a higher surface energy over an extended period.

The data suggests that fluorinated plasma treatment (PT3) could be beneficial for applications where enhanced surface energy is required for up to two weeks, with relatively stable performance after the initial aging period.

4.5.2.3 Lap shear

Lap shear strength tests are pivotal in assessing the adhesive performance of MTM44-1 composites under shear stress conditions, which are common in structural applications. This test measures the force required to slide one layer of composite material over another, providing a quantitative evaluation of the adhesive bond strength. High lap shear strength values indicate robust adhesive bonds capable of withstanding significant mechanical loads without failure. These results are critical for applications in aerospace and other industries where reliable adhesion is essential for structural integrity and safety. By analysing lap shear strength in conjunction with surface energy and contact angle measurements, we gain comprehensive insights into the adhesive properties and performance of MTM44-1 composites under practical conditions.

The breakage strength of the samples was evaluated along with the breakage mechanisms of each joint. These visual and categorical analyses provide critical insights into the effectiveness of different plasma treatments and the role of contamination in determining the failure modes of adhesively bonded joints. They also highlight the importance of comprehensive surface preparation in ensuring the durability and strength of bonded assemblies.

In section 4.2.3, Araldite 420 adhesive was used, which was a strong, liquid application adhesive. It was difficult to ensure constant bond line thickness with this adhesive and the strength of this adhesive was too high to give a comparison between treated and non-treated samples, which showed to be largely the same. For this study, a thin film adhesive, FM300 0.33mm, was used, supplied to the study from the National Composites Centre. This contained a mesh to ensure an equal bond line thickness across the bonding area.

Figure 4-47 shows the breakage force (kN) of lap shear samples subjected to different plasma treatment conditions, comparing the performance of uncontaminated (blue bars) and contaminated (orange bars) samples. The plasma treatments are denoted as Untreated, PT1, PT2, PT3, and PT4, as described in Table 3-1.

The breakage force for uncontaminated untreated samples was recorded at 4.2kN (+/-0.18), whereas contaminated untreated samples exhibited a substantial reduction in strength, with a breakage force of only 0.25kN (+0.75/-0.25). This highlights the significant detrimental effect of contamination on adhesion strength in the absence of plasma treatment.

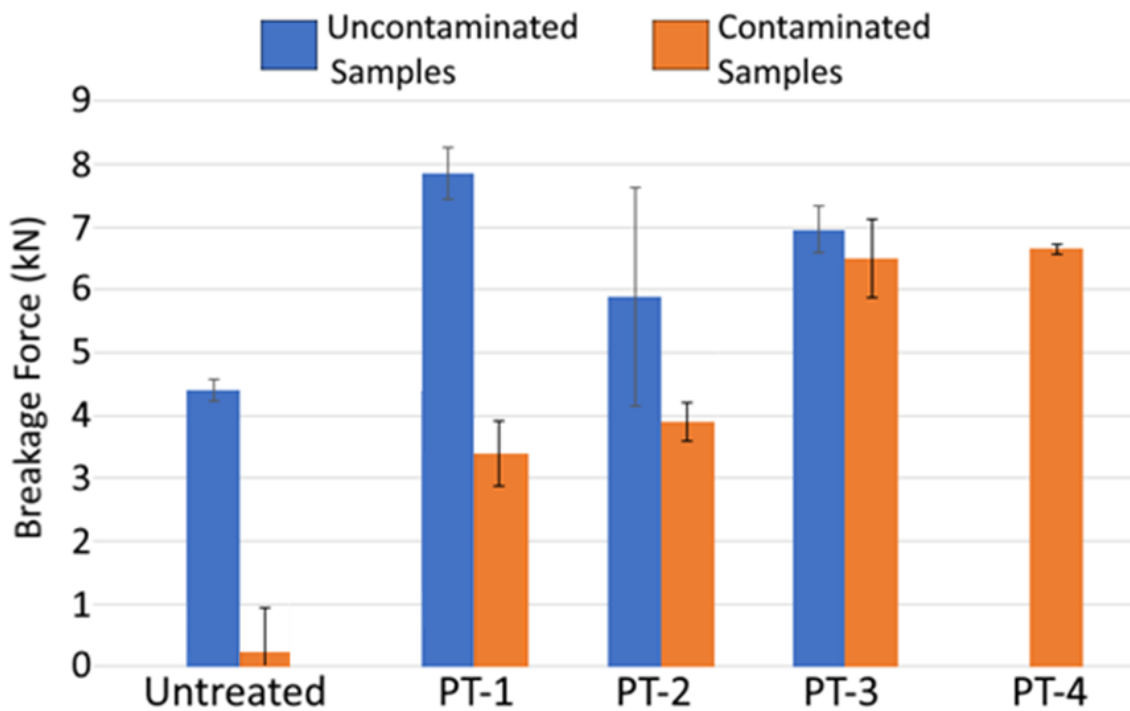


Figure 4-47 Lap Shear samples under various plasma conditions, comparing original samples (blue) and coated samples (orange). The untreated samples exhibit a significant difference in breakage force, with uncontaminated samples exceeding 4 kN and contaminated samples breaking below 1kN. Plasma treatments PT-1, PT-2, PT-3, and PT-4 all enhance the breakage force of both original and coated samples.

Uncontaminated samples treated with PT1 (argon) displayed a marked increase in breakage force to 7.9kN (+/-0.4), indicating a significant enhancement in adhesion strength due to the plasma treatment. However, when contaminated, the breakage force of PT-1 treated samples decreased to 3.4kN (+/-0.53), suggesting that while the treatment mitigates the adverse effects of contamination, it does not fully eliminate them.

The PT-2 treated uncontaminated samples demonstrated a breakage force of 5.9kN (+/-1.8), which, while showing improvement, was slightly lower than that observed with PT-1, and slightly overlaps within PT-1's error. Contaminated samples treated with PT-2 showed an increase in breakage force to 3.9kN (+/0.3), indicating that this treatment could possibly be marginally more effective in maintaining adhesion strength in the presence of contamination compared to PT-1, although this also falls within the error of PT-1.

Samples treated with PT3 showed a breakage force of 7kN (+/-0.34) for uncontaminated samples, comparable to PT1 in terms of enhancement. Notably, the breakage force for contaminated PT3 treated samples remained high, at around 6.5kN (+/-0.63), indicating that PT3 is highly effective in maintaining adhesion strength even under contaminated conditions.

The breakage force for contaminated samples treated with PT4 was averaged around 6.7kN (+/-0.1), suggesting that PT4 offers strong adhesion capabilities under contaminated conditions. It is worth noting that data for uncontaminated samples under PT-4 conditions were not tested due to material availability of the samples.

The data indicate that all plasma treatments (PT1, PT2, PT3, and PT4) significantly enhance the adhesion strength of lap shear samples relative to untreated samples. The highest breakage forces were observed with PT1 and PT-3 treatments. Contamination was found to substantially reduce the breakage force in untreated samples; however, the application of plasma treatments, particularly PT3 and PT4, was shown to effectively mitigate the impact of contamination, maintaining relatively high adhesion strength even in the presence of contaminants.

To better understand the failure mechanisms in adhesively bonded lap shear samples, the breakage types were analysed post-failure. The images provided in Figure 4-48 display evidence of the different failure modes. Table 4-20 summarises the different failure modes identified for both clean and contaminated samples across various surface preparation conditions.

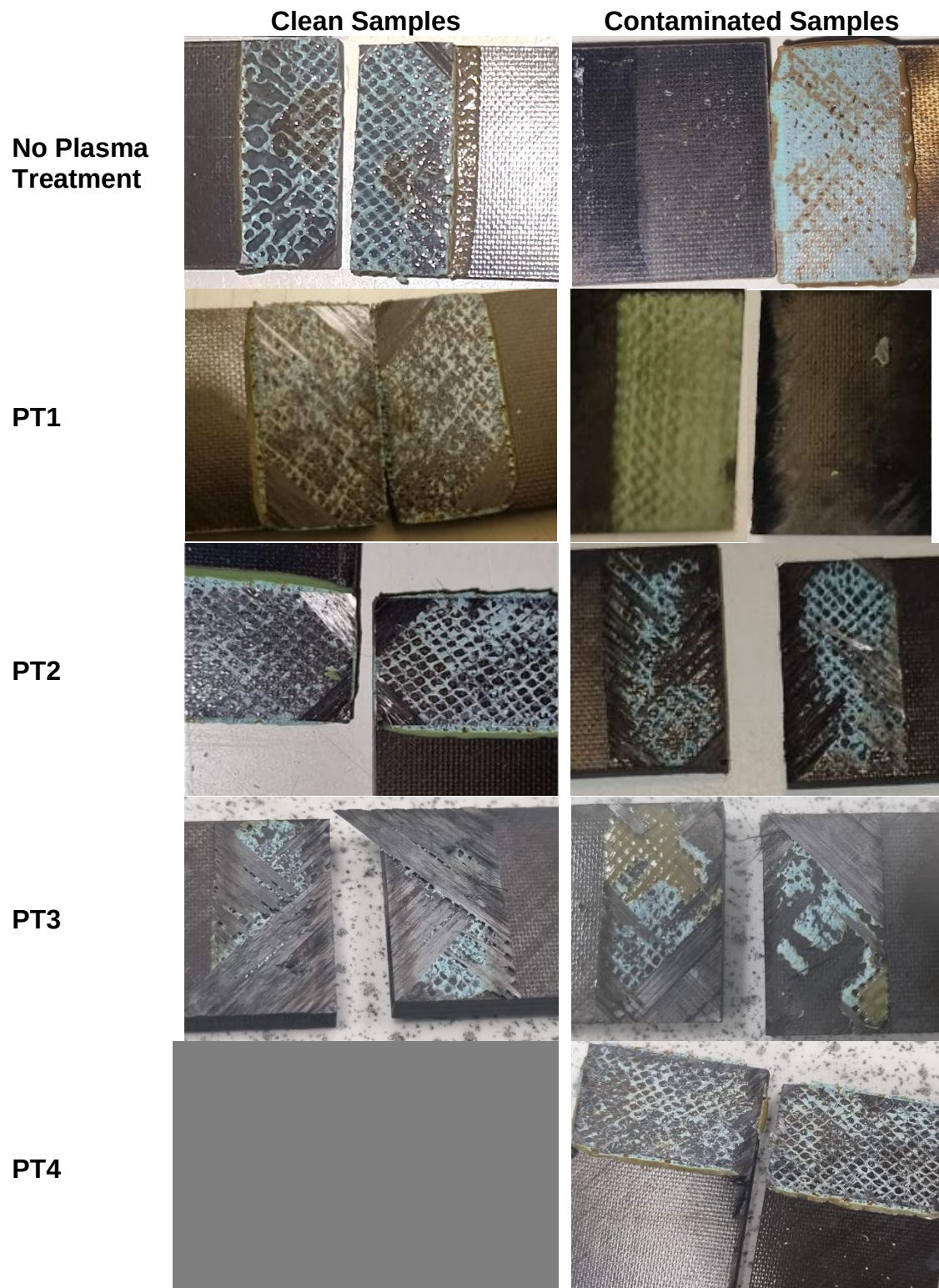


Figure 4-48 displaying photos taken after failure of a lap shear joint. These photos document various failure types, with some joints featuring multiple failure areas as detailed in PT3 contaminated samples which features all 3 failure methods.

Table 4-20 showing the different failure methods found at the surface of lap shear samples under different preparation conditions.

	Clean Samples	Contaminated Samples
No Plasma	Mixture of all 3 failure mechanisms.	Adhesive Failure.
PT1	Mixture of Cohesive Failure & Substrate/Adherend Failure.	<i>Predominantly Adhesive/Interface Failure.</i>
PT2	<i>Predominantly Cohesive Failure.</i>	Mixture of all 3 failure mechanisms
PT3	<i>Predominantly Substrate/Adherend Failure</i>	Mixture of all 3 failure mechanisms
PT4		Mixture of Cohesive Failure and Substrate/Adherend Failure

For clean samples, untreated surfaces exhibited a mixture of all three failure mechanisms, indicating inconsistent bonding. Plasma-treated samples (PT1, PT2, PT3, PT4) generally showed more cohesive and adherend failures, signifying stronger adhesion and bonding strength. In contrast, contaminated samples typically showed more adhesive failures, with some plasma treatments (e.g., PT1, PT2, and PT3) still resulting in mixed failure modes, though with a predominance of adhesive failure in certain cases.

In some cases, a single joint is depicted that exhibits all three failure modes as displayed in Figure 4-46. Although most joints primarily fail in one mode, this sample illustrates the potential for multiple concurrent failure mechanisms, likely influenced by a combination of surface treatment, contamination, and the inherent material properties. It also visualises where the three different failure mechanisms were determined. Interface failure is characterised by a dark green epoxy layer on one side of the sample, with a relatively clean looking epoxy finish surface layer on the adjoining coupon, similar to that of the unbonded section. The cohesive failure mechanism can be characterised by layers of light green-blue adhesive present on both sides of the broken sample. Substrate failure is characterised by the presence of bare carbon fibre, likely present on both sides.

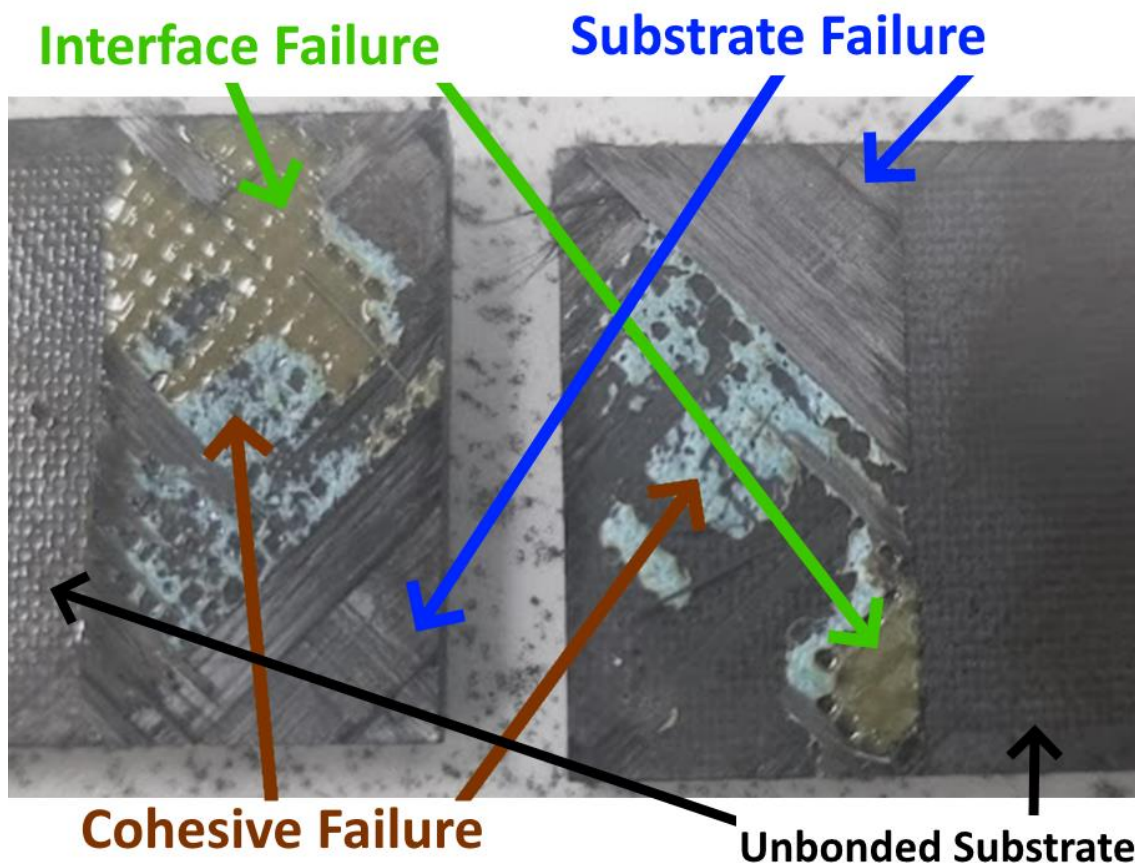


Figure 4-49 displaying a failed joint displaying all 3 modes of failure. Although most joints would predominantly break at only one mode of failure, this breakage was the result of all 3.

The analysis of breakage types is crucial in evaluating the effectiveness of surface treatments. Interface failure, or adhesive failure, occurs when there is a clear separation between the adhesive and the substrate, indicating suboptimal surface preparation. This type of failure suggests that the bonding between the adhesive and the substrate is weaker than the cohesive strength of the adhesive itself or the substrate's structural integrity.

On the other hand, the absence of interface failure generally points to a successful surface treatment, where the failure shifts to within the adhesive layer (cohesive failure) or within the substrate itself (substrate or adherend failure).

Cohesive failure indicates a strong bond between the adhesive and the substrate but a weakness within the adhesive material, whereas adherend failure suggests that the bond strength exceeds the structural integrity of the substrate. This latter

scenario could potentially raise concerns about whether the surface treatment might have compromised the substrate, although SEM studies, as shown in Figure 3-15, revealed no significant damage to the carbon fibres or the epoxy surface post-treatment.

4.5.2.4 Summary

The water contact angle measurements revealed that plasma treatments significantly improve surface wettability, indicating higher adhesive potential. Surface energy analysis further confirmed that plasma treatment enhances interfacial compatibility, with higher surface energy values correlating with stronger adhesive bonds.

When looking into the long-term effects of plasma processing, the effect seemed promising post 48 hours after treatment. Although the difference in plasma treatment mechanism resulting surface energy seemed negligible post 1 hour after surface treatment, the data indicates that post 1 week, a more intense surface treatment, such as is found in PT3, compared to PT2 (i.e. 6x as many passes due to every 1mm vs 6mm pass regime) seemed to reduce hydrophobic recovery time. This may be due to most samples reaching the maximum surface energy possible for the sample type, with the effect of PT3 reaching further down towards the subsurface, allowing for a thicker layer to prevent hydrophobic recovery. It could also be due to the more intense treatment of PT3 resulting in a physical surface roughening approach, that would not be visible under SEM.

Owen and Smith (26) suggests that plasma treatment creates a thin, silica-like, brittle layer on the surface, which initially increases wettability by introducing polar groups. However, over time, untreated polymer chains from the bulk can migrate through cracks in this brittle layer, leading to the surface becoming hydrophobic again. They note that more intense plasma treatments, which create thicker and stronger silica layers, can slow down the migration of these polymer chains, thereby delaying the hydrophobic recovery.

The intense treatments are likely to remove more contaminants and create a surface that is less likely to revert to its original state due to a more thorough modification of the surface chemistry. The repeated passes in PT3 could enhance these effects by ensuring that the entire surface is uniformly treated, further reducing the likelihood of hydrophobic recovery.

Lap shear tests provided practical insights into the structural integrity and adhesive performance of treated and untreated composites under mechanical stress. The results showed that specific plasma treatments, depending on the existence of contamination or not, led to cohesive or substrate failure modes rather than interface failures, suggesting improved bonding due to enhanced surface conditions. Importantly, the use of a thin film adhesive with consistent bond line thickness allowed for a clearer distinction between treated and untreated samples.

Overall, section 4.5.2.3 showed that fluorinated plasma, at either higher concentrations of SF₆ or longer treatment methods, shows a more effective treatment on contaminated samples, likely at the cause of fluorine-silicon interactions, although for non-contaminated samples argon plasma alone proved the most beneficial, likely due to better ionisation of pure argon when compared to fluorinated argon.

4.5.3 Summary of the effects of thermal radio frequency (RF) plasma

The effects of thermal radio frequency (RF) plasma, specifically reactive atom plasma (RAP), on the surface modification of MTM44-1 composites was explored, with a focus on surface chemistry, topography, and adhesive properties. The RAP 300 was chosen due to its success in etching silicon-based materials, making it a viable option for treating silicon-contaminated composites.

High temperatures generated by thermal RF plasma posed a significant challenge, as they could cause composites to burn or degrade. To mitigate these risks, an adapted raster pattern was implemented, spacing plasma passes at 1mm to allow for cooling, which distributed heat more evenly across the sample surface. SEM analysis revealed that while RAP effectively treated the surface, it did not show significant damage due to high temperature.

XPS was used to examine the chemical composition of the composites after plasma treatment. Argon plasma treatment led to oxidation of the surface, increasing the presence of oxygen-containing groups and reducing fluorine content. Fluorinated plasma treatment introduced fluorine-containing groups, significantly altering the surface chemistry by reducing C-C/C-H/C-Si bonds and increasing C=O and O=C-O groups. Overall, in contaminated samples, fluorinated plasma reduced the percentage of silicon, indicating effective etching and oxidation.

Plasma treatment significantly increased the surface energy of MTM44-1 composites, improving their wettability and adhesion properties. Surface energy measurements showed substantial increases after treatment, especially with fluorinated plasma, which maintained higher surface energy over time compared to pre-plasma treatment. Lap shear tests confirmed that plasma-treated samples had improved adhesive strength, with fluorinated plasma providing superior adhesion on contaminated surfaces. The failure analysis indicated that plasma-treated samples primarily experienced cohesive or substrate failures, reflecting stronger adhesive bonds compared to untreated samples, which mostly exhibited adhesive failures.

5 Conclusions

This thesis explored the application of atmospheric pressure plasma (APP) as a surface treatment technique for carbon-fibre epoxy composites, specifically focusing on the challenge of removing silicone-based release agents, which posed a barrier to effective adhesive bonding in aerospace composite manufacturing. Prior to this study, no successful method had been validated for the reliable removal of such contamination without damaging the surface.

5.1 Summary of findings addressing aims and objectives

1. Investigate both non-thermal and thermal plasma for increasing adhesion

The first objective was achieved, using a mix of non-thermal sources, and one RF thermal torch using either argon or argon and fluorine. Both plasma types were indicated to increased adhesion. Thermal RF showed the highest removal efficiency of silicone contaminants without visible surface degradation.

2. Measure the impact of plasma treatment on surface energy using contact angle analysis

Plasma treatment decreased water contact angles significantly, increasing wettability regardless of contamination or plasma source.

3. Assess short- and long-term ageing effects on surface energy

Short-term ageing (<48 hrs) retained high surface energy. Longer-term studies indicate partial reversion depending on environmental exposure.

4. Optimise treatment speed for a uniform surface treatment

1 m/min treatment speed with a spiral raster pattern was found to provide an effective surface treatment and thermal management without damage.

5. Investigate plasma treatment for silicone removal

Plasma (thermal RF with fluorinated gas) was effective in significantly reducing silicone content, as validated by XPS and lap shear testing.

5.2 Main findings

Regardless of thermal RF or non-thermal MW/DBD plasma, or choice of gas used between argon, fluorinated argon or nitrogen, the study supported that atmospheric pressure plasma (APP) was a viable method for surface treatment of carbon fibre epoxy composites, particularly the aerospace grade composite MTM44-1. All results showed that APP was capable of increasing surface energy and/or decreasing the water contact angles, or composite surfaces, when compared to before treatment.

Non-thermal dielectric barrier discharge (DBD) nitrogen plasma exerts a notable influence on both uncontaminated and silicone-contaminated CFRP surfaces. In uncontaminated samples, the plasma predominantly enhances surface oxidation, leading to an increase in carbonyl and hydroxyl functionalities that elevate surface energy and promote improved wettability. However, in heavily silicone-contaminated samples, the same treatment is only partially effective in oxidising and reducing the silicone layer, leaving residual contaminants that continue to impede adhesion. These findings indicate that while DBD nitrogen plasma is a useful tool for surface activation, it may require further optimisation or complementary treatments to fully remove persistent contaminants like silicone-based release agents.

Across all plasma treatment regimens, one consistent outcome is the improvement in wettability, as evidenced by reduced water contact angles on treated surfaces. This enhancement is achieved whether plasma fully eradicates the silicone layer or causes surface chemistry interactions of the contamination layer itself. However, when contamination is not, or only partially, removed, the remaining silicone can still form a barrier to optimal adhesion, despite its temporary increase in surface energy. Lap shear tests confirm that complete or near-complete removal of silicone contamination correlates strongly with robust, reliable bonding, underscoring the importance of thorough surface decontamination for high-performance CFRP applications.

Argon plasma alone introduces polar functional groups through surface oxidation and mild etching, effectively increasing the density of carbonyl or carboxyl groups.

This process contributes to better adhesive bonding by creating chemically active sites on the epoxy surface.

Fluorinated plasma had been shown in previous studies to remove surface contamination, when used with a thermal RF torch. The fluorine atoms effectively target Si–O and Si–CH₃ bonds, significantly reducing silicone content. The combination of higher temperatures, with the use of a fluorine and argon gas mixture, resulted in significant removal of silicon at the surface of samples, to much lower levels. As a result, lap shear results show that this surface treatment has a comparable lap shear breakage force to that of uncontaminated samples which have undergone plasma treatment, particularly when tripling the fluorine content of the plasma's feed gas.

This high temperature technique (Thermal RF plasma) was originally not explored due to the possibility that it may cause samples to burn or degrade. Experimental results confirm that thermal RF plasma, when applied in a spiral raster pattern at a moderate treatment speed, does not induce observable thermal degradation in CFRP substrates. Scanning electron microscopy (SEM) images showed no significant signs of surface degradation from plasma, at speeds of 1m/min with a spiral raster pattern used to allow the surface to cool in between passes. As a result, it was concluded that a well-managed process can effectively remove silicone contamination without compromising the composite's structural integrity.

Overall, this research demonstrates that atmospheric pressure plasma can be tailored through gas composition, plasma type, and treatment parameters to provide effective surface preparation for adhesive bonding of CFRP composites. The ability to remove silicone-based contaminants without mechanical abrasion or solvent cleaning has strong implications for aerospace manufacturing, particularly in automation and cleanroom environments. Thermal RF plasma using a fluorine-argon mixture achieved the most effective removal of silicone contamination, leading to lap shear strength comparable to uncontaminated samples, especially when the fluorine content was tripled in the gas mixture.

5.3 Recommendations for industrial applications

When considering the industrial applications of this study, Atmospheric pressure plasma (APP) is strongly recommended as a viable and scalable surface treatment for carbon fibre reinforced polymer (CFRP) composites in industrial settings, particularly where silicone-based release agents are used in the manufacturing process. The results suggest that plasma treatment not only enhances surface wettability but, when optimally configured, can effectively remove surface contaminants that traditionally hinder adhesive bonding.

For applications requiring the removal of silicone-based release agents (as often is the case involving aerospace-grade composites like MTM44-1) the use of thermal RF plasma with a fluorinated argon gas mixture is recommended. Specifically, increasing the fluorine concentration in the feed gas (up to three times the standard level) yielded the most significant reduction in silicone contamination, while maintaining surface integrity. When applied at a speed of 1 m/min using a spiral raster pattern, this configuration provided excellent adhesion results, comparable to those of uncontaminated control samples. This setup also prevented thermal degradation, as confirmed by SEM imaging.

In contrast, argon-only and non-thermal plasma delivered moderate oxidation effects that improved adhesion but was less effective in removing silicone contamination. This configuration may still be suitable for less critical bonding operations or for substrates that have already undergone surface cleaning through other methods.

Therefore, for critical bonding applications, particularly in the aerospace and defence sectors, the recommendation is to adopt thermal RF plasma systems with fluorinated argon, optimised at 1 m/min treatment speed with spiral rastering to ensure consistent exposure and adequate cooling. This method offers a promising, contamination-removing alternative to traditional surface preparation methods and can be integrated into automated, high-throughput manufacturing lines with relatively low risk of substrate damage.

6 Further Work

Future studies could focus on understanding the thermal effects and morphological changes induced by plasma on the composite materials. While the current work has provided significant insights into the surface temperatures, further investigations using temperature-controlled experiments would help quantify the thermal load transferred to the substrate during plasma processing. Continuous heat monitoring, paired with advanced thermographic techniques, could provide a clearer picture of how temperature fluctuations during plasma treatment affect the surface and bulk properties of the composite material.

Additional surface investigations using scanning electron microscopy (SEM), coupled with X-ray photoelectron spectroscopy (XPS) depth profiling, would be beneficial. Such techniques would offer detailed insight into the microstructural changes and the effective depth of plasma treatment. The extent of surface etching and contamination removal could be evaluated, providing a more comprehensive understanding of the plasma's impact on surface roughness and topography. Further XPS studies could assist in quantifying the remaining contamination layers after plasma treatment and how these evolve with increased plasma exposure or variations in gas composition.

To allow for the adoption of this technique into industry, additional studies are required to explore optimised processing speeds. The results of this study suggest that treatment speeds can significantly influence the adhesion properties of composite surfaces; however, the trade-off between treatment efficiency and time needs further exploration to enhance processing rates for industrial applications without sacrificing treatment quality.

Further investigations into the aging effects of plasma-treated surfaces are also necessary to determine the longevity of the enhanced adhesion properties. Understanding how the surface chemistry, energy and lap shear strength decay over time would allow proper storage and handling of composite post-processing and understand the maximum time post-treatment that sample surfaces can still be adhered to.

Additionally, studies on scaling up the plasma treatment process should focus on uniformity of treatment across larger surface areas. The feasibility of integrating multiple plasma torches or continuous treatment systems could be evaluated, especially for larger industrial components. Lastly, investigations into the effects of gas concentrations and mixtures, such as altering the concentrations of SF₆ to argon, would provide valuable information on optimising plasma chemistry for different types of contamination and surface types. This could allow for more tailored plasma treatments.

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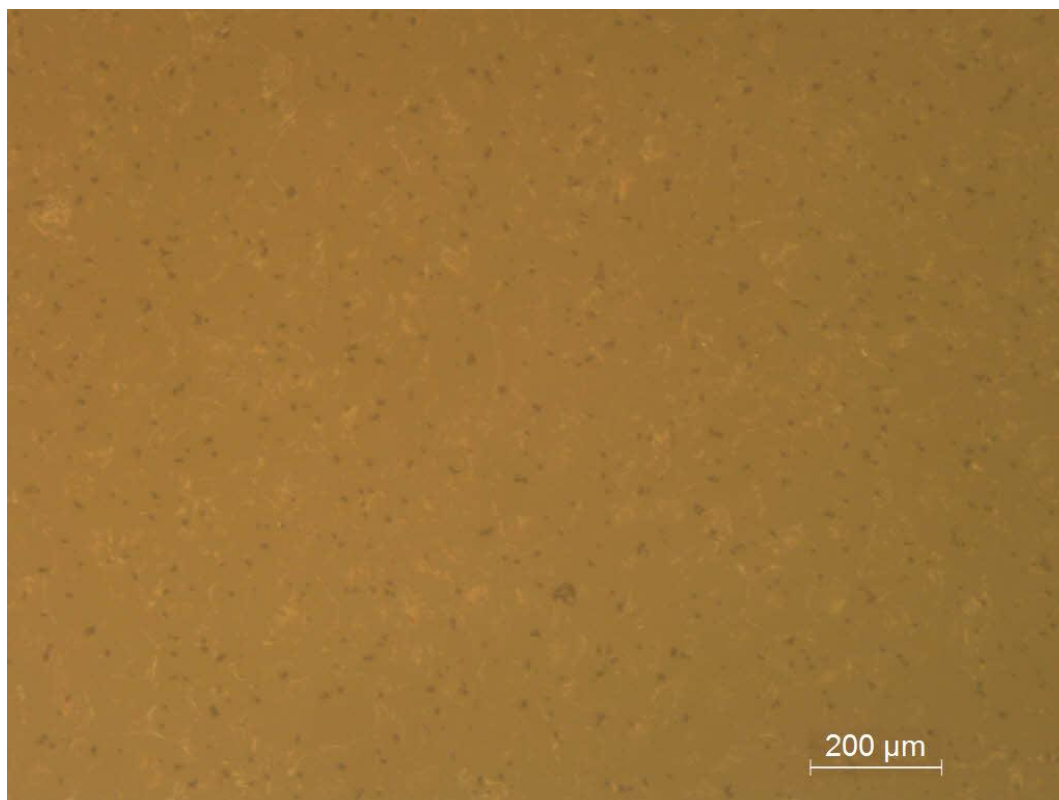
APPENDICES

Appendix A Initial Chemlease Coating Studies

An optical microscope, followed by SEM was used to determine optimal parameters to produce an even coating of contaminant.

A.1 Glass Slide Studies

A clean glass slide was imaged initially to show the clean surface.



1:1 IPA: Chemlease was spun coat at 200 RPM and 250RPM onto glass slides.

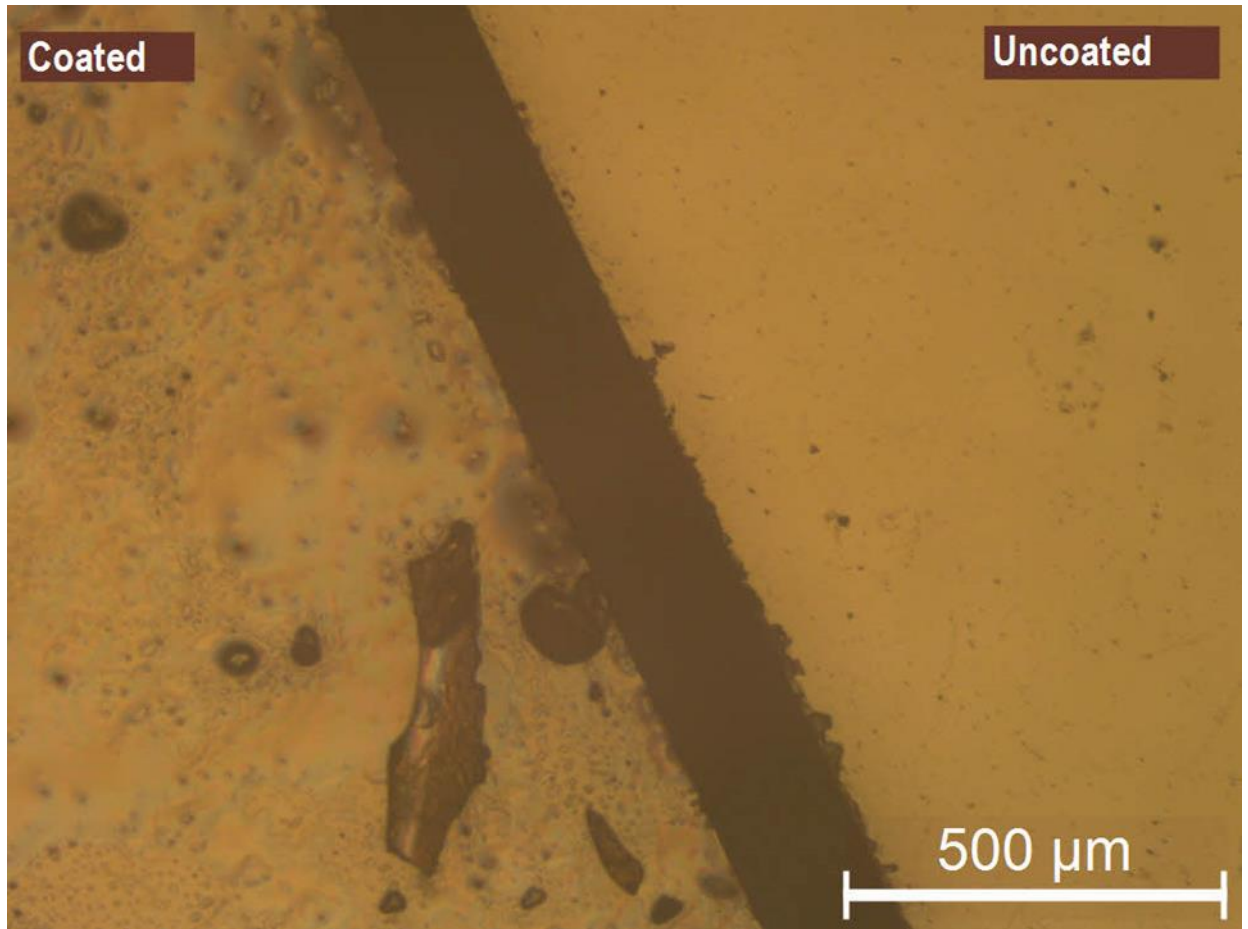


Figure 6-1 200RPM

Appendix B Uniformity of Surface Energy Analysis

B.1 Adapted Spray Wetting Test

The change in surface energy across a sample was initially measured using an adapted version of the spray wetting test. This test was initially trailed on mylar samples using microwave plasma and measurement via optical microscopes. A single pass of plasma was processed across a sample, and water was sprayed onto the sample to visualise where the water could gather in high surface energy zones. Although this was not a precise measurement, it gave an approximation for where effective wetting could take place across the sample, as shown in Figure 6-2. However, as CFRP samples were darker in colour, this method was too difficult to utilise in composite studies.

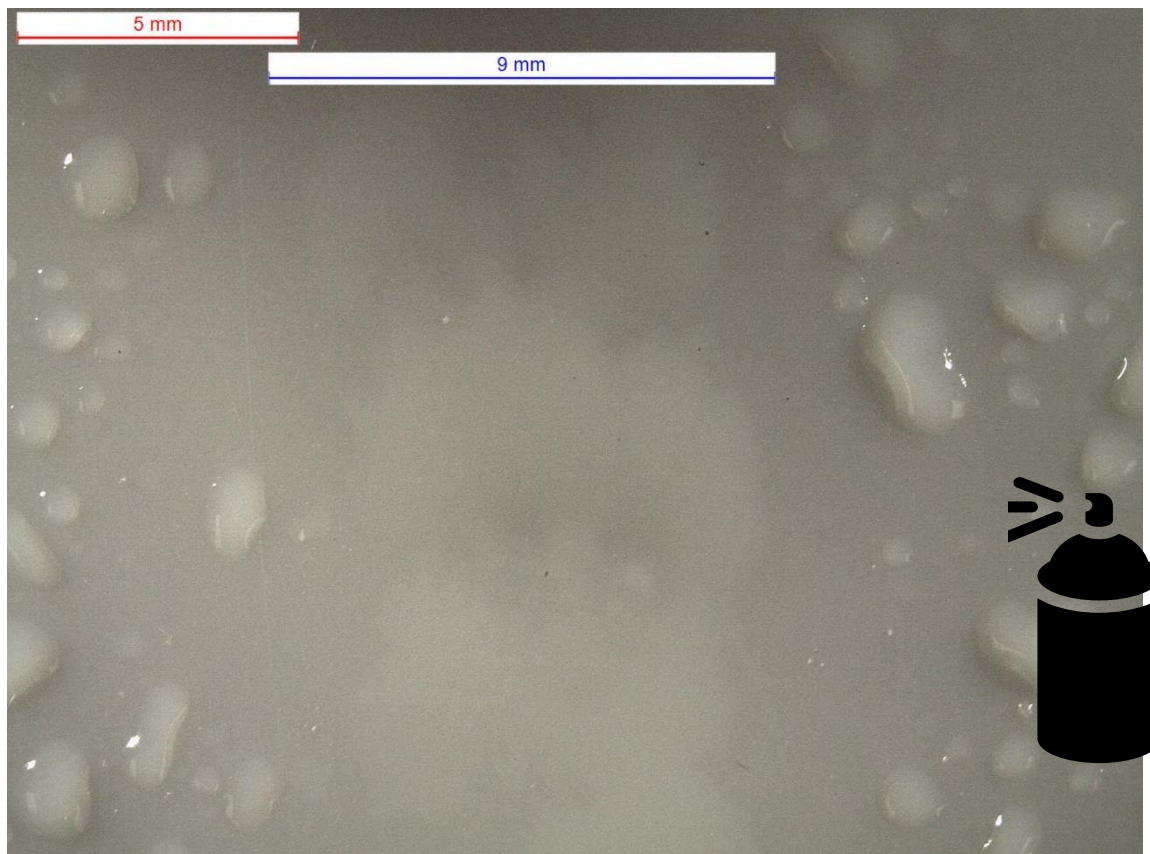


Figure 6-2 The results of an adapted spray wetting test on mylar samples

B.2 Using water contact angle to measure uniformity

In order to better understand uniformity, water contact angles were measured across a sample where a plasma pass had occurred in a configuration demonstrated in Figure 6-3. The results of this were visualised in a graph as shown in Figure 6-4

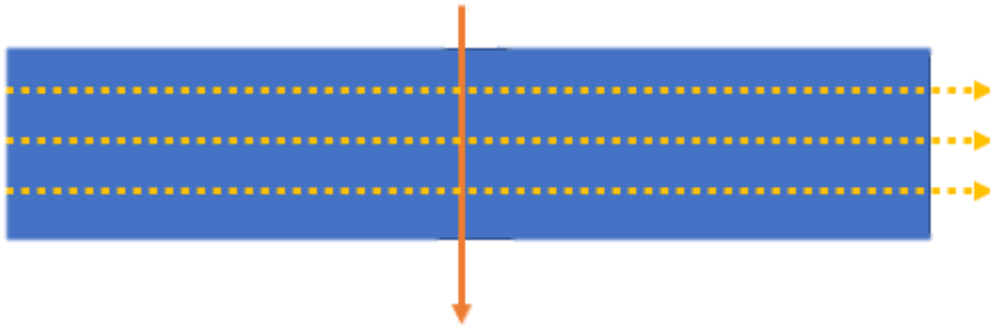


Figure 6-3 The location of water contact angle measurements across a sample (yellow) where a plasma pass had occurred (orange arrow)

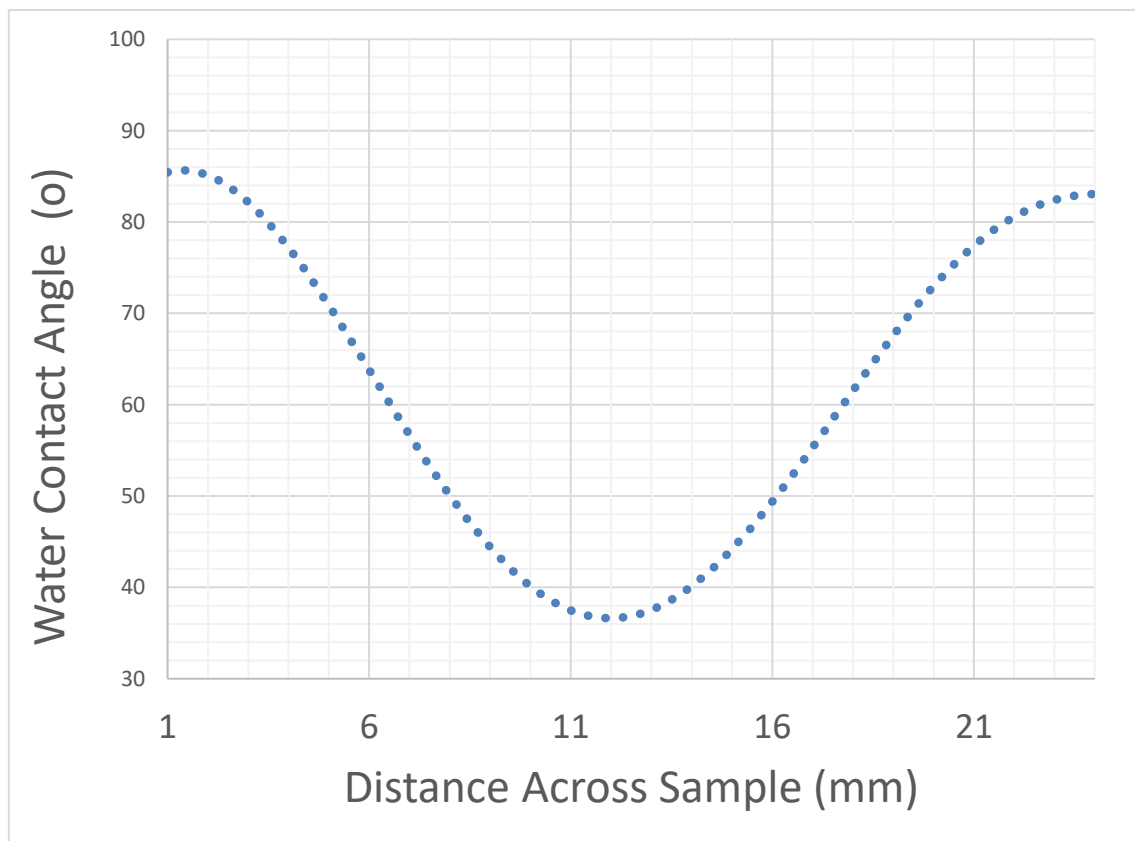


Figure 6-4 Displaying the average water contact angle change across a sample where a single plasma processing pass had accounted.

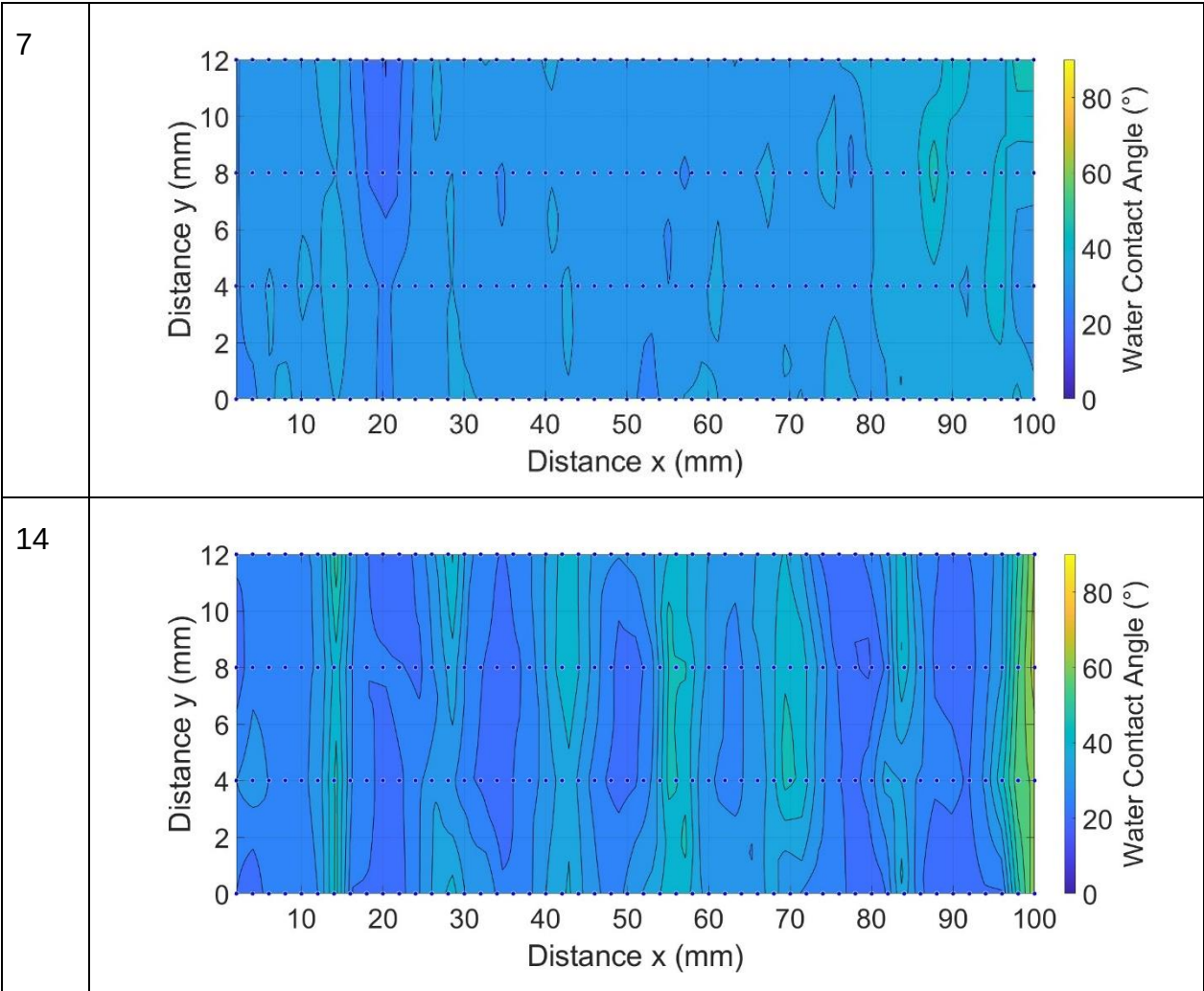
**B.3 Further studies on Water Contact Angles on the surfaces
MTM44-1 samples treated with MIP argon plasma.**

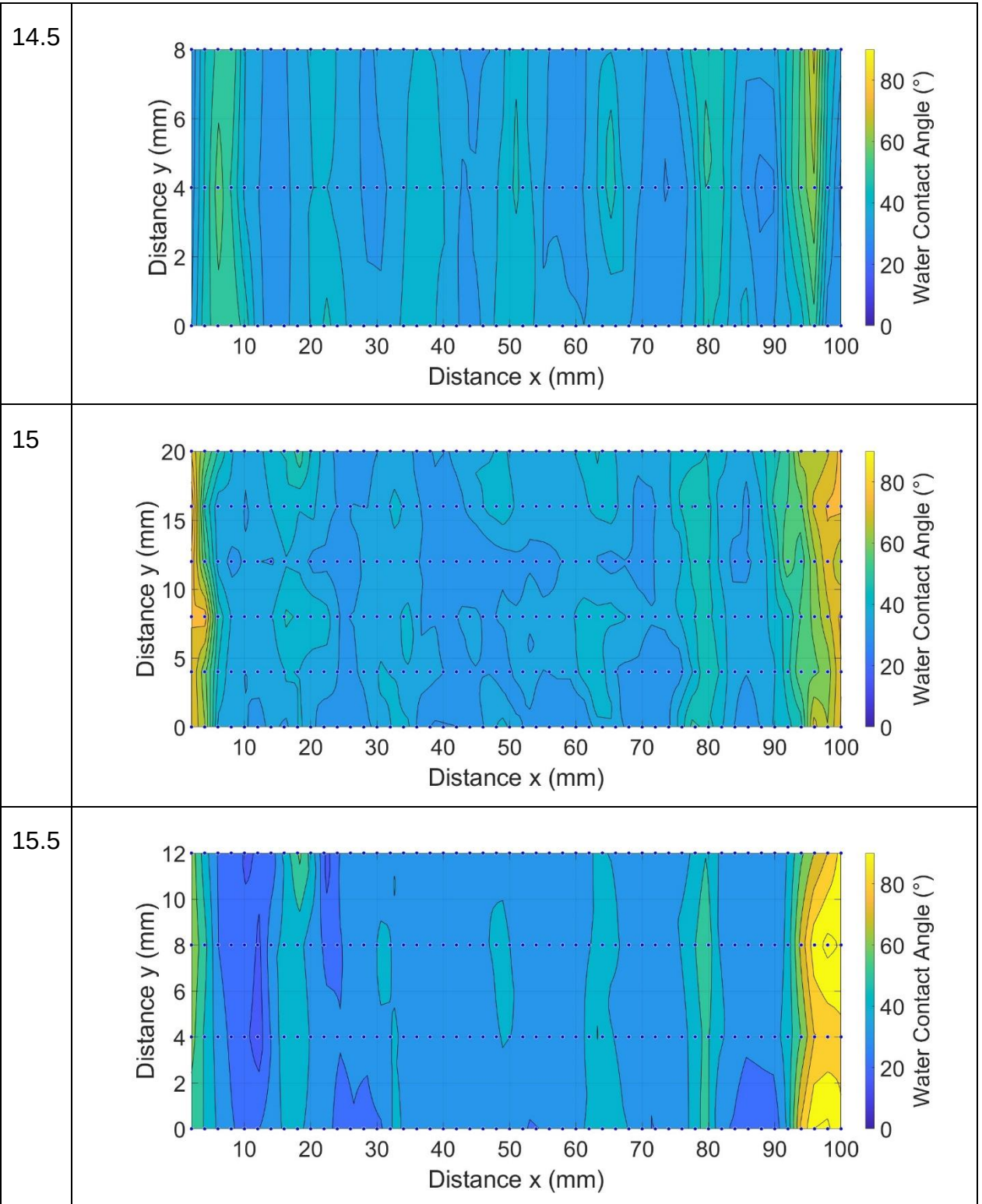
This appendices displays further results studied in assessing idea plasma pass parameters.

B.3.1 Treatment speeds of 1m/min

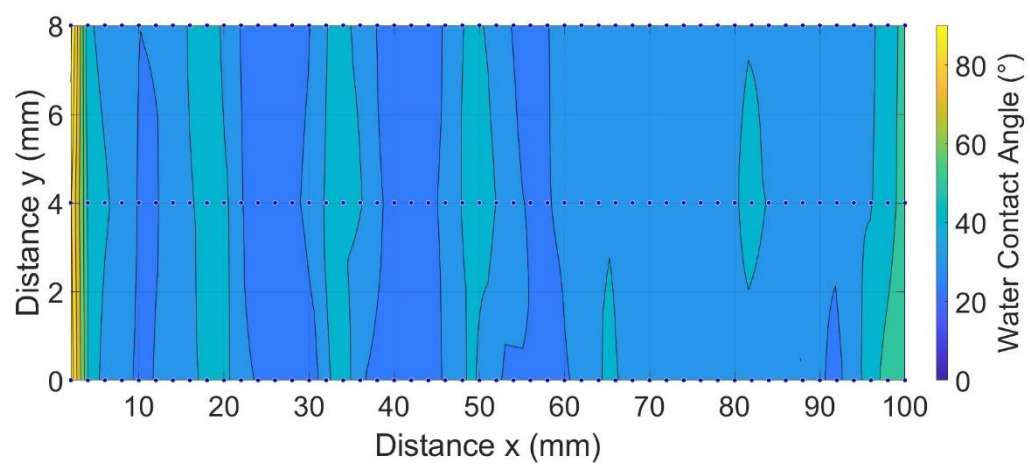
This includes looking at pass dynamics of passes 14, 14.5, 15, 15.5 and 16mm apart.

Table 6-1 displaying maps of WCA across MTM44-1 samples with varying distances in between plasma passes in mm





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Appendix C Pie Charts of Deconvoluted Peaks of Contaminated Samples

In order to better visualise potential surface changes from section 4.5.1.2, a series of pie charts were created as shown in _ for the Carbon C1s peak, _ for the Silicon Si2p peak and _ for the O1s peak. This was particularly beneficial in understanding the overall change in the O1s region as described in 4.5.1.2.1.

Table 6-2 Carbon C1s bonding environment percentages. Plasma treatment decrease % of C-C/C-Si bonds and creates Carbon-Oxygen bonds

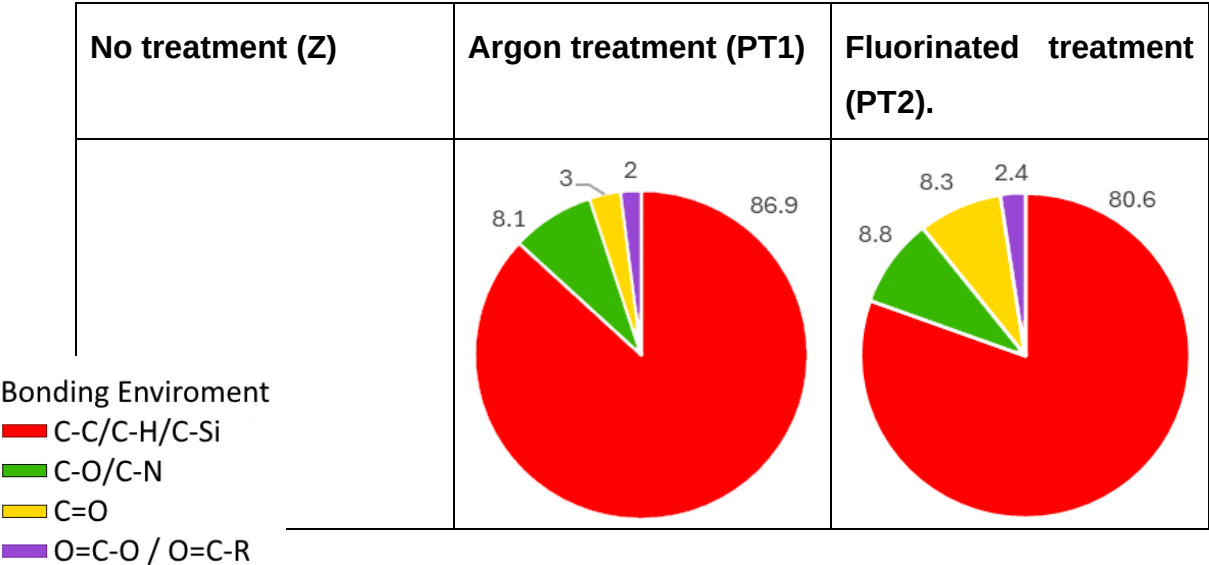


Table 6-3 Silicon Si2p bonding environment percentages. Plasma treatment causes Si-O to be converted to Si-O2

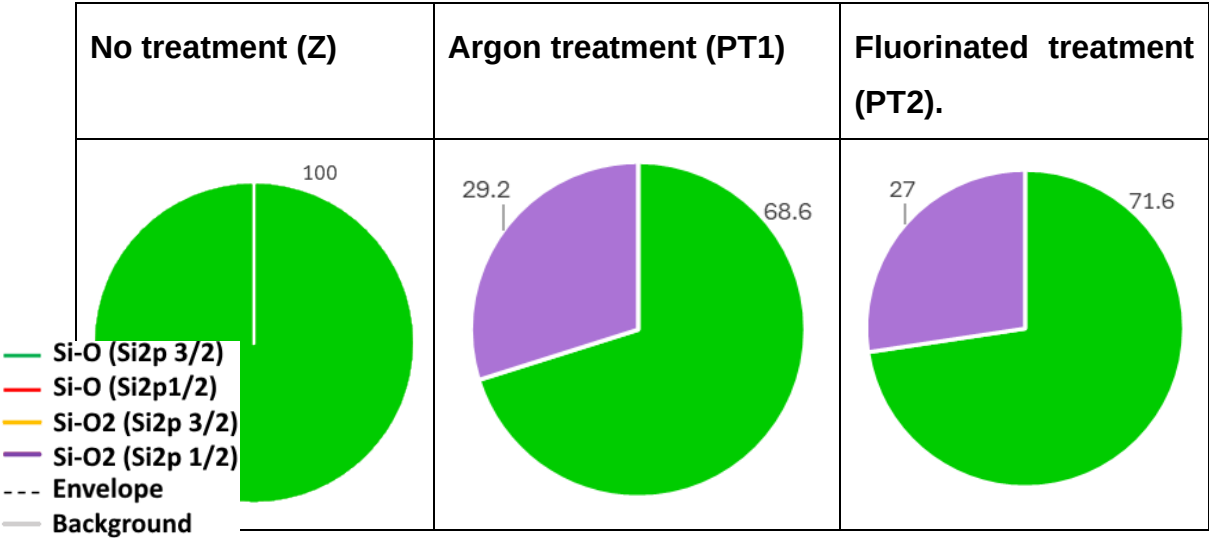


Table 6-4 Oxygen O1s bonding environment percentages. The first row shows just the data from the deconvoluted peaks, where the second region displays the oxygen binding region, with information from the C1s and Si2p regions combined. O1s region shows a conversion of Si-O to Si-O₂, which is supported when looking at the Si2p & C1s region

