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Doctoral Dissertation

Doctoral Program in Mechanical Engineering (38th cycle)

**From Surface Activation to Delamination Resistance:
Nitrogen Atmospheric Pressure Plasma Jet Effects on
Unidirectional Carbon Fiber Composites for
Sustainable Mobility Applications**

By

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Declaration

I hereby declare that, the contents and organization of this dissertation constitute my own original work and does not compromise in any way the rights of third parties, including those relating to the security of personal data.

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2026

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Abstract

Fiber-reinforced epoxy composites represent the foundation of lightweight structures for sustainable mobility applications, where delamination is often the primary failure mode limiting structural performance and durability. This thesis investigates nitrogen-based Atmospheric Pressure Plasma Jet (APP Jet) surface treatments applied to industrial-grade unidirectional (UD) carbon fiber textiles through a multiscale experimental framework that spans surface treatment design, surface characterization and mechanical testing. The work is structured around the progressive assessment of the treated reinforcements at micro-, meso- and macro-scale, with the aim of clarifying how processing parameters affect surface state and how these changes translate, when possible, into interfacial and laminate-level responses.

The experimental campaign begins with the definition of a suitable APP Jet process window, based on primary and secondary plasma parameters namely jet power, stand-off plasma-substrate distance, exposure time and gas flow, in order to balance cleaning, etching and functionalization while preserving fiber integrity. Surface characterization by Optical Emission Spectroscopy (OES), Fourier Transform Infrared in Attenuated Total Reflectance (FTIR-ATR) spectroscopy, X-ray Photoelectron Spectroscopy (XPS), SEM-EDS and micro-Raman spectroscopy show effective removal of peel-ply residues and sizing contaminants, an increase in oxygen-to-carbon ratio and the introduction of polar functional groups ($-\text{OH}$, $-\text{C}=\text{O}$, $-\text{COOH}$), while preserving graphitic order and fiber morphology. These observations provide a surface-level basis for evaluating the treatment effectiveness and for defining the most suitable processing conditions.

To assess the practical value of the treatment across scales, the thesis combines microbond tests, transverse fiber bundle tensile tests (TFBT), Mode I Double Cantilever Beam (DCB) tests, and dynamic impact testing. Microbond testing is used as a first screening tool for local interfacial response, while TFBT provides a meso-

scale assessment of bundle-level behavior and failure modes. At the laminate scale, DCB testing reveals an increase in Mode I fracture toughness for the treated system, whereas dynamic impact tests show a less pronounced treatment effect under high strain-rate loading. Taken together, these results indicate that the plasma treatment is effective in quasi-static delamination-dominated conditions, but that its influence becomes less detectable when bulk damage mechanisms dominate.

A key element of the work is the critical evaluation of micro- and meso-scale testing as quantitative predictors of interface strength in industrial UD textiles. The study shows that these methods are useful for ranking surface states and for identifying qualitative changes in failure behavior, but their quantitative predictivity is limited by specimen geometry, treatment sensitivity, and the complexity of the failure mechanisms involved in industrial UD reinforcements. In this sense, the work does not treat small-scale testing as a substitute for laminate validation, but as a hierarchical screening route that helps reduce material consumption, testing time, and experimental effort before committing to full-scale mechanical characterization.

By integrating multiscale mechanical data with detailed surface analysis, the thesis defines an APP Jet process window that delivers reproducible gains in quasi-static delamination toughness on UD laminates, while maintaining compatibility with industrial constraints. Compared to traditional wet oxidation or solvent-based surface treatments, the nitrogen APP Jet approach is dry, solvent-free and inline-compatible, reducing process steps and drying times and offering clear opportunities for energy and environmental impact reduction. These surface treatment technology effects are hence presented in the thesis in terms of interfacial improvement under quasi-static conditions and according to its methodological limits of inferring laminate performance from smaller-scale tests alone. The resulting multiscale framework supports a more cautious and structured interpretation of plasma-assisted interface modification in industrial composites.

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Chapter 1

Introduction

1.1 Application Context

Over the last decades, increasingly stringent climate and energy regulations have pushed the transportation and aerospace sectors towards drastic reductions in greenhouse gas emissions, fuel consumption and life-cycle environmental impact [3]. In both fields, one of the most effective strategies to achieve these goals is weight reduction, as every kilogram saved at vehicle or aircraft level directly translates into lower energy demand and extended range [4]. As a result, there has been a progressive shift from traditional steel-intensive designs to lighter metallic solutions, such as aluminum and titanium alloys, and, more recently, to advanced fiber-reinforced polymer composites, which offer high specific stiffness and strength together with excellent fatigue and corrosion resistance as stated by Sharma et al. [5], providing the material rationale for the composite systems investigated here. Figure 1.1, for instance, illustrates the material distribution by weight in the Boeing 787 airframe, highlighting the dominance of composites (50%) over metals like aluminum (20%), titanium (15%), steel (10%), and others (5%).

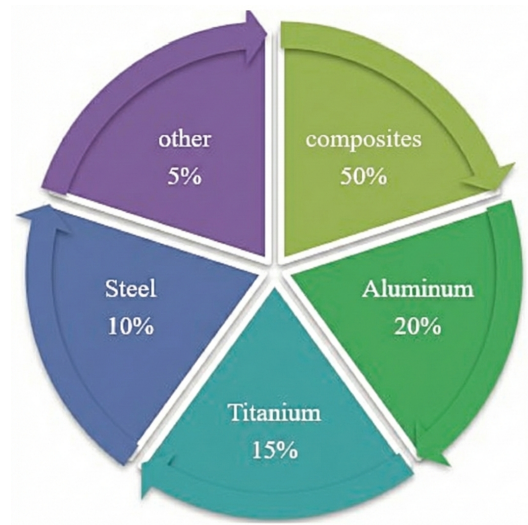


Fig. 1.1 Example of materials usage in aerospace field, in particular in boeing787 body. Adapted from Mahesh et al. [6]

These lightweight materials are particularly attractive for next-generation sustainable mobility concepts, including battery-electric, hybrid and hydrogen-based architectures, as well as for modern aircraft and spacecraft, where mass penalties associated with energy storage systems, tanks, satellites or additional control equipment must be compensated by structural weight savings. In this broader perspective, composite materials are increasingly viewed not only as load-bearing solutions for current aerospace structures, but also as enabling materials for future mobility platforms, where their role extends across structural, functional, and interior components, as schematically summarized in Figure 1.2. The associated reference is therefore not merely illustrative, but helps contextualize the application range that motivates the present study.

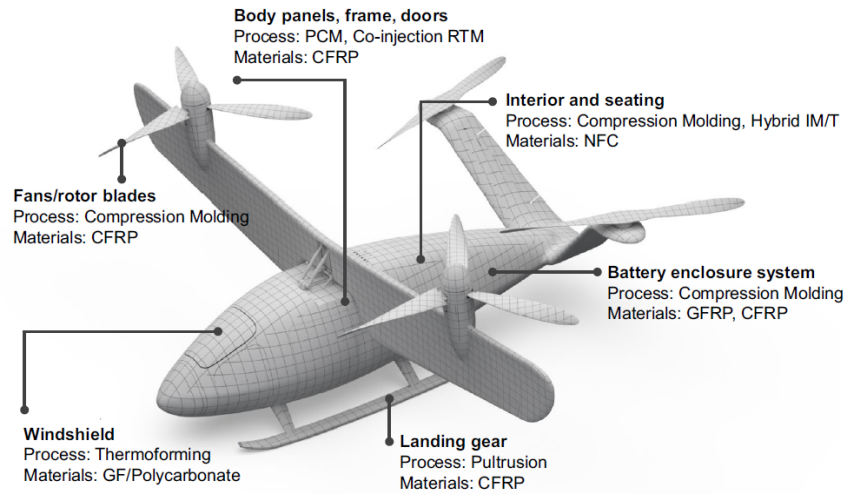


Fig. 1.2 Composite applications for future mobility platforms [7].

At the same time, the widespread adoption of composite materials raises new challenges in terms of manufacturing robustness, long-term durability and damage tolerance as presented by Simões [8]. The latter article is relevant because it points to the non trivial reliability issues that accompany the use of composites in structural applications. Specifically, the integrity of the fiber–matrix interface and the resistance to interlaminar delamination become critical design drivers for primary and secondary structures in both aeronautical components and advanced ground vehicles. In particular, delamination resistance emerges as critical across loading regimes—from quasi-static to dynamic/impact conditions—while the fiber-matrix interface remains the primary determinant of interlaminar integrity in primary structures as stated by de Castro Saiki[9].

While macroscale mechanical characterization, such as Mode I Double Cantilever Beam (DCB) and In-plane impact test (according to standard ASTM D7136 and built-in texting fixture [10]), provides useful validation of delamination resistance and interfacial performance, these protocols are inherently time-intensive [11]. This motivates the multiscale screening strategy developed in the thesis. Laminate fabrication via vacuum resin infusion, specimen preparation and testing, typically span weeks per batch, limiting rapid screening during process adaption to achieve enhanced component delamination resistance.

Beyond material selection and structural design, sustainability targets also call for cleaner and more efficient manufacturing routes. Conventional surface preparation

and adhesion-promoting treatments still rely on wet chemical processes, aggressive reagents and energy-intensive drying steps [12]. These routes introduce safety and environmental issues, generate chemical waste and increase production costs and cycle times [12]. Therefore, there is a growing demand for dry, scalable, and scalable surface engineering technologies that can be integrated into automated composite manufacturing lines, improving interfacial performance without relying on solvents or complex chemical conditioning, as stated by Asmatulu et al. [13] and Marques et al. [14].

The present thesis investigates nitrogen-based Atmospheric Pressure Plasma (APP) Jet surface treatment for unidirectional (UD) carbon-fiber/epoxy composites through a comprehensive multiscale approach aimed at accelerating interface characterization. The work evaluates a dry, solvent-free APP Jet process to enhance fiber–matrix adhesion and delamination resistance across length scales and loading rates, while developing micro/meso-scale testing protocols intended to reduce the time and resources of macroscale validation. The purpose of this work is to establish correlations between surface chemistry modifications and macroscale mechanical performance, particularly under quasi-static delamination. It assesses the capabilities and limitations of micro/meso-scale screening for industrial-grade UD fabrics. These methods revealed challenges in sensitivity and calibration between untreated (NT) and N_2 -treated carbon fibers. Ultimately, the work delivers mechanical performance insights alongside a proper evaluation of multiscale characterization strategies.

1.2 Research Motivation

Advanced composites perform in specific stiffness/strength but the weakness of the fiber-matrix interface still remains, dictating structural reliability. Carbon fibers' graphitic inertness (low %O/C ~ 0.05 – 0.1) and commercial sizings (peel-ply residues) yield poor epoxy wettability, $\theta > 90^\circ$ of polar and non-polar contact angle, compromising chemical bonding (van der Waals, hydrogen and covalent bonds) and mechanical interlocking. Previous work dissected this chemo-physical barrier in twill CF/epoxy [15], revealing modest Mode I/II gains (+14–16% (G_{IC})-(G_{IIC}) and increased stability in crack propagation) via mixed-gas APP jet, in particular N_2 and N_2/H_2 gas sources as also found by Sampino et al. [16], as closest methodological antecedent to the present study.

Mechanically, suboptimal adhesion manifests as interlaminar delamination, composites' predominant failure mode in service. M. R. Wisnom [17] linked this behavior directly to through-thickness failure owing to interlaminar stresses caused by out-of-plane loading, curved or tapered geometry, or discontinuities owing to cracks, ply drops or free edges. The author has also underlined the crucial role of delamination in in-plane failure related to transverse matrix cracks, which is why the comparison with respect to the aforementioned work is useful for framing the failure mechanisms considered later in the present work.

Mode I crack propagation dominates quasi-static/fatigue scenarios, while dynamic/impact loading aggravates damage via matrix-dominated cracking and fiber kinking [18] [19]. In UD laminates—hallmark of industrial aero preforms—delamination critically reduces compressive-after-impact (CAI) strength and fatigue endurance, curtailing primary load-bearing applications. Sato et al. [20], confirmed the critical nature of delamination and fiber kinking for the prediction of CAI strength, with numerical analysis accurately forecasting delamination areas and CAI strength within $\pm 15\%$ accuracy, making this work relevant as a benchmark for the impact of delamination on residual performance. Established literature positions the fiber-matrix interface as the primary determinant of interlaminar shear strength (ILSS) and overall Mode I/II fracture toughness. Fu et al. [21], treated via plasma carbon fibers to improve the interfacial adhesion of UHMWPE composites. The authors showed that a plasma route can increase roughness without apparent fiber damage while promoting adhesion through innested polar functional groups such as OH, COOH via FTIR. The ILSS increased by 18% from smooth fiber debonding to mechanical interlocking without fiber damage. This necessitates scalable surface engineering to supplant wet chemical pretreatments such as acid oxidation (e.g., HNO₃ oxidation) and solvent etching.

While conventional methods effectively increase surface oxygen content and introduce polar functional groups, they suffer from drawbacks including fiber damage risk, hydrophobic recovery (ageing), volatile organic compound (VOC) emissions from solvents (acetone, IPA), and extended cycle times due to drying requirements [22] [23] [24], which is why these references are cited here as evidence of the limitations that motivate dry alternatives. In contrast, plasma-based technologies provide dry, inline-compatible processing with tunable cleaning, etching, and activation capabilities, eliminating chemical waste and enabling high throughput without compromising environmental sustainability [23] [25]. Bonandini et al. [26], im-

proved wettability and hydrophilicity (+38% in contact angle, θ_{adv} $68^\circ \rightarrow 41^\circ$) of PET fibers using roll-to-roll atmospheric-pressure glow-discharge plasma, APGD. Morphological changes (+47% roughness increase, R_{pv} $18 \rightarrow 27$ nm) and introduction of COOH groups occurred as the main factors responsible for the promoted adhesion characteristics. The APGD methodology was assessed as a green and alternative method to reach proper adhesion characteristics without using wet treatments. The author hence demonstrated, on a different polymer system, that atmospheric plasma can alter both morphology and surface chemistry.

Within this context, the motivation of the present PhD work lies in addressing two closely connected needs. The first is the improvement of fiber–matrix adhesion as a key route to enhancing the interlaminar mechanical response of UD carbon-fiber/epoxy composites, starting from micro- and meso-scale analysis until macro-scale validation. The second is the need for more efficient characterization strategies, capable of reducing the time, material consumption, and experimental effort associated with full macro-scale validation.

Previous plasma-related experience on twill 2×2 carbon fabrics, shown in Figure 1.3, provided a useful methodological background [16]. However, the present research is conceived as a distinct investigation centered on industrial UD reinforcements, on delamination-related mechanical performance, and on the practical significance and limitations of micro- and meso-scale characterization in preliminary interface assessment. The multiscale framework is intended not as a substitute for laminate-level validation, but as a hierarchical screening strategy that balances experimental efficiency with structural relevance. Micro- and meso-scale tests reduce material consumption and testing time, yet their quantitative predictability is limited by industrial filament geometry and by the complexity of the governing failure modes.

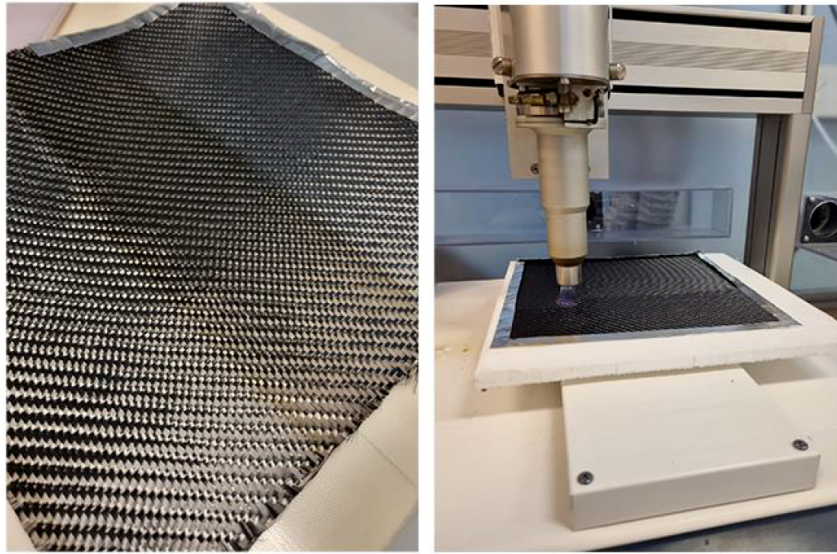


Fig. 1.3 (left) Twill - Warp and Weft CF fabric sample and (right) APP Jet treatment run for surface enhancement.

1.3 Thesis Objectives

This doctoral investigation aims to examine the potential of N_2 APP Jet treatment for unidirectional (UD) carbon fiber textiles to improve delamination resistance through enhanced fiber–matrix interfacial adhesion, while preserving fiber integrity, laminate manufacturability, and the low-impact character of the process within practical industrial constraints.

To achieve this main goal, the research pursues several interconnected objectives, each addressing a key step from plasma process definition to multiscale mechanical assessment.

The first objective focuses on identifying suitable N_2 APP Jet treatment conditions for UD carbon fiber fabrics, aiming to induce surface modifications associated with improved fiber–matrix adhesion and delamination-related mechanical performance. To this end, the influence of the main process variables (jet power, nozzle-to-substrate standoff distance, exposure time, and gas flow) is examined with respect to both surface activation and fiber integrity. Particular attention is given to the use of nitrogen as the working gas, since its selection was guided by recent literature evidence on N_2 -based APP Jet behavior and target interaction, together

with its practical availability within the adopted plasma setup [27] [28]. The selection of the investigated parameter ranges is supported by previous results obtained on twill carbon-fabric systems with the same fiber chemistry [16], as well as by relevant prior studies on comparable substrates. These conditions are then assessed on UD textiles through targeted surface characterization, including optical emission spectroscopy (OES), micro-Raman spectroscopy, and SEM–EDS analysis, in order to identify treatment settings that induce effective surface modification without causing morphological damage to the reinforcement that will be used for the micro-, meso- and macro-scale components to be tested.

The second objective systematically investigates conventional micro- and meso-scale testing methodologies—non-standard microbond (MB) shear strength evaluation and transverse fiber bundle tensile (TFBT) testing—as potential tools for interface quality assessment within industrial UD textile systems. These protocols, commonly employed as material-efficient preliminary screening approaches ahead of resource-intensive full-laminate production, are subjected to detailed evaluation concerning their sensitivity, reproducibility, failure mode interpretability, and predictive capacity relative to macro-scale mechanical validation outcomes [29] [30]. The analysis specifically examines sources of experimental variability—including droplet geometry inconsistencies in MB testing of epoxy resin droplet and carbon/glass fibers, and challenges distinguishing true interfacial debonding from internal bundle cohesion in TFBT—together with their ability to detect moderate adhesion modifications. Through this investigation, the thesis aims to clarify both the practical limitations of these methods and the diagnostic insight they can still provide, thereby contributing to a more informed understanding of their role within multiscale interface characterization frameworks.

The third objective focuses on establishing quantitative structure-property relationships linking these plasma-induced chemo-physical surface modifications to macroscopic delamination performance at the laminate scale. Through controlled fabrication of vacuum-infused UD carbon fiber/epoxy laminates from both plasma-treated and untreated textiles, the research quantifies enhancements in interlaminar fracture toughness—specifically critical energy release rate (G_{IC}) under Mode I DCB loading and alongside dynamic (drop-dart impact) configurations—whilst elucidating the mechanistic pathways through which improved surface polarity, wettability, and functional group chemistry translate into measurable structural benefits across loading rates. This objective is supported by the literature cited above because it

extends the surface-treatment rationale to laminate-scale validation under the two loading regimes that are most relevant for the present work.

Collectively, these objectives define a coherent, hierarchical multiscale workflow that systematically connects plasma-induced surface modification (Chapter 3 and 4) with the resulting mechanical response of the treated composite (Chapter 6), while simultaneously addressing the practical need for faster and less material-intensive preliminary screening routes (Chapter 5) before committing to full macro-scale validation.

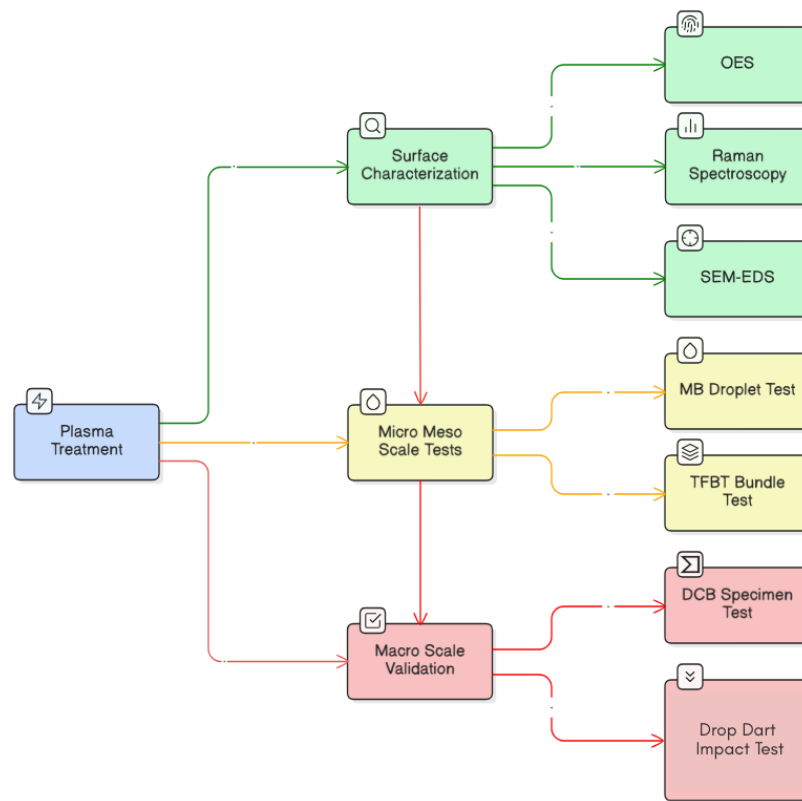


Fig. 1.4 Hierarchical multiscale workflow following APP Jet treatment of UD carbon fiber textiles: (green) surface characterization; (yellow) micro-/meso-scale tests; (red) macro-scale validation.

Figure 1.4 is not just schematic but provides a visual summary of this research logic, illustrating the progression from (green) APP Jet treatment and subsequent surface characterization (OES, Raman, SEM-EDS), through (yellow) micro/meso-scale interface assessment (MB and TFBT test), to (red) macro-scale mechanical

validation (DCB, drop-dart impact test). This structured tries to ensure that each characterization step builds upon the previous one, progressively linking surface chemistry changes to observable improvements in interface strength and, ultimately, to enhanced delamination resistance at laminate level.

Chapter 2

Literature Review

2.1 Adhesion Mechanisms in Polymer Matrix Composites

In polymer matrix composites, the interfacial adhesion between synthetic fibers and resin represents a critical factor that determines the overall mechanical performance of the material, particularly its resistance to delamination and structural toughness under quasi-static and dynamic loading. Among the most common synthetic fibers, carbon and glass fibers play a predominant role: carbon fibers were selected as the primary reinforcement in this thesis due to their exceptional strength-to-weight ratio (commercial T300 registers tensile strength ~ 2.1 - 2.5 GPa, elastic modulus ~ 240 - 390 GPa, three times higher than glass [31]) and thermal/electrical conductivity [32], while E-glass fibers were specifically used for microscale test calibration, such as the microbond test, leveraging their significantly larger single-fiber diameter (~ 10 - $20\mu\text{m}$ versus ~ 5 - $7\mu\text{m}$ for PAN-based carbon [33] [34]), which facilitates manual handling, precise resin droplet deposition, and reliable debonding force measurement without excessive surface imperfection sensitivity. Prashanth et al. [35] have summarized the advantages for fiber/epoxy composites: for 55% CF/SMC tow, density is 1.45 g/cm^3 with tensile modulus 55.1 GPa and compressive yield strength 275 MPa, while highest grade CF/epoxy fabric (12k-24k fiber count per bundle) reaches 2100 MPa tensile strength and 1720 MPa compressive yield; in contrast, E-glass woven cloth shows tensile strength 300 MPa, flexural strength 400 MPa, and impact strength 150 kJ/m^2 . This comparison is useful here because it

justifies the selection of carbon fibers as the primary reinforcement while retaining glass fibers as a practical calibration material in this work. These differences are summarized in Table 2.1 and Table 2.2.

Table 2.1 Comparison between carbon fiber/epoxy products.

Property	55% CF SMC	Lowest grade CF epoxy	Highest grade CF epoxy
Density (g/cm ³)	1.45	1.15	1.8
Tensile str. (N/mm ²)	289	50	2100
Modulus (10 ³ N/mm ²)	55.1	6.6	520
Comp. yield (N/mm ²)	275	50	1720

Table 2.2 Mechanical properties of glass fiber products.

Property	Woven cloth	Chopped strand mat	Continuous roving
Tensile str. (N/mm ²)	300	100	800
Flexural str. (N/mm ²)	400	150	1000
Flexural modulus (N/mm ²)	15000	7000	40000
Impact str. (kJ/m ²)	150	75	250

The manufacturing of carbon fibers begins with the polyacrylonitrile (PAN) precursor, obtained through aqueous emulsion polymerization of the acrylonitrile monomer ($\text{CH}_2=\text{CH-CN}$) with specific comonomers to control cyclization, followed by a multistage thermal process outlined in Figure 2.2: oxidation/stabilization at 200-300°C in air to break CN bonds and form ladder structures (tetrahydropyridine), low-temperature carbonization (400-600°C), and high-temperature carbonization (up to 1300-3000°C) in an inert atmosphere (argon) for dehydrogenation, nitrogen expulsion, and lateral fusion of ribbon-like chains into a core-skin graphitic structure. The inner core exhibits ordered crystals with high binding energy (hexagonal ABA structure) while the outer skin is amorphous, lacking active sites, with low oxygen/nitrogen concentrations and polar dispersive components, rendering it intrinsically hydrophobic and chemically inert. Nunna et al.[36] defined the skin-core heterogeneity using synchrotron ATR-FTIR mapping and micro Raman spectroscopy, revealing “cup and cone” distributions of $\text{C}\equiv\text{N}$ and $\text{C}=\text{N}$ groups with higher cyclization in the core rather than on the skin. This reference is particularly valuable because it supports the idea that the low reactivity of the outer skin is structurally rooted rather than incidental. The same study also showed that dehydrogenation/oxidation followed similar gradients, but sp^2 carbon concentration revealed distinct cross-linking

mechanisms -ketone/hydroxyl pyridine in oxygen-rich skin versus carbonyl/CH-rich core- confirmed by nanoindentation showing lower core modulus, supporting heterogeneous stabilization as origin of radial defects.

From a physico-chemical standpoint, this weak interfacial performance originates in the surface architecture of PAN-based fibers rather than in their bulk mechanical capacity. Tang et al. [37] showed that the interphase is controlled by the fiber surface chemical groups, microstructure, morphology, surface area, and surface free energy, all of which govern the ability of the matrix to establish effective load transfer across the interface. The author offered a conceptual basis for linking surface state to adhesion rather than treating adhesion as a purely mechanical quantity, aspect relevant for the purpose of the thesis. In PAN-derived carbon fibers, the outer skin is frequently enriched in highly oriented graphitic basal planes and contains only a limited population of “unbalanced” surface carbon atoms, namely sites with asymmetric bonding and higher reactivity, which become progressively scarcer as graphitization proceeds toward higher-modulus grades. This surface evolution produces an intrinsically inert, low-polarity outer layer, with a reduced density of oxygen-containing functionalities and a correspondingly low polar contribution to the surface free energy. The anisotropic internal organization of PAN-based carbon fibers is schematically illustrated in Figure 2.1 that visually supports the skin-core argument made in the text. The fiber surface offers few chemically active sites for acid–base interactions, hydrogen bonding, or covalent coupling with epoxy networks. Moreover, the native PAN-based surface is not only chemically limited but also structurally heterogeneous, since the presence of striations, pits, and turbostratic microfibrillar domains does not automatically translate into improved adhesion unless these features are made chemically accessible by removing weak outer layers or introducing new functional groups. Commercial carbon fibers are often further modified by a sizing layer, typically applied to protect the reinforcement during handling, weaving, and processing, while also improving initial compatibility with the target matrix. Nevertheless, the sizing film can partially mask the native carbon surface and reduce direct fiber–matrix contact, thereby influencing wettability, interfacial chemistry, and the measured adhesion response as defined by Laukmanis et al. [38]. This latter work, is pertinent because it shows that sizing does not merely protect the fiber, but also alters the interfacial interpretation of adhesion tests. For this reason, desized fibers are often preferred when the objective is to assess the intrinsic contribution of the carbon surface itself, without the additional screening

effect of the sizing layer [39]. The consequence is a surface that is mechanically strong in the bulk but interfacially underperforming in its as-received state, often favoring interfacial debonding or crack propagation along a weak boundary layer rather than cohesive failure within the matrix.

This skin inertness, a legacy of the graphitization process that minimizes defects to maximize bulk properties (reducing porosity and impurities), imposes inherent limitations on adhesion to epoxy matrices as also encountered in the candidate previous work [15]: poor wettability (contact angle $>130^\circ$), weak interaction with epoxy groups, and susceptibility to premature delamination under shear or Mode I-II loading, with interlaminar fracture toughness values of G_{IC} , $\sim 0.28\text{--}0.43\text{ kJ/m}^2$ and $G_{IIC} \sim 1.2\text{--}1.42\text{ kJ/m}^2$ in untreated CFRP composites, compromising laminate integrity in DCB (ASTM D5528 [40]) and ENF (ASTM D7905 [41]) tests—values consistent with literature reports of $0.13\text{--}0.33\text{ kJ/m}^2$ for CFRP/epoxy.

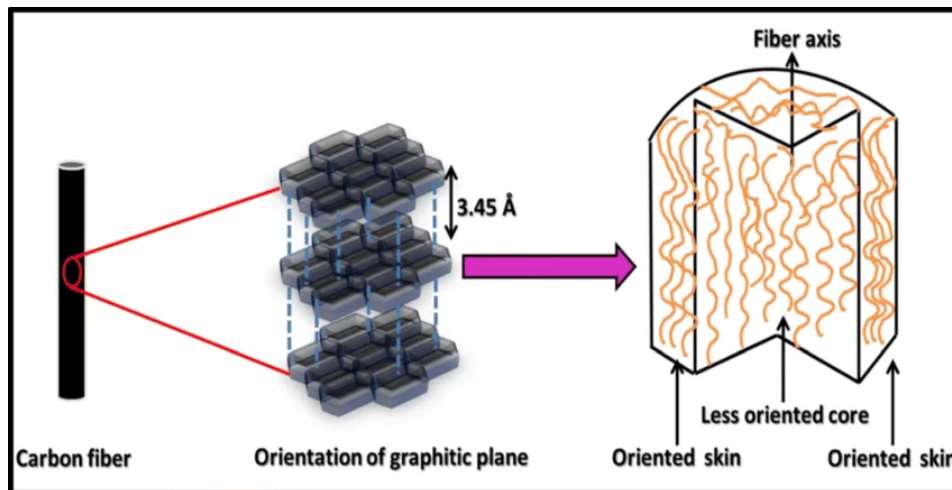


Fig. 2.1 Internal structure of PAN based carbon fiber: core and outer skin. Adapted from [42]

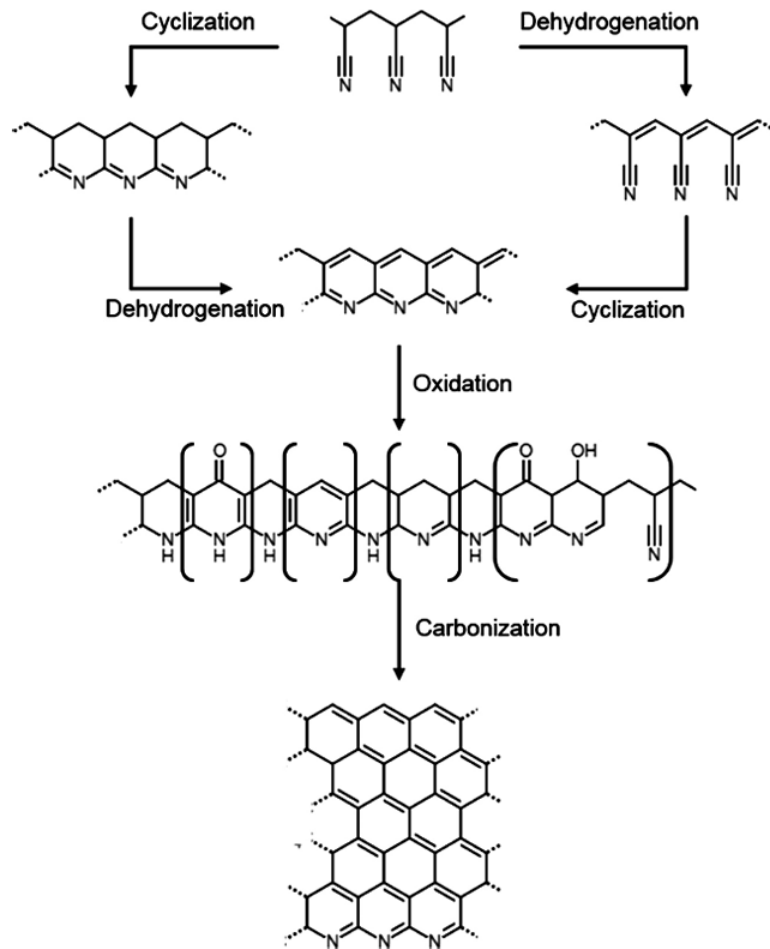


Fig. 2.2 Stabilization reactions: nitrile cyclization, dehydrogenation, aromatization in PAN precursor [43]

These limitations are overcome through multiscale adhesion mechanisms: the chemical mechanism, dominant in carbon/epoxy systems, relies on grafting polar functional groups ($-\text{OH}$, $-\text{COOH}$, $-\text{C}=\text{O}$, $-\text{NH}_2$ also arising from the reassembling of amino-based traces with oxygen from the surrounding environment) onto active surface sites. This favorable surface condition can be achieved via surface treatments, for instance APP Jet treatments with N_2 or nitrogen-based mix gases. As explained before, it promotes the development of more reactive interfacial sites (verified by proper spectroscopic inspections), enabling stronger chemical affinity and hydrogen-bonding interactions with the epoxy matrix and ultimately improving interfacial adhesion and toughness [44] [16]. Physical adhesion involves van der Waals forces and hydrogen bonds. In particular this is amplified by increased surface

free energy and wettability post surface treatment, enhancing the compatibility with thermosetting resins. The intrinsic adhesion limitations of PAN-based carbon fibers are therefore not merely a consequence of poor compatibility with epoxy matrices, but rather the combined effect of a graphitized, chemically inert outer skin and the presence of a sizing layer that can simultaneously protect the reinforcement and hinder direct interfacial interaction.

2.2 Surface Modification Techniques

To address the intrinsic chemical inertness and poor wettability of graphitized carbon-fiber surfaces, a variety of surface-modification strategies have been developed, including desizing, wet-chemical and dry physical approaches. Figure 2.3 provides a compact framework for comparing the main treatment families discussed in the literature and for positioning the methods relevant to the present experimental campaign. In the context of this work, the discussion is limited to selected representative approaches relevant to carbon-fiber fabrics and to the surface conditions encountered in the present experimental campaign, namely sizing removal, wet chemical oxidation and dry physical treatments. Within these categories, emphasis is placed on a few specific examples, including nitric acid-based treatments on the wet side, and UV laser ablation, DBD, low-pressure plasma, vacuum plasma, atmospheric-pressure plasma processing on the dry side. These strategies are generally aimed at improving fiber–matrix adhesion by tailoring surface chemistry, surface energy, and near-surface topography, thereby promoting chemical affinity, wettability, and mechanical interlocking at the interphase. In this sense, the discussion is then framed by the need to interpret the resulting surface and mechanical responses across micro-, meso-, and macroscopic scales.

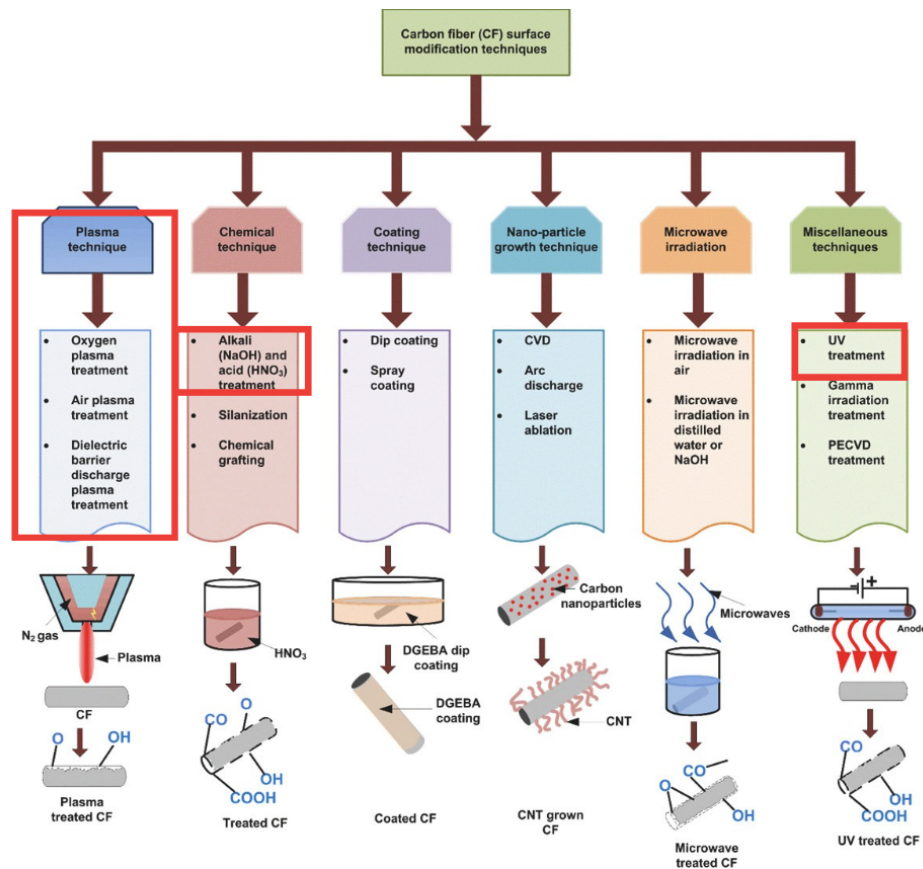


Fig. 2.3 Classification of the main carbon-fiber surface modification techniques. Highlighted methods are the explicated ones in the 2.2.1-2.2.3 subsections. Adapted from Ansari et al. [45]

2.2.1 Desizing/Sizing Removal

Commercial carbon fabrics commonly retain polymeric sizing (typically epoxy/PVA, 1-2 wt%) applied during manufacturing to facilitate handling and stabilize tow structure, but can also inhibits resin wetting, bundle infiltration, and limit fiber-matrix adhesion. This is why desizing is discussed here not as a stand-alone strengthening route, but as a preparatory step that allows the intrinsic contribution of the fiber surface to be isolated. Kim et al. [46] demonstrated that sizing removal via acetone extraction (60°C, 0.5 h) achieves complete sizing removal without tensile degradation, while thermal desizing up to 500°C preserves fiber integrity but risks oxidation at higher temperatures. These findings is pertinent because it demonstrates that sizing can be removed without necessarily damaging the reinforcement, although

the surface still requires subsequent activation. Exposed pristine surfaces remain relatively hydrophobic ($\theta_{\text{water}} \sim 110 - 130^\circ$), reducing ILSS by 10-20% without subsequent activation.

Further evidence of CF sizing influence is found in Sampino et al [16]. Surface analysis of as received CF showed that particular sizing was present and consistent with typically an unsaturated polyester (e.g., poly-4,4-dipropoxy-2,2-diphenylpropane fumarate [16]) applied to the reverse side of 2x2 twill fabric. It also affects wettability, vacuum infusion permeability, and the interpretation of interfacial tests. In that work, the sizing layer was associated with reduced direct fiber–matrix contact and a partial screening of the native surface chemistry, which is precisely the kind of effect that must be considered when comparing untreated and plasma-treated reinforcements. Similar conclusions were reported by Dilsiz et al. [47], who linked the surface-energy components of sized fibers to their interfacial behavior, showing that the presence of sizing can alter the balance between polar and dispersive contributions.

From a processing viewpoint, thermal desizing (300-500°C, 1-10 min, N₂ inert atmosphere) volatilizes organics (epoxy $\rightarrow$ CO₂/H₂O) but with practical possible limitations: thermal routes may risk surface oxidation (>500°C: tensile loss 5-15%) and incomplete bundle penetration due to tow densification, while solvent routes require additional drying and handling steps. Kim et al. [46] showed that acetone extraction (60°C, 0.5-2 h) can achieve 95% sizing removal without defects (tensile retention $\sim$ 98%). The same study is also useful here because it indicates that solvent-based desizing can be optimized not only for sizing removal, but also for preserving reinforcement integrity and improving filament accessibility. In the same context, Ultrasonic assistance (25-60 kHz, 4-10 min) has been reported as a way to facilitate tow opening and improve solvent penetration via cavitation-driven mass transfer, improving filament accessibility for subsequent resin infusion.

Morphological evidence of thermal desizing is shown in Figure 2.4, adapted from Kiss et al. [39], where epoxy-sized filaments appear smooth and partially bonded by the sizing layer, while IR-desized fibers show a cleaner and more ridged surface with no evident damage after treatment at 400°C. This confirms that desizing effectively removes the protective polymer layer and re-exposes the native carbon surface. Desized pristine graphite surfaces nevertheless exhibit inherent low polarity ($\theta_{\text{water}} \sim 120^\circ$, $\gamma_{\text{surface}} \sim 40$ mN/m) due to removal of polar sizing groups, reverting rapidly

post-exposure via surface reconstruction. The authors demonstrated that thermally desized CF requires immediate plasma/oxidation activation to prevent hydrophobicity recovery and achieve effective fiber-matrix bonding. Desizing thus serves as essential pre-treatment but cannot standalone replace surface functionalization strategies.

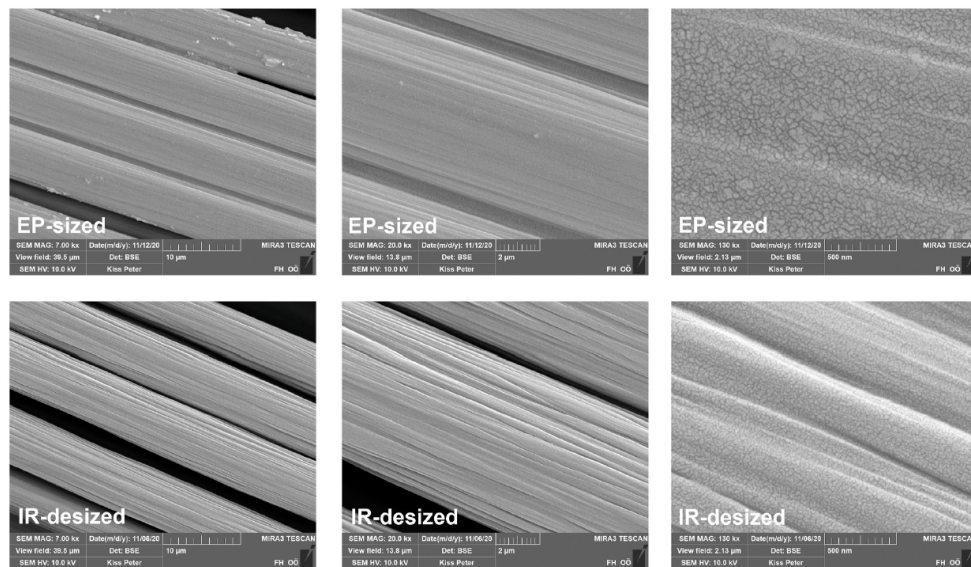


Fig. 2.4 SEM comparison of epoxy-sized and thermally desized PAN-based carbon fibres at different magnifications [39].

Overall, desizing is best interpreted as a means to expose the native carbon surface and reduce the influence of the original sizing layer, rather than as a complete solution for adhesion improvement. This is the reason it is treated in the present chapter as a preparatory step before wet-chemical or dry-plasma activation.

2.2.2 Wet Chemical Treatments

Wet chemical oxidation represents the industrial standard for carbon fiber surface activation, primarily through immersion in strong oxidizing agents. Roseno et al. [48] involved nitric acid (HNO_3 , concentrated 65%, 100°C , 30-120 min) to achieve certain oxidation effect. This choice allowed to introduce oxygen-containing functional groups ($\text{C}=\text{O}$, $\text{C}\equiv\text{N}$ via FTIR), increase surface roughness, and improve wettability/resin bonding as illustrated in the Figure 2.5. This result is relevant here because it provides a direct benchmark for the type of chemical activation that plasma treatment is intended to replicate without wet processing. Sulfuric acid (H_2SO_4)

treatments was also prevalent and reported as wet chemical treatment technology example. Wu et al. [49] for instance reported optimal HNO_3 treatment at 115°C for 20-90 min yielding maximum tensile strength before pitting-induced degradation, while electrochemical oxidation in alkaline/acidic electrolytes enables continuous processing with precise control of pit morphology and functional group density. These methods showed a uniform functionalization across fiber tows but suffer critical limitations: generation of hazardous chemical waste, extended drying cycles (3-4 h at 100°C), fiber damage risk (up to 56% tensile strength loss), and hydrophobic recovery (contact angle rebound within 1 week) [16] [48]. Such drawbacks reduce the appeal of wet chemistry for sustainable and inline composite manufacturing workflows, and they also make it less convenient for preliminary prototypal studies at sub-macroscale levels, where wet treatments on single fibers or bundles can more readily compromise reinforcement integrity than dry methods.

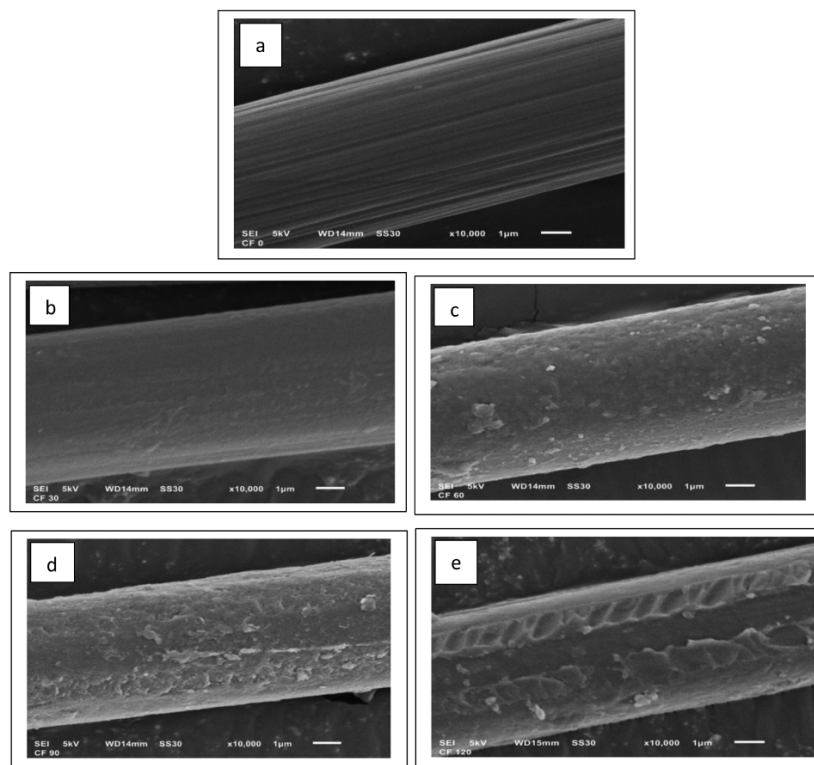


Fig. 2.5 SEM images of carbon fibers: (a) untreated (smooth), (b-e) HNO_3 oxidized (30-120 min) showing progressive pitting/roughness [48].

2.2.3 Dry Physical Treatments

Dry methods eliminate liquid chemical waste and post-treatment washing streams while offering tunable cleaning, etching, and activation. Laser ablation (CO_2 , 10.6 μm ; UV excimer, 248 nm) provides micron-precision morphological modification (R_a 0.5-5 μm) and localized C-C bond scission, achieving 15-25% ILSS gains without contact damage, though limited scanning speeds (0.1-1 m/min) restrict throughput [50]. This demonstrates that dry activation can be effective (but not necessarily scalable for textile-level processing). As a direct example of dry plasma that improves interfacial performance while preserving integrity, Xiao et al. [51] report ILSS increase from 64.9 to 80.0 MPa via air plasma DBD etching (roughness $R_a\uparrow$, O/C $\uparrow$) without reinforcement bulk damage. Kusano et al. [52] demonstrated atmospheric pressure DBD plasma (air/He/ O_2) treatment of carbon fibers, achieving O/C ratio enhancement and improved epoxy adhesion via continuous etching and polar group introduction. High treatment speeds (>10 m/min) eliminate chemical waste, but electrode-sample distance limitations and modest functionalization depth restrict efficacy compared to direct APP Jet systems for tow-level treatment.

Low-pressure plasma (LPP, 0.1-10 Pa, RF 13.56 MHz) represents the reference standard for surface activation, but atmospheric low-temperature plasma offers continuous processing. Li et al. [53] achieved O/C enhancement, contact angles $<40^\circ$, and tensile shear strength $\uparrow 119\%$ via etching and polar group (C-O, C=O) grafting, though excessive treatment (>50 s) causes fiber damage. The strength of this finding is related to the highlighted trade-off between activation intensity and reinforcement preservation.

Atmospheric pressure plasma technologies bridge this gap, combining LPP-quality activation with continuous inline processing. Corona variants sacrifice depth penetration for speed, while DBD and APP Jet balance uniformity and reactivity using technical gases (N_2 , air) rather than expensive He/Ar. APP Jet systems achieve treatment speeds of 1-20 m/min with energy efficiencies of 0.5-2 kWh/m², positioning them as optimal for textile preforms. Detailed APP Jet physics and carbon fiber-specific optimization form the subject of Section 2.3.

2.2.4 Comparative Performance Analysis

Table 2.3 provides a compact comparison of the main carbon fiber surface treatment technologies in terms of surface evidence, mechanical response, scalability, and waste generation. The comparison highlights that wet oxidation and desizing are effective in modifying the fiber surface but remain limited by batch processing and, in the case of wet chemistry, by high waste generation [48] [49] [46] [39] [54]. The aforementioned citations are grouped here because they collectively support the statement that conventional wet routes are effective but process-intensive. Dry technologies offer a more favorable balance between activation and process sustainability: CO₂/UV laser provides localized and programmable treatment [50] [55] [56], corona discharge enables continuous inline processing [51] [57] [58], low-pressure plasma ensures strong surface activation but is constrained by vacuum operation and operational costs [53] [59], and APP jet combines atmospheric operation with continuous processing [16] [60] [61]. All these cited works collectively justify the selection of APP Jet as the most balanced option for the present study. Overall, the comparative survey indicates that, for carbon-based substrates and especially for reinforcement fabrics in CFRP systems, atmospheric-pressure plasma routes offer the most balanced solution when surface functionalization, mechanical enhancement, scalability, and sustainability are considered together. Among these, APP jet emerges as the most promising option for the subsequent analysis, where its applicability across multiscale conditions will be examined.

Table 2.3 Semi-quantitative and comparative performance of carbon fiber surface treatment technologies.

Method	Surface evidence reported	Mechanical evidence reported	Scalability	Waste Generation
Desizing	Residue removal, O/C change, surface energy	Tensile: no deterioration, improved wet-out and interfacial adhesion (ILSS +16.1%)	Batch or semi-batch	Low to moderate
Wet oxidation	+Acidity, +surface area, O-functionalization	Tensile (+16%), IFSS (+10–15%)	Batch, slow	High
UV laser	Cleaning/activation, +Ra (woven 1.212->5.350 μm , tape 0.340->5.960 μm), + θ (-20–35%)	+7–22% Lap shear str., +19–22% fract. tough.	Localized, programmable	None
Corona discharge	Wettability, surface activ.	Improved adhesion; Tg and flex. strength increase	Continuous, inline possible	None
Low-pressure plasma	O/C 0.35->1.38, roughness, Surf. energy 23.18->97.5 mJ/m^2	ILSS (+10–23%), tens. strength (+>100%), but shape restriction	Batch/ vacuum	None
APP jet	O/C, roughness, wettability	Fracture tough. (+10–20%), tensile retention	Inline / continuous	None

Note: O/C = oxygen-to-carbon ratio; IFSS = interfacial shear strength; ILSS = interlaminar shear strength; Tg = glass transition temperature; θ = contact angle

2.3 Atmospheric Pressure Plasma Jet (APP Jet)

Atmospheric Pressure Plasma Jets (APP Jets) produce non-equilibrium, non-thermal plasmas at atmospheric pressure via radio frequency (RF) capacitive discharges in coaxial electrode configurations, accelerating electrons (~ 2 eV) to ionize feed gases without significantly heating neutrals ($T_g \sim 120^\circ\text{C}$) [62]: $n_e \sim 3 \times 10^{11} \text{ cm}^{-3}$ and α -mode condition preserves fiber integrity unlike aggressive filamentary-based plasma, which may damage the substrate with undesirable arcing/etching. Quasi-neutrality is preserved by short Debye lengths ($\lambda_D \sim 10\text{--}100\mu\text{m}$), with plasma frequency $\omega_p \sim 10^9\text{--}10^{10} \text{ Hz}$ enabling stable homogeneous discharge (non-filamentary) through frequent collisions ($\nu_c \sim 10^{11}\text{--}10^{12} \text{ s}^{-1}$); key diagnostics include Schottky theory for electron density $n_e \sim 10^{10}\text{--}10^{14} \text{ cm}^{-3}$ [62].

A general schematic of an APP Jet treatment configuration is shown in Figure 2.6, where the main system elements and process variables governing plasma–substrate interaction can be identified, including the gas supply, electrode/nozzle assembly, nozzle-to-substrate standoff distance, and relative scanning motion [1].

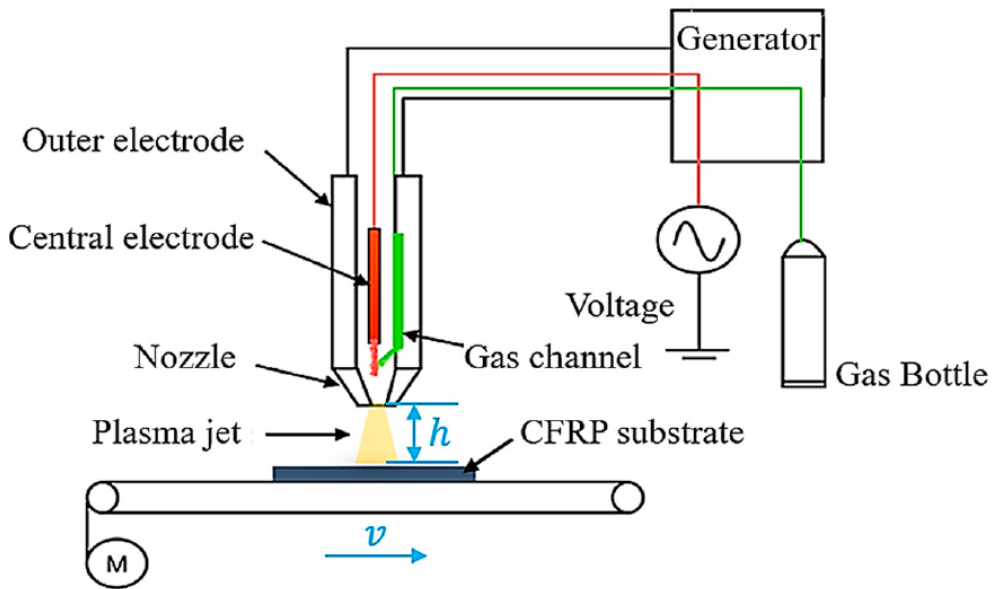


Fig. 2.6 General schematic of an atmospheric-pressure plasma jet (APP Jet) treatment configuration [1].

In N_2 APP Jets, dominant species encompass vibrationally excited $\text{N}_2(X^1\Sigma_g^+)$, $\text{N}_2(X, v > 13)$ metastables, atomic N, N_2^+ , and trace NH/NH_x , alongside post-

discharge O-atoms from air entrainment (impurity) enabling ROS/RNS functionalization, with densities $nN \sim (2-6) \times 10^{14} \text{ cm}^{-3}$, $nN_2(A) \sim 10^{10}-10^{11} \text{ cm}^{-3}$. These drive Penning ionization ($N_2(A^3\Sigma_u^+) + O_2 \rightarrow O + NO + N_2$), surface bombardment, and etching, with species fluxes tuned by power/standoff for balanced ablation/activation on graphitic CF, as presented by Ricard et al. [63]. The authors work is useful to links plasma chemistry to the types of surface modification that are relevant for adhesion enhancement in carbon fiber composites.

Critical parameters form a process window optimizing cleaning / etching / functionalization without bulk damage; primary (power, frequency RF, gas flow N_2 , Ar, Air etc.) control discharge stability/ion flux, secondary (nozzle distance, exposure time) dictate fluence ($\sim 10^{16}-10^{18} \text{ species/cm}^2$) [16] [61]. These variable control the balance between cleaning, etching and functionalization, important aspect in this work because excessive etching can damage the reinforcement, whereas insufficient exposure may not produce enough chemical activation to improve adhesion.

Inline APP Jet modes, such as roll-to-roll or scanning configurations, represent the cornerstone of high-throughput large-area industrial processing, enabling continuous, vacuum-free surface modification across diverse substrates—from screen-printed electrode pastes to synthetic fibers like glass or carbon—while preserving bulk properties and minimizing thermal budgets ($T_{\max} \sim 550^\circ\text{C}$, exposure $\sim 10 \text{ s/scan}$) [60]. Unlike batch vacuum plasma, scanning APP Jet excels in scalability (35×35 cm panels <4 min), precise flux control (scan speed 1–20 m/min, stand-off 10–20 mm), and extended post-discharge chemistry (10–50 mm metastable reach), delivering ultrafast activation with controlled fluence and low thermal load ($T_g < 200^\circ\text{C}$), as demonstrated for example, in DC-pulse N_2 APP Jet for rGO supercapacitors where optimized scans enhanced capacitance 3.6× via EC decomposition and wettability without rGO damage. These advantages support the three core sequential mechanisms mentioned above:

- cleaning, achieved through volatilization of sizing agents and peel-ply residues, reducing water contact angle from hydrophobic $\theta_w \sim 120^\circ$ to hydrophilic 90° or less;
- etching and ablation, involving C-C bond scission increasing roughness $Ra \sim 0.1-1 \mu\text{m}$ (XPS $\pi \rightarrow \sigma \text{ sp}^3$ detection);

- activation, grafting polar groups -OH, -CO, -COOH, -NH_x elevating SFE $\sim 40 \rightarrow 60$ mN/m.

In summary, N₂-based APP Jets enable continuous modulation of reactive species flux toward the reinforcement surface, providing fine control over the balance between these three sequential mechanisms. The following section analyzes these mechanisms specifically for carbon fiber surfaces, progressing from single filaments to twill and industrial UD textile architectures, with particular attention to wettability implications and process design considerations for industrial implementation.

2.4 Plasma Treatment of Carbon fiber Surfaces

Atmospheric pressure plasma treatments of carbon fiber surfaces address the intrinsic chemical inertness and excessive smoothness resulting from high-temperature PAN graphitization, which yields low polar group content, limited surface free energy, and poor wettability toward epoxy resins. By combining cleaning, etching, and activation effects, plasma processing enables targeted enhancement of the multiple adhesion mechanisms (chemical, mechanical, and physical) outlined in Chapter 2.1, with process outcomes critically dependent on both plasma parameters and substrate architecture. Figure 2.7 displays the sequence of plasma effect on carbon fiber surface with initial activation effect and then subsequent functionalization and potential polymerization with the matrix (or coating) for the enhanced interface development. Table 2.4 summarizes the key APP Jet parameters and their primary effects on CF surfaces (from single fibers to CFRP laminates), highlighting the crucial role of balancing etching (power/distance), uniformity (frequency), and reactive dose control (scan speed, gas flow) to achieve cleaning and activation without excessive ablation.

Table 2.4 Key APP Jet parameters and effects on CF surfaces (fibers and CFRP).

Parameter	Range	Effect	Typical
Power	200–800 W	Etching-O/C $\uparrow$	400–600 W
Frequency	10–25 kHz	Uniformity	20–25 kHz
Distance	10–20 mm	Flux balance	8–16 mm
Scan speed	1–20 m/min	Dose control	2–10 m/min
Gas flow	20–60 slm	Ionization	30–40 slm

At the morphological level, atmospheric plasma produces three distinct effects. First, it removes continuous organic films such as binders, excess sizing, and peel-ply residues, restoring the native filament profile. Second, through controlled C–C bond scission and surface ablation, it introduces moderate micro-roughness that enhances mechanical interlocking without compromising filament integrity. Barrie et al. [64] demonstrated these effects on ultra-high modulus UD composites, achieving minor surface roughening—well below mechanical interlocking levels—while completely avoiding the subsurface fiber damage and brittle fracture through graphitic layers typical of abrasive preparation methods. The aforementioned work provides a direct comparison between plasma treatment and mechanically aggressive preparation routes, supporting the use of plasma when surface modification must remain shallow and controlled. Unlike wet chemical oxidations (e.g., HNO_3) that frequently generate deep pits and tensile strength loss, properly calibrated N_2 APP Jets typically produce first-level surface texturing (striations, micro-asperities) while preserving the graphitic core structure.

Chemically, the primary contribution involves controlled introduction of polar functional groups $-\text{OH}$, $-\text{CO}$, $-\text{COOH}$, and nitrogen-containing species ($-\text{C}-\text{N}$, $-\text{CONH}-$, $-\text{NH}_x$) when using nitrogen-based gases. This produces measurable increases in O/C (and relevantly N/C) ratios via XPS analysis. FTIR-ATR and Raman spectroscopy associate these modifications with reorganization of G/D carbon bands and emergence of characteristic functional group signatures, consistent with literature reports on both twill fabrics and single filaments. Critical process optimization balances mere binder/sizing ablation (exposing still-low-polarity graphitic surfaces), excessive oxidation (creating fragile unstable layers), and deep functionalization yielding high reactive site density toward epoxy.

The combined morphological and chemical modifications directly enhance wettability and surface free energy. Untreated CF surfaces exhibit characteristically high contact angles with water and epoxy systems (hydrophobic behavior), while APP Jet treatments produce marked surface energy increases and contact angle reductions well below 90° . Studies on twill fabrics treated with $\text{N}_2/\text{N}_2\text{H}_2$ APP Jets demonstrate transition from distinctly hydrophobic to significantly hydrophilic behavior, correlating with XPS/FTIR-ATR detected polar group increases and improved fabric-level resin wettability with enhanced fiber-matrix interface continuity post-infusion [16]. The transfer of the same treatment logic to industrial UD textile is not automatic,

because tow shielding, binder distribution, and filament packing can limit reactive species penetration and make the effective dose non-uniform.

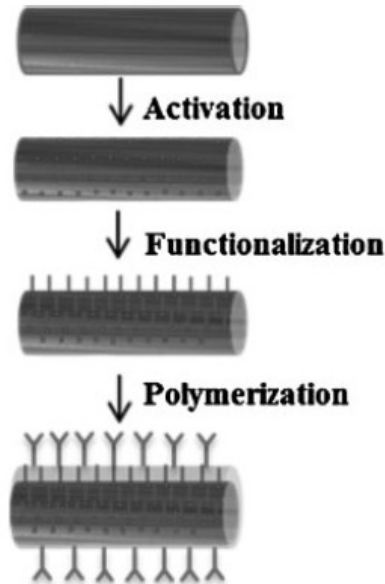


Fig. 2.7 Schematic of sequential plasma effects on carbon fiber surface: (a) activation cleans and exposes reactive sites, (b) functionalization introduces polar groups ($-\text{OH}$, $-\text{COOH}$), (c) potential polymerization for interphase development. Adapted from Chen et al. [65].

The transition from single filaments to twill and industrial UD textiles introduces progressively complex treatment dynamics. Single fiber studies provide isolated mechanism insights under uniform reactive species exposure without significant shadowing or tow diffusion effects. Gravis et al. [66] demonstrated this on single CF strands via precise wetting profile analysis, achieving dramatic O/C increases (XPS) and surface energy enhancement up to 44 mJ/m^2 , changes relevant because it shows the maximum response that can be expected under favorable exposure conditions. However, excessive oxidation risks altering crystalline structure (Raman IG/ID shift), rapid aging effects (environmental reaction), and poor scalability to production lines limit industrial relevance.

Twill fabrics (2×2 , 3k architectures) introduce substantial local exposure heterogeneities due to yarn crimp and mutual filament shielding, alongside micro-cavities where reactive species flux becomes partially screened. Binder/sizing distributions, often non-uniform or single-sided, further complicate uniform treatment [16]. APP Jet $\text{N}_2/\text{N}_2\text{H}_2$ studies on twill demonstrate effective binder removal from treated faces,

preferential functionalization of surface-exposed filaments versus tow interiors [66], and significant G_{IC}/G_{IIC} improvements at laminate scale—albeit with more complex local property distributions than isolated fibers.

Industrial UD textiles represent the most challenging case, characterized by high filament areal density, stabilizing binder distribution, and unidirectional architecture that generate strongly anisotropic treatment fields. The frontal tow receives primary plasma fire zone exposure, while internal bundle regions rely on post-discharge species penetration and inter-filament void diffusion. Residues of peel ply, sizing or binder lead to an increased risk of shielding if not cleaned properly. Relative to twill fabrics, UD systems thus demand even finer treatment dose control (power $\times$ time $\times$ distance, scan passes) to avoid excessive frontal etching while pursuing internal activation—though micro/meso-scale tests reveal predictive limitations for full fabric-level assessment.

This architecture-dependent response—including differences in specimen geometry (thickness), test setup (rotative vs blade-like nozzle), and afterglow dynamics—underscores that identical APP Jet configurations (gas composition, power, standoff jet-component distance) produce different surface states across reinforcement types despite identical base carbon chemistry [16].

For UD textile optimization targeting structural applications, direct process calibration on target fabrics becomes essential, combining high-resolution surface characterization and plasma analysis (Raman, XPS, FTIR-ATR, SEM-EDS on treated surface and OES on plasma source) with wettability measurements and, despite their known limitations, multiscale mechanical testing. The defined process window might guarantee complete cleaning and effective activation with etching strictly limited to filament integrity-compatible levels, positioning N_2 APP Jet as a scalable, solvent-free alternative to wet chemistry for aerospace-grade CFRP preform preparation. These architecture-specific considerations frame the experimental validation of APP Jet effects on adhesive performance, as detailed in the following section.

2.5 Effects on Adhesive Properties: Literature and Prior Work

Beyond surface-level modifications, APP Jet treatments must guarantee quantifiable improvements in adhesion on relevant scales, from micro-interfacial to full laminate performance. This section reviews key methodologies employed in literature, highlighting their diagnostic value and limitations when applied to plasma-activated CFRP.

Mode I and II interlaminar fracture toughness constitute primary macro-scale metrics, with DCB (ASTM D5528) and ENF (ASTM D7905) tests routinely demonstrating G_{IC}/G_{IIC} enhancements of >30% post-plasma relative to untreated baselines, albeit via configurations distinct from single-pass N₂ APP Jets (e.g., pulsed arrays or DBD). Wang et al. [67], employing high-frequency pulsed microsecond plasma jet arrays on CF prepregs, nonetheless illustrate shared principles of surface activation, achieving +19.49% peak load alongside +29.94% G_{IC} . This work further support the same general mechanism by showing that plasma activation can translate into measurable laminate-scale gains even though their configuration differs from the specific setup adopted in this thesis. Yildirim et al. [68], investigating APA on AFP CF/PEKK adherends, report unprecedented 34–84× G_{IC} despite multi-adhesive variability, reinforcing plasma’s universal potential for cohesive failure promotion via chemistry/topography synergy. This is an example of effectiveness with compatible adherend surface and adhesive system.

While macro-scale delamination captures integrated laminate response, micro- and meso-scale tests offer isolated interrogation of fiber-matrix adhesion, circumventing ply interactions and providing direct predictors of interlaminar performance. These methodologies bridge single-filament behavior to bundle-level mechanics, particularly relevant for plasma-activated industrial tows where tow-level wetting governs infusion quality.

At micro-scale, microbond tests provide isolated quantification of apparent interfacial shear strength (τ_{app}), routinely documenting 20–40% enhancements post-functionalization, even though plagued by well-documented scaling artifacts inherent to nanoliter resin droplets. Thomason et al. [30] demonstrate glass/VE IFSS doubling (12–36 MPa) simply by substituting epoxy for cyanoacrylate mounting, attributing artifacts to adhesive vapor deposition on fiber sizings, a methodological and significant

caveat for plasma-activated systems where surface chemistry amplifies contamination sensitivity. Complementarily, Xypolias [69] elucidates universal scaling challenges: vinyl ester microdroplets manifest dual T_g transitions, pronounced oxygen inhibition, and styrene volatilization absent in macroscale equivalents, yielding systematically unrepresentative τ_{app} unless rigorously N_2 -purged during cure, paralleling APP Jet activation imperatives.

These methodological insights directly inform CF/epoxy: Kim et al. [70] report electrochemical oxidation boosting IFSS via oxygen groups/roughness; Zhao [71] confirms atmospheric He/O_2 plasma enhances IFSS through elevated O-content and surface crevicing without fiber strength loss. Such controlled gains, despite short terms ageing stability in certain cases, underscore microbond's diagnostic value when artifacts are mitigated, bridging to meso-scale bundle mechanics.

Meso-scale approaches, such as transverse fiber bundle tensile (TFBT) and Iosipescu V-notch shear testing, bridge single-filament micro-mechanics to laminate-level response, isolating bundle cohesion where tow-level wetting and inter-filament interactions critically govern industrial infusion behavior.

Kaybal et al. [29] exemplify this synergy through comprehensive multi-scale characterization of Elium thermoplastic composites: TFBT reveals glass/Elium superiority (1043 N load, 43.46 MPa shear stress) over carbon (931.8 N, ~ 35 MPa), scaling seamlessly to SBS ILSS (53.36 vs 41.19 MPa)—quantitatively linking wettability gradients (53 – 86° contact angles) to macro performance across glass / carbon / basalt / aramid systems. The latter reference work is relevant because it shows how surface chemistry can be followed consistently across scales. Stojceveski [72] also underlines that Iosipescu-type approaches for CF/epoxy tows, remain useful only within a limited filament-count range, making them more appropriate as complementary tools than as universal predictors of full laminate behavior. Complementarily, Guimarães [73] nitric acid oxidation of 3K/12K CFs boosts tensile strength 11–26% and modulus 6–16% via SEM/EDS-confirmed roughening/O-N enrichment, mechanistically analogous to plasma etching without processing defects compromising absolute values.

Collectively, these meso-scale approaches confirm ILSS (ASTM D2344) 10–30% uplifts arise from interface-driven cracking suppression, yet remain embedded within composite complexity. Prior work on 3k twill APP Jet (N_2 660 W/12 mm, N_2H_2 810 W/16 mm) validated +14.3% P_{max} , +3.3% G_{IC} , +16.1% G_{IIC} (PC) [16]

via macroscale DCB/ENF, but did not incorporate micro/meso-scale interrogation and was restricted to mixed-gas activation on twill fabrics. The present investigation therefore extends APP Jet treatment to pure N₂ and UD textiles, embedding it in a multiscale assessment of CF/epoxy interfacial adhesion.

2.6 Scientific Gap and Project Focus

While Sections 2.3–2.5 delineate APP Jet principles, CF surface responses, and multiscale diagnostic methodologies—culminating in prior twill macroscale validation (+14.3% $P_{\max}$, +3.3% G_{IC} , +16.1% G_{IIC} PC via N₂/N₂H₂ [16])—persistent gaps preclude industrial UD deployment and green integration.

Continuous single-pass APP Jet on UD CF textiles lacks systematic exploration: as presented in the previous paragraph, literature favors pulsed arrays on prepregs [67] or DBD on AFP adherends [68], configurations that are not directly transferable to Vacuum Resin Infusion preform lines, where 3k UD tow wetting dictates permeability and infusion uniformity. In addition, even when applied from both sides, plasma treatment may remain non-uniform within industrial UD textiles because tow packing and residual binder can shield the internal filaments from full exposure, as cited in previous Section 2.4. This lack of systematic studies on process trade-offs that can quantify the compromises between power / distance / flow / exposure for the removal of specific UD dimensions without excessive ablation hinders in-line scalability (1-5 m/min), which is absent from studies focusing on twill.

Multiscale delamination-focused frameworks remain fragmented: micro/meso predictors (IFSS_{microbond}, τ_{TFBT}) rarely cascade to G_C with surface linkages (OES / XPS / Raman), particularly for plasma-UD where bundle-internal modes obscure true adhesion gains [29, 72]. Stojceveski warned about wetting failures of >12k tow, while APP Jet-induced tow-opening effects sizing removal, surface etching, filament separation remain unlinked from integrated hierarchies bridging wettability gradients (θ 53–86°, [29]) to Short Beam Shear ILSS (41–53 MPa).

The green and low-impact aspect is still marginal in the literature: APP Jet can replace HNO₃/acetone baths which involves hazardous waste, 3–4 h drying at 100°C and 5–56% tensile loss as reported by Guimaraes[73], and it also avoids

batch-like vacuum plasma processing, yet LCA metrics (kWh/m², CO₂/kg fabric) and cycle-time benchmarks against wet baselines remain largely unexplored.

Therefore, this PhD proposes pure N₂ single-pass APP Jet (OES-guided, 660 W/12 mm) on industrial 3k UD, dry, continuous, solvent-free, low-energy, to boost fiber-matrix adhesion/delamination resistance (G_{IC} +36% propagation), while preserving resin vacuum infusion compatibility and fiber integrity.

UD micro/meso limits sharpen macro prioritization: microbond τ_{app} (13–27 MPa) yields $\sim 25\%$ std from D_g 100–200 μm (vs. 65–110 μm) and $L_{emb}/D_f > 10$ friction, evidencing adhesive-to-cohesive shifts through resin residues but no reliable IFSS– G_{IC} scaling; TFBT shows post-plasma bundle cohesion dominance ($\tau_{interface} > \tau_{bundle}$), reducing sensitivity to adhesion changes amid porosity and wetting artifacts, with these limitations amplified for industrial tows relative to lab-scale filaments.

Thus, surface-macro correlations anchor the hierarchical workflow, extending twill and mixed-gas prior work to pure N₂ UD, and providing a scalable green engineering route for delamination-critical structures, while micro/meso tests remain qualitative adjuncts that expose methodological pitfalls in real-world UD assessment.

Chapter 3

Materials and Methods

3.1 Materials

The experimental campaign conducted within this doctoral investigation relied upon industrially relevant materials carefully selected to balance scientific rigor with practical applicability to aerospace and sustainable mobility applications. Commercial unidirectional (UD) carbon fiber fabrics served as the primary reinforcement phase throughout. “200 g unidirectional carbon fiber cloth (1000 mm)” based on Grafil 34-700 24K PAN-based carbon fiber tows were used [2]. The reinforcement exhibits an areal weight of 200 g/m², nominal tape width of 1000 mm and a nominal dry thickness of 0.2 mm, with unidirectional format and filament count of 24K, specifically designed to provide 100% strength in a single preferred direction within structural laminates.

In the preliminary phase of the project, an earlier UD variant with nominal dry thickness of 0.1 mm, based on a high-strength PAN fiber (TR30S 3L, $\sigma_t \approx 4.1$ GPa, $E \approx 234$ GPa, $\rho \approx 1.80$ g/cm³), was also employed. This thinner configuration was used for preliminary laminate trials and meso-scale investigations, including transverse fiber bundle tensile (TFBT) tests, in order to assess the influence of textile thickness and surface wettability on impregnation quality, bundle compaction, and the resulting fracture modes. In this regard, the thinner reinforcement provided a convenient specimen architecture for probing the coupled effects of through-thickness flow, compaction behavior, and liquid spreading within the textile structure, which are all known to affect impregnation efficiency and wetting response in fibrous

reinforcements [74] [75]. The 0.2 mm configuration was therefore adopted for all macro-scale delamination tests, as it offered a more representative reinforcement architecture for laminate-level validation and improved consistency with the coupon set used throughout the final macro-scale test campaign. At fiber level, Grafil 34-700 delivers a typical tow tensile strength of 4830 MPa, modulus of 234 GPa and density of 1.80 g/cm^3 , confirming its classification as a high-strength PAN-based grade suitable for aerospace-relevant applications [76]. These fabrics are shown in Figure 3.1 while the summary of the employed fabrics' properties are presented in Table 3.1.

For selected microscale investigations, in particular MicroBond calibration tests, fibers from a 200 g/m^2 2/2 twill woven E-glass fabric (1 m width, nominal dry thickness 0.2 mm) [2], were also employed, providing larger single-fiber diameters and improved handling compared to carbon, while remaining fully compatible with the epoxy matrix [2].

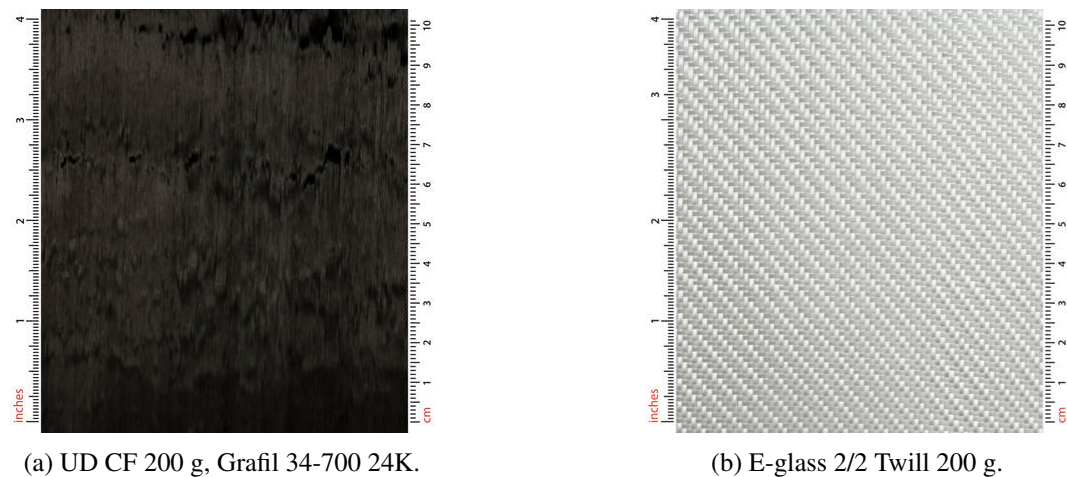


Fig. 3.1 Reinforcement and matrix materials employed in the experimental campaign: (a) UD carbon fiber fabric (0.2 mm thick) for macro-scale laminates, (b) woven E-glass fabric for microscale calibration [2].

As-received UD fabrics present the characteristic surface condition of commercial products, where the unidirectional tows are held together by binder-based traces to ensure handling stability and maintain fiber alignment during cutting, lay-up and positioning, while also potentially screening portions of the carbon surface from direct matrix contact and locally affecting resin impregnation, permeability and capillary flow during vacuum infusion [77] [78] [79]. These features, combined with the intrinsically low-polar, graphitic outer skin of PAN-based fibers highlighted in

the Chapter 2, motivate the adoption of atmospheric pressure plasma jet treatments to selectively clean, etch and activate the UD reinforcement prior to composite fabrication. Furthermore, the literature support the choice of a bio-derived epoxy system that can still approach mechanical-relevant performance levels.

The matrix phase consisted of IB2 epoxy infusion bio resin, supplied by Easy Composites, a low-viscosity two-component epoxy system with approximately 38% resin plant-derived content obtained by manufacturing epichlorohydrin from renewable glycerol instead of petroleum-based propylene [2]. Reported datasheet values for the cured resin include a density of 1.12 g/cm³, tensile strength of 65.0 MPa, flexural strength of 107.0 MPa, flexural modulus of 2.8 GPa, and elongation at break of 5.3%, together with impact, shear, and compressive properties compatible with structural composite applications [2]. The IB2 system was selected over its fully petrochemical counterpart IN2 [2], in line with recent literature: Ramon et al. [80] demonstrated that plant-derived epoxy formulations deliver performances approaching aerospace-grade standards (e.g., RTM6), while Quirino et al. [81] emphasized their environmental benefits through reduced petroleum feedstocks. Boursier et al. [82] reported that commercially available bio-based epoxy composites can exhibit quasi-static properties comparable to those of conventional epoxy systems, while Ge et al. [83] showed that low-viscosity bio-based epoxy formulations can achieve high thermal and mechanical performance in vacuum assisted resin transfer molding-compatible systems. Reported literature on bio-based epoxy systems hence suggests that such resins can combine low viscosity, vacuum-infusion compatibility, and thermomechanical properties suitable for carbon-fiber composite applications, while maintaining quasi-static performance comparable to conventional epoxy systems.

Critically for the plasma treatment workflow, the IB2 system exhibits a pot life of about 1 h 25 min at 20 °C (500 g mix) and a demould time of approximately 21 h 30 min at the same temperature, enabling reliable synchronization between surface activation and subsequent infusion without compromising resin flow characteristics or cure kinetics. Full mechanical development is achieved through the manufacturer's recommended ambient cure followed by optional post-curing cycles (up to 80 °C - 3h), yielding matrix-dominated properties comparable to fully petrochemical epoxies.

A significant consideration governing the experimental protocol was the limited temporal stability of the plasma-induced surface activation. In plasma-treated ma-

terials, the initially enhanced hydrophilicity may partially decay over time due to hydrophobic recovery, a phenomenon associated with surface reorientation and relaxation processes [84]. This issue is particularly relevant for carbon-based surfaces, where plasma activation has been shown to age rapidly, leading to a partial loss of surface activity and an increase in water contact angle upon storage in ambient conditions [85]. To limit post-treatment ageing of the engineered surface chemistry — principally hydroxyl (OH), carboxyl (COOH) and amine (NH_x) groups essential for epoxy covalent bonding and hydrogen bridging — the time between APP Jet treatment and vacuum infusion was minimized and the treated fabrics were handled in laboratory conditions with moderate ambient humidity, reducing uncontrolled air exposure as far as practically possible. This dry processing strategy eliminated the volatile organic compound emissions and drying cycles associated with wet chemical activation alternatives, facilitating integration into high-throughput, environmentally responsible vacuum-assisted resin transfer molding manufacturing lines.

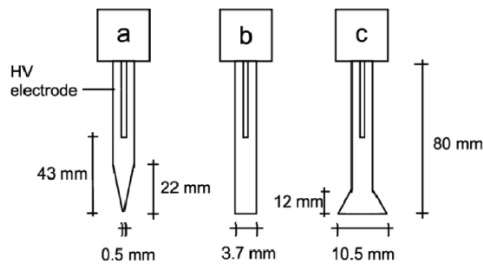
Table 3.1 Summary of fiber reinforcements employed in the experimental campaign.

Substrate	fiber type	Format	Areal wt. (g/m ²)	Thick. (mm)
UD CF 200 g	Grafil 34-700	UD tape	200	0.20
UD CF 100 g	TR30S 3L	UD tape	~100	0.10
E-glass 2/2 twill 200 g	E-glass	2/2 twill	200	0.20

3.2 Plasma Jet Treatment Setup

The surface activation of the UD carbon fiber textiles was carried out using an industrial APP Jet installation located at Environmental Park (Turin, Italy), which acted as project partner within the NODES Spoke 1 framework [16]. This technology generates a non-thermal plasma discharge through dielectric barrier discharge (DBD) or radiofrequency excitation of a process gas (Air, N₂, Nitrogen-based mixture etc.), producing a high density of reactive species (metastable N₂^{*}, atomic N, OH, O) at near-ambient temperatures (<100°C) without requiring vacuum systems. For the specific treatment of UD carbon fabrics (0.1–0.2 mm), a non-rotating blade nozzle was selected instead of the conventional rotating configuration that was adopted for the author's previous work on carbon fiber twill warp and weft fabrics. Non-rotating nozzles typically produce an elongated plasma plume with ~ 8 mm working width, which was considered suitable for the unidirectional tape architecture because it

allows line-wise activation along the fiber direction while limiting lateral overspray and tow disturbance [86]. Non-circular nozzle geometries have been demonstrated to improve treated area and plasma chemistry control without power density loss, making them particularly suited for tape-like substrates as defined by Ricci et al. [87]; nozzles configuration of the latter reference study is shown in Figure 3.2 (a) while in Figure 3.2 (b) three Plasmatreat nozzle configurations with different outlet geometries and, consequently, different effective working widths of the plasma aperture, are displayed. These three configurations (front and up view shown) count for narrow-punctual, rotating and static-blade plasma jet respectively, from left to right in the Figure 3.2 (b). The static-blade is the one adopted in the present work for both UD carbon fabric treatment and glass fiber twill fabric. The cited literature show that non-circular nozzle geometries can improve area coverage and process control on tape-like materials.



(a) Nozzle geometries comparison (Ricci Castro et al.[49]), from left to right: tapered ($D_{out} = 0.5$ mm), straight ($D_{out} = 3.7$ mm), enlarged ($D_{out} = 10.5$ mm) [87].



(b) Front and up view of equivalent Plasmatreat configurations, from left to right: straight, rotating, static blade-like (8 mm width, selected for UD).

Fig. 3.2 Nozzle geometry comparison: (a) reference example [87] and (b) in-house Plasmatreat configuration.

The treatment line was based on an Openair[®] PFW1004 plasma system (Plasmatreat GmbH, Steinhagen, Germany) equipped with a FG5001 radio-frequency generator, a dedicated power control unit (PCU) and rotative/static RD1004 torch [88]. Initial machine calibration involved a parameter screening with two robot translation speeds and three nozzle-to-sample distances, which was used to identify a working window suitable for UD textile processing, as discussed in Chapter 4. On the basis of the spectroscopic analyses presented in that mentioned Chapter 4, the final setup delivered a reproducible discharge condition at an excitation frequency of

approximately 23 kHz and nominal plasma power of about 660 W (100% reference voltage, plasma voltage ≈ 334 V). Technical nitrogen (N_2) was adopted as process gas, supplied at 4 bar with a mass flow of ~ 31 L/min, thus ensuring a reproducible ionisation regime and consistent density of reactive species within the jet. The main components of the plasma system adopted are shown in Figure 3.3, from the electrical generator to the robot movimentation system that allows the plasma torch movement and precise positioning in vertical axes towards the substrates that will be treated.

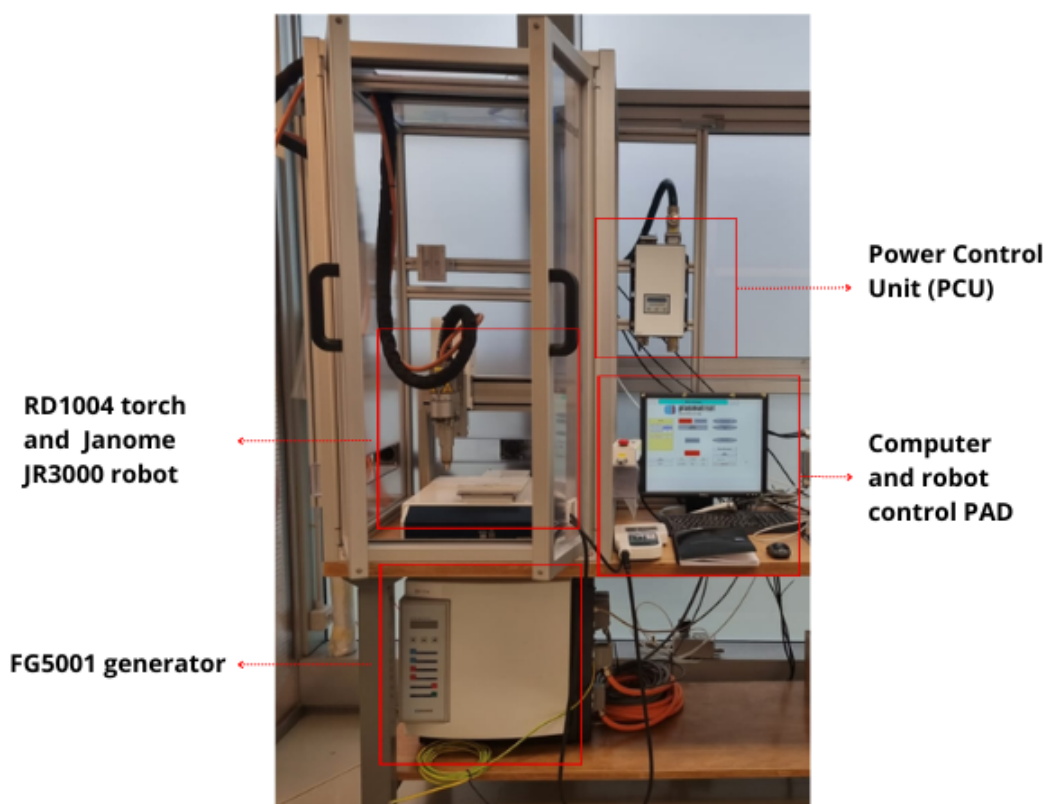


Fig. 3.3 Openair APP Jet system: PCU, FG5001 generator, RD1004 torch, Janome robot movimentation system and computer/PAD for machine control.

The blade nozzle was mounted on a three-axis gantry system (Janome JR3000 series, Janome Industrial Equipment, Tokyo, Japan) that allowed fully programmable trajectories over the fabric panels, including control of scan direction, overlap between adjacent passes and acceleration/deceleration ramps at the edges of the treatment area. Spatial parameters (i.e.: x and y torch coordinates) were modified directly through the PAD (Figure 3.3) or by means of the dedicated robot movimentation

software. Hence treatment paths were specifically programmed as serpentine patterns optimized for the panel dimensions and machine working envelope, with minimal overlap between adjacent passes to avoid over-exposure while ensuring complete coverage of the UD fabric area. UD fabrics were laid flat on a grounded metallic support plate, with the fiber direction aligned with the principal scan direction, and clamped along the edges to prevent fluttering or wrinkling under the action of the plasma jet. In this configuration, the APP Jet system operated in open air without vacuum chambers, while maintaining a gas temperature in the cold-plasma regime compatible with the mechanical integrity of the reinforcement.

Process parameters were organised into primary and secondary sets. The primary parameters comprised the plasma power, excitation frequency and nitrogen flow rate, which collectively governed the ionisation degree and population of excited N_2/N species. Secondary parameters included the nozzle-to-substrate standoff distance d , the line speed and the programmed line spacing Δx between adjacent passes, which controlled the local exposure time and spatial uniformity of activation. Following the preliminary screening campaign (2 speeds $\times$ 3 distances) adapted from the twill fabric experience, the UD-specific setup was opportunely studied with a nozzle-to-substrate standoff distance of 8 mm and line velocity of 160 mm/s, as result of spectroscopic campaign on both plasma and functionalized surfaces shown in Chapter 4. These conditions enabled efficient treatment of $300 \times 300 \text{ mm}^2$ UD panels within the laboratory machine envelope while maintaining uniform activation across the unidirectional tape architecture.

3.3 Chemical Surface Characterization Techniques

Surface modifications induced by the N_2 APP Jet treatment were systematically characterized across lengthscales using complementary techniques targeting chemical functionality, graphitic order, plasma chemistry and morphology. Measurements were performed using intradepartmental facilities at DIMEAS–DJLab@Polito and external collaborations. Specific instrumentation details are provided in the following subsections.

3.3.1 Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscopy (FESEM), coupled with Energy Dispersive X-ray Spectroscopy (EDS), provided high-resolution morphological characterization and elemental mapping across lengthscales, from microscale fracture surfaces of glass fibers in Microbond testing to macroscale UD fabric tow morphology and plasma-treatment uniformity. The instrument's external configuration and internal chamber layout are illustrated in Figure 3.4. FESEM leverages field emission electron sources to achieve superior lateral resolution (~ 1 nm) and depth-of-field compared to tungsten-filament SEM, particularly valuable for resolving nanoscale surface features such as plasma-induced micro-roughness, sizing ablation residues, and interfacial debonding signatures without metallisation artefacts. EDS, exploiting characteristic X-ray emission from core-level ionisation under beam bombardment, enabled semi-quantitative C/O/N mapping (detection limit ~ 0.1 wt.%) to confirm functionalization gradients across filaments.

Imaging was conducted using a Tescan Mira 3 GMH field emission scanning electron microscope, distinguished by its high-brightness Schottky field emission gun capable of accelerating voltages from 1 to 30 kV, optimally set to 3–5 kV for high-resolution topographic imaging and 10–15 kV when coupled with EDS for compositional analysis. The instrument features an In-lens secondary electron detector for ultimate surface detail alongside a retractable four-quadrant backscattered electron detector for compositional contrast, with optional In-Beam and low-energy BSE configurations available to enhance performance at reduced landing energies. Operating in high-vacuum mode ($p < 10^{-4}$ Pa) to minimise beam scattering, the system incorporates a fully motorised compucentric stage offering extensive X/Y travel (130 mm), Z range (100 mm), continuous 360° rotation, and tilt capability from -30° to $+90^\circ$, accommodating samples up to 10 kg with effective vibration isolation. Bruker XFlash EDS integration facilitated semi-quantitative C/N/O mapping across fiber tows. For non-conductive specimens, samples were mounted on polished aluminum stubs and received a thin carbon sputter coating to mitigate charging artefacts; the microscope's automated drift compensation and multi-point mapping routines proved invaluable for comprehensive surveys of UD fabric architectures [89].

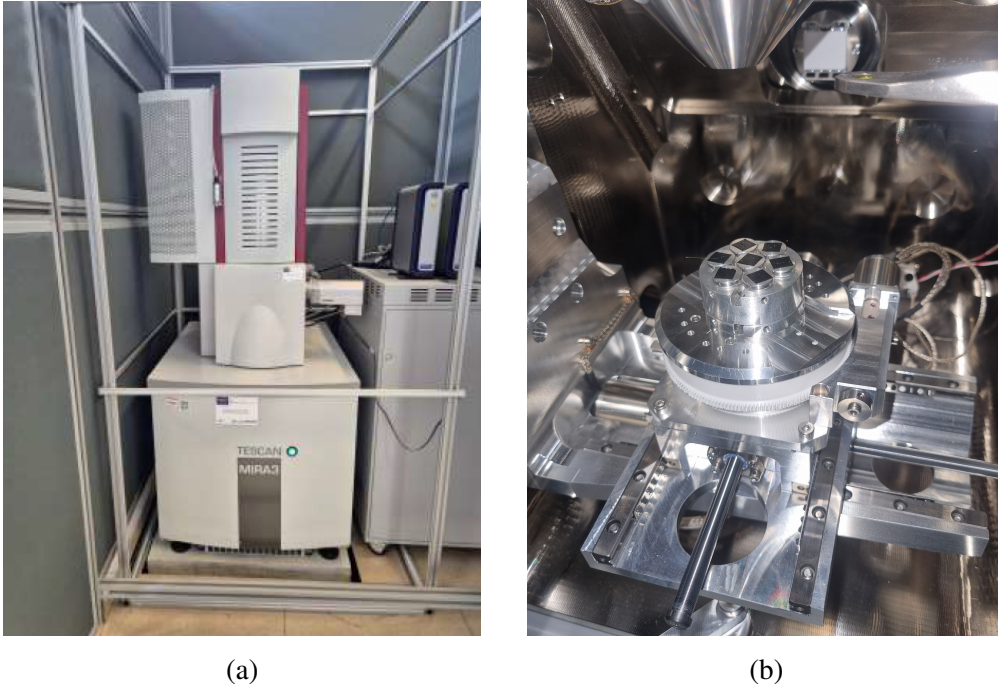


Fig. 3.4 Field emission scanning electron microscopy instrumentation used for morphological characterisation: (a) Tescan Mira 3 GMH FESEM available at Polito; (b) internal specimen holder arrangement adopted for the positioning and observation of fiber-based samples during SEM analysis.

3.3.2 Micro-Raman spectroscopy

Micro-Raman spectroscopy characterised modifications to the graphitic structure of PAN-based carbon fibers through quantitative analysis of the disorder-to-order band intensity ratio, a metric particularly sensitive to surface-level defect engineering induced by plasma exposure. The graphitisation process of PAN-based carbon fibers and the corresponding Raman evolution are schematically illustrated in Figure 3.5. The underlying Raman effect arises from inelastic photon scattering when a high-intensity laser irradiates the sample: while the vast majority of incident photons (ν_{inc}) undergo elastic Rayleigh scattering without energy exchange ($\nu_{\text{scat}} = \nu_{\text{inc}}$), only a minuscule fraction ($\sim 10^{-6}$ – 10^{-8}) interacts with molecular vibrations, giving rise to anelastic scattering. In Stokes-Raman scattering, the molecule absorbs vibrational energy such that scattered photons are red-shifted ($\nu_{\text{Stokes}} = \nu_{\text{inc}} - \Delta\tilde{\nu}$), whereas the inverse anti-Stokes process ($\nu_{\text{anti-Stokes}} = \nu_{\text{inc}} + \Delta\tilde{\nu}$) occurs from thermally populated excited states. The Raman shift $\Delta\tilde{\nu}$ (cm^{-1}), i.e. the difference in wavenumber

between incident and scattered photons, uniquely fingerprints vibrational modes and thus enables material-specific identification [90] [91].

For disordered carbons such as the skin layer of PAN-based CFs, spectral deconvolution targets the D₁ breathing mode ($\sim 1350 \text{ cm}^{-1}$, associated with sp^3 sites and edge/defect activation) and the G tangential mode ($\sim 1580 \text{ cm}^{-1}$, characteristic of sp^2 graphitic order). The key Raman indicator adopted in this work is the D-to-G intensity ratio, defined for each spectrum as

$$R_1 = \frac{I_{\text{D1}}}{I_{\text{G}}}, \quad (3.1)$$

which inversely gauges lateral crystallite perfection (qualitatively, $L_a \propto 1/R_1$). Plasma processing generally elevates R_1 through preferential π -bond scission in low - coordination surface sites, partially hybridising $\text{sp}^2 \rightarrow \text{sp}^3$ and simultaneously facilitating nitrogen incorporation from the discharge, with the formation of additional amine/amide functional groups that support enhanced chemisorption of the epoxy matrix.

Stokes-shifted spectra (1000–2000 cm^{-1} fingerprint) employed 532 nm Nd:YAG excitation ($\sim 1 \text{ }\mu\text{m}$ spot via confocal optics) mounted on Jobin Yvon HR800 LabRAM spectrometer. The high-throughput Czerny-Turner monochromator, thermo electrically-cooled CCD detector, and automated multi-point mapping enabled statistically robust D1/G deconvolution (Lorentzian/Gaussian Voigt fitting) across tow filaments, mitigating local sizing heterogeneity. This technique is hence cited because the D/G ratio is used as a proxy for disorder induced by plasma exposure on the carbon surface, linked with surface reactivity with epoxy matrix.

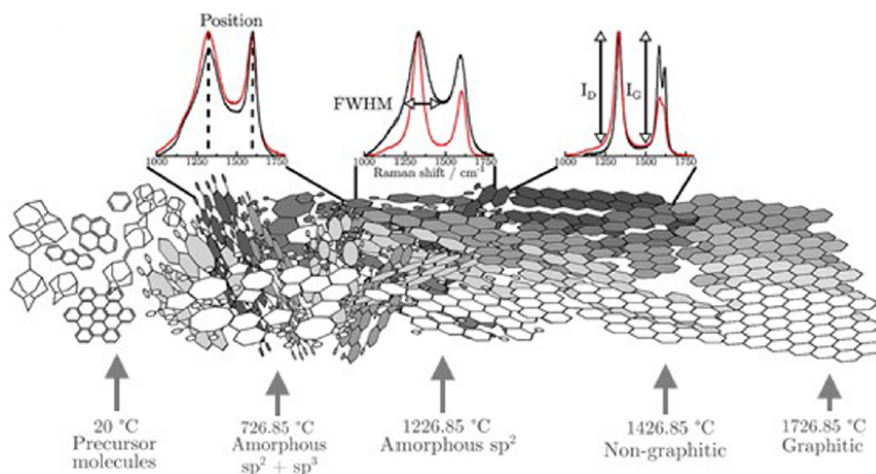


Fig. 3.5 Schematic of PAN CF graphitisation and Raman response [91]

3.3.3 Optical Emission Spectroscopy (OES)

Optical Emission Spectroscopy (OES) was employed to characterize the plasma discharge itself, providing real-time information on the reactive species population generated within the N₂ jet, identifying vibrational-electronic bands diagnostic of nitrogen dissociation and ionisation pathways critical for downstream surface activation. OES exploits radiative de-excitation of electronically/vibrationally excited species generated primarily through electron-impact collisions within the plasma, such as $e^- + \text{N}_2 \rightarrow \text{N}_2^* + 2e^-$ with characteristic threshold energies spanning 11.1 eV for the second positive system up to 18.7 eV for stepwise excitation of the first negative system. The observed emission line intensity follows $I_{ki} \propto n_i A_{ki}$ where n_i represents the population density of the upper energy level k and A_{ki} the Einstein transition probability to the lower level i , enabling non-intrusive quantification of species densities, electron temperature T_e , and $n_e \sim 10^{11} - 10^{14} \text{ cm}^{-3}$ that ultimately correlate with CF surface grafting efficacy [92].

Emission spectra spanning 150–1100 nm were acquired using an Ocean Optics LIBS2500+ compact spectrometer (Environmental Park, Turin) coupled via fiber optic probe to OceanView 2.0.8 software. The characterization instrument is shown in Figure 3.6. Probe positioned near nozzle exit in overpressure isolated carrier-gas chemistry from ambient entrainment, resolving N₂ first positive (1^+ : $\text{B}^3\Pi_g \rightarrow \text{A}^3\Sigma_u^+$, 500–900 nm afterglow, prominent $\sim 589/660/742 \text{ nm}$), first negative (1^- : $\text{B}^3\Sigma_u^+ \rightarrow \text{A}^3\Sigma_u^+$, $\sim 389 \text{ nm}$), and second positive (2^+ : $\text{C}^3\Pi_u \rightarrow \text{B}^3\Pi_g$, $\Delta v = 2$, 300–

400 nm: $\sim 334/337$ (N_2^*), 354, 372, 388, 392 nm) systems. The 300–400 nm window sensitively tracks power-driven ionisation, while 500–900 nm captures metastable post-discharge flux to CF.



Fig. 3.6 Ocean Optics LIBS2500+ spectrometer equipped with fiber optic probe.

3.3.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) provided quantitative surface chemical composition and bonding state analysis by measuring the kinetic energy of photoelectrons ejected from core-level orbitals (top ~ 5 – 10 nm depth) upon monochromatic X-ray irradiation, governed by the photoelectric effect with binding energy

$$E_b = h\nu - E_k - \phi, \quad (3.2)$$

where $h\nu$ is photon energy, E_k the kinetic energy and ϕ is a work function. The system featured a twin-anode monochromatic X-ray source (Al $K\alpha$ $h\nu = 1486.6$ eV / Mg $K\alpha$ 1253.6 eV) coupled to a hemispherical energy analyser for high energy-resolution, with low-energy Ar^+ ion source enabling sputter cleaning (~ 0.5 – 2 nm/min) and depth profiling. Survey scans preceded high-resolution C 1s, O 1s, N 1s ac-

quisitions for peak deconvolution, quantifying graphitic C–C/sp² (~ 284.5 eV), oxygenated (C–O ~ 286 eV, C=O ~ 288 eV, COOH ~ 289 eV) and nitrogenated (pyridinic N ~ 398 eV, pyrrolic ~ 400 eV, graphitic ~ 401 eV) functionalities on UD carbon fabrics and glass Microbond samples revealing plasma-induced polar grafting.

Additional surface observations different from the aforementioned methodology were finally provided by high-resolution optical microscopy documented meso-scale transverse fiber bundle tensile (TFBT) fracture surfaces from UD carbon samples, capturing tow morphology, crack paths and interfacial debonding. SEM/EDS complemented all scales with qualitative binder ablation, rugosity enhancement and absence of thermal damage confirmation. XPS therefore supplements these analyses because quantify changes in surface composition and bonding states, particularly the increase in oxygen- and nitrogen-containing functionalities after treatment.

3.4 Mechanical Characterization Specimen Fabrication

As-received and plasma-treated fabric samples for the chemical-surface characterization campaign did not require any special fabrication as they were simply cut into 1–2 cm² pieces directly from the larger (treated and untreated) textile substrate to ensure representative surface analysis. Crucially, all fiber-based specimens were derived from these pre-treated fabrics; individual fiber-level plasma treatment was avoided not only to maintain high throughput and industrial relevance but also to prevent potential localized morphological damage resulting from excessive plasma exposure or thermal degradation.

On the contrary, specimen fabrication across micro-, meso-, and macro-scales was conducted following well-defined and reproducible procedures (ASTM and similar guidelines [93] [40] [30]) specifically designed to ensure full compatibility with the subsequent multiscale mechanical testing campaign while critically minimising the time interval between APP Jet surface treatment and resin infusion. This temporal constraint – typically maintained below 12–24 hours under controlled storage conditions (sealed vacuum bags, 20–25°C, low humidity) – was essential to preserve the activated surface chemistry induced by nitrogen plasma exposure,

thereby preventing hydrophobic recovery and loss of polar functional groups that would otherwise compromise fiber-matrix interfacial adhesion during composite consolidation. Micro-scale specimens employed individual E-glass fibers for Microbond calibration via custom in-house testing apparatus, meso-scale testing leveraged fiber bundles extracted from UD carbon textiles using purpose-built silicone molds (Grafil 34-700 12K, 200 g/m², 0.2 mm thick dense architecture vs. 0.1 mm sparse variants), and macro-scale validation comprised vacuum-infused UD carbon/epoxy laminates using bio-derived IB2 resin, with preliminary DCB testing on 0.1 mm textiles transitioning to production-scale 0.2 mm architectures for comprehensive delamination characterization.

3.4.1 Micro-Scale Specimen Fabrication

Single E-glass fibers (diameter $\sim 15\text{--}20\ \mu\text{m}$, were selected over carbon fibers of $7\ \mu\text{m}$ diameter to provide superior manual handling precision, reduced surface imperfection sensitivity, and well-characterized baseline adhesion to epoxy systems) were carefully extracted from commercial twill weave fabrics to establish quantitative reference standards for fiber-matrix interfacial shear characterization. Rather than conventional blade-wedge incision of cured droplets, an original methodology was developed featuring precise fiber centring within a G34 commercial needle (internal diameter $100\ \mu\text{m}$). Epoxy resin droplets (IB2 formulation, nominal diameter D_g $100\text{--}200\ \mu\text{m}$) were deposited atop the needle aperture with the embedded fiber tensioned through its polished circular corona (surface mechanically polished to eliminate characteristic needle tip geometry, yielding a rectilinear edge profile for uniform circumferential stress distribution).

To ensure appropriate specimen reliability, several curing parameters and process variants were systematically evaluated, as summarized in Table 3.2. Following this assessment, the curing cycle that requires 16h at room temperature followed by 8h at 80° was selected as standard protocol, as it provided a suitable balance between complete cure, geometry retention, and droplet symmetry. Consequently only specimens produced under this revised condition were included in the final analysis, allowing that the interfacial shear characterization was performed on droplets with superior morphological quality and consistent alignment relative to embedded fiber. Additional process variables were also examined during specimen preparation, including resin degassing and oven ventilation. Given the very small resin volumes

involved, degassing was initially omitted and later introduced only as a precautionary step on an excess resin batch from which the droplets were subsequently extracted. No marked change in the mechanical response or in the qualitative appearance of the debonding curves was observed. Similarly, forced ventilation during the high-temperature cure was considered as a possible source of droplet asymmetry or local structural non-uniformity; however, its effect remained primarily qualitative, leading at most to a visually smoother droplet geometry without measurable influence on the final test outcomes.

Table 3.2 Summary of evaluated cure schedules.

Cure Schedule	Outcome	Assessment
3h RT + 3h 80°C	Partial cure; voids	Intermediate
No pre-cure + 6h 60°C	Brittle failure; voids	Not suitable
16h RT + 6h 80°C	Minor brittle response	Acceptable
16h RT + 8h 80°C	Stable geometry; repeatable	Highly acceptable

Additionally, to disentangle plasma-specific effects from commercial sizing influence, as explored in detail in the following Section 3.4.2 and literature (Section 2.2.1), a desized GF series was prepared for baseline Microbond testing. Starting from representative samples extracted from the original fabric, single filaments were isolated following an aggressive dual-cleaning process: thermal desorption at 300°C for 1 h (N₂ inert) followed by 2 h acetone immersion, yielding sizing-free graphitic surfaces verified via FESEM pre-testing. This controlled variant (n=19 specimens) enabled direct assessment of intrinsic fiber response absent artificial screening.

During controlled crosshead displacement (0.2 mm/min, MTS Tensile Loading machine, 10 N load cell), the receding droplet becomes progressively entrapped by the needle's circular rim, developing perfectly axisymmetric debonding stresses until catastrophic interfacial failure at peak load – fundamentally distinct from traditional asymmetric wedge geometries that introduce non-uniform stress concentrations and edge effects.

The MicroBond testing apparatus (Figure 3.7) was designed and fabricated in-house to enable precise, repeatable debonding under these novel boundary conditions. A 3D-printed support structure (PLA filament) was engineered for rigid integration with standard universal testing machine frames, featuring a fixed base plate securely clamped to the machine frame and precision alignment system. A dovetail guide (Norolem, Italy [94]) with micrometric screw adjustment (0.01 mm resolu-

tion) accommodated the needle-fixture assembly, allowing acceptable fiber-needle concentricity and eliminating undesirable rotations during testing.

Pre-debonding droplet geometry (D_g , embedded length L_{emb} , meniscus contact angle) was rigorously documented via high-resolution optical microscopy (500x magnification, 1 μm resolution). Post-fracture surface morphology are reported in Section 5.1 and it was systematically characterized using the FESEM Tescan Mira 3 (DIMEAS-DJLab@Polito), documenting the diagnostic transition from clean adhesive failure in untreated references to partial cohesive matrix failure with extensive resin retention in plasma-treated specimens.

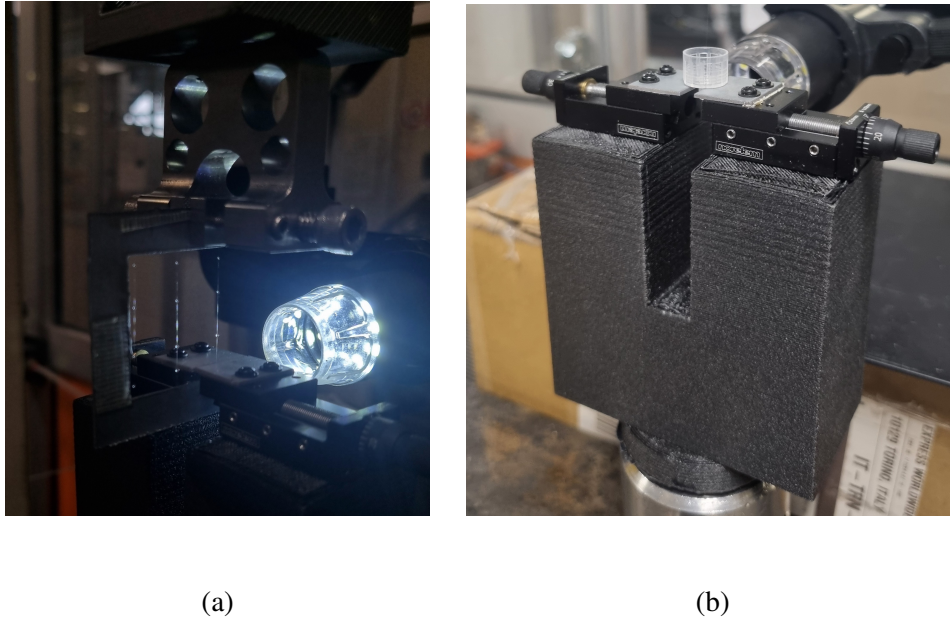


Fig. 3.7 In-house built Microbond testing configurations: (a) preliminary configuration based on blade-assisted droplet debonding; (b) final circular debonding configuration with fiber centering through a polished G34 insulin needle.

3.4.2 Meso-Scale Specimen Fabrication

Meso-scale transverse fiber bundle tensile (TFBT) specimens were systematically extracted from UD carbon textiles spanning both high filament packing density architectures (0.2 mm nominal thickness, directly representative of macro-scale preform consolidation behavior) and lower-density screening variants (0.1 mm thickness, enhanced interface exposure for sensitivity analysis). As shown in Figure 3.8, custom silicone molds were fabricated specifically for TFBT specimen production, featuring

dogbone geometries precisely dimensioned per ASTM D638 type IV configuration [95], to position fiber bundles at the exact center of the reduced cross-section. These molds enabled controlled resin infiltration and uniform curing around bundles during room temperature initial cure followed by 80°C post-cure, eliminating geometric variability and allowing good transverse stress distribution during testing. The final specimen was polished in the vicinity of the embedded fiber bundle to avoid localized reinforcement effects.

Mechanical characterization employed grip separation at 10 mm/min displacement rate on an Instron 5569 universal testing frame fitted with 5 kN load cell capacity. Comprehensive fracture surface analysis via optical microscopy (100x) consistently documented the characteristic transition from pristine adhesive debonding (optically clean fiber surfaces) in as-received (NT) bundles to partially cohesive failure morphologies exhibiting quantifiable resin retention, enhanced surface roughness, and matrix ligament bridging in APP Jet-treated specimens; representative observations are reported in Section 5.2.

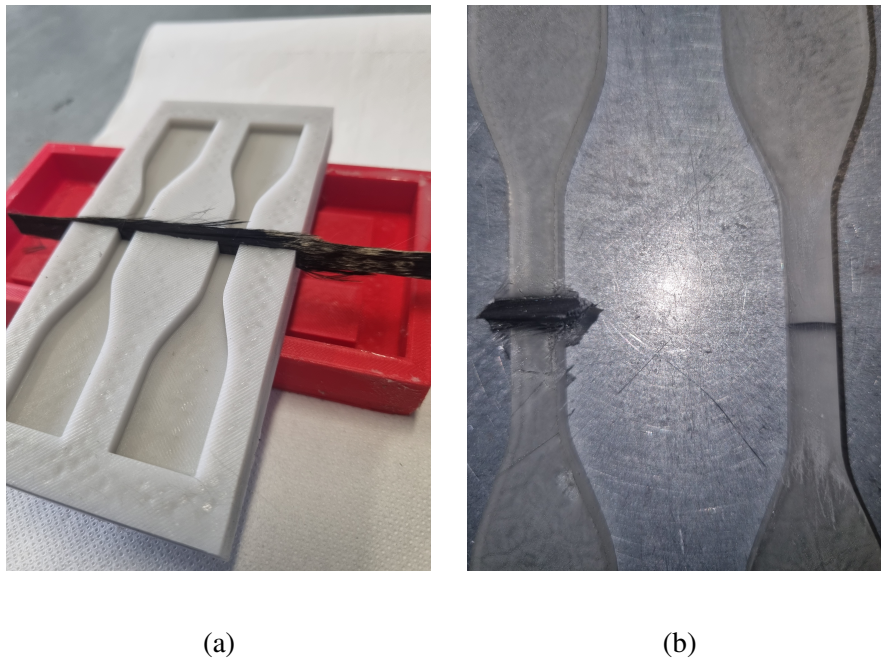


Fig. 3.8 TFBT meso-scale specimen fabrication: (a) custom silicone dogbone mould with fiber bundle in correspondence with the reduced cross-section prior to resin curing; (b) representative cured specimens before and after local grinding/polishing of the fiber region.

3.4.3 Laminate and Macro-Scale Specimen Fabrication

Macro-scale composite laminates were manufactured by vacuum resin infusion. The scheme of the manufacturing process is shown in Figure 3.9: following manual mixing of IB2 epoxy resin with hardener, the formulation was infused into the vacuum bag via controlled vacuum-assisted resin infusion, utilizing the same vacuum pump that maintained bagging integrity during pre-infusion degassing to preclude air entrapment. Within the sealed vacuum envelope, layers $[0^\circ]$ UD carbon fiber preforms were precisely hand-laid up with unidirectional alignment parallel to the programmed resin flow path, ensuring homogeneous fiber wet-out. Optimal infusion uniformity and subsequent demolding without surface discontinuities were achieved through the strategic deployment of resin distribution mesh and a release system comprising wax-coated working plane and peel-ply film on the tool face. The cured laminate was then cut to final geometries by waterjet machining (220V/60Hz Wazer-Pro cut machine). Three main specimen families were produced, namely preliminary DCB specimens based on thinner UD carbon textiles, final DCB specimens based on thicker and more representative UD reinforcements, and larger coupons for dynamic impact testing. Example of the fabricated coupons are displayed in Figure 3.10. Since the final cured laminate thickness differed depending on textile architecture and target application, specimen description is herein provided in terms of final coupon geometry.

Preliminary Double Cantilever Beam (DCB) specimens were manufactured from laminates based on 0.1 mm-thick UD carbon fabrics and machined to a nominal geometry of $140 \times 25 \times 2.5$ mm. A second and more representative DCB configuration was then produced using 0.2 mm-thick UD carbon textiles, yielding specimens with nominal dimensions of $140 \times 25 \times 4.5$ mm. In both cases, a central aluminum foil insert was introduced during laminate fabrication in order to generate the artificial starter crack required for Mode I delamination testing. The insert was wax-coated on both faces to prevent unintended adhesion during infusion and curing. The adopted geometries were selected so as to satisfy the ASTM D5528 thickness-to-precrack constraint, maintaining the condition $a_0/h > 10$ [40].

Load introduction for DCB testing can in principle be achieved either by means of piano hinges or adhesively bonded loading blocks. In the present work, the latter solution was adopted, using aluminum loading blocks bonded with room-

temperature-curing structural adhesive. This configuration was preferred to ensure stable load transfer and compatibility with the selected testing arrangement.

Dynamic impact test specimens were fabricated from vacuum-infused laminates based on 0.2 mm UD carbon textiles, using the same panel production route adopted for the thicker DCB configuration. However, the final coupon geometry was specifically modified to suit the impact and crashworthiness-inspired loading setup [96]. In particular, specimens were waterjet-cut to nominal dimensions of $150 \times 50 \times 3.5$ mm.

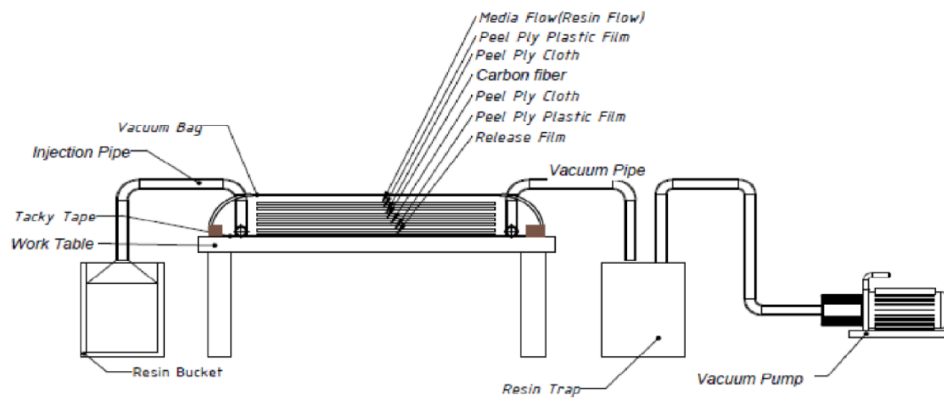
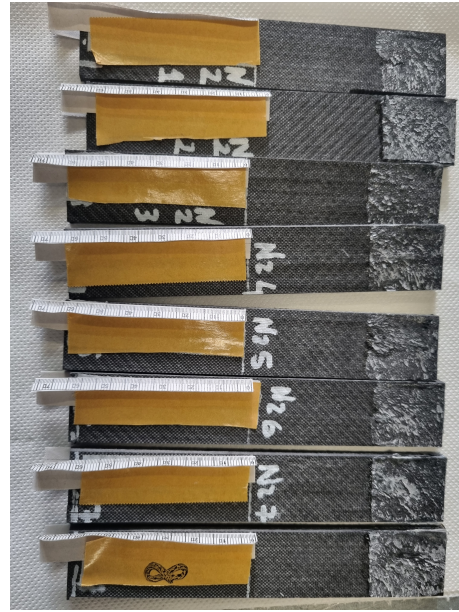


Fig. 3.9 Vacuum Assisted Resin Infusion system [48].



(a)



(b)

Fig. 3.10 Vacuum resin infusion composite fabrication and final specimen preparation: (a) setup adopted for the manufacture of UD carbon/epoxy laminates (NT and plasma-treated N₂ textile configuration); (b) example of DCB specimens ready for bonding to loading blocks and with rulers for crack monitoring.

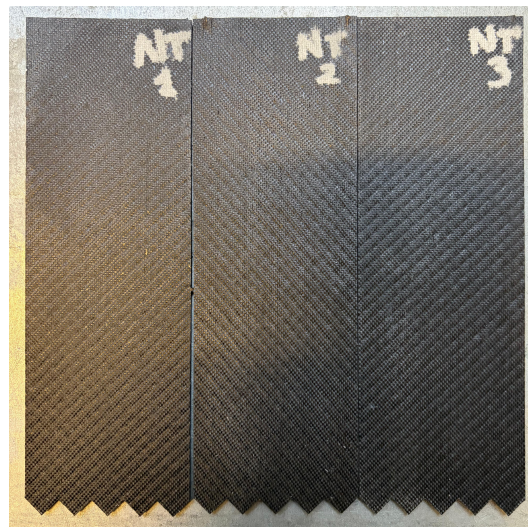


Fig. 3.11 Representative impact test coupons.

3.5 Mechanical Testing Procedures

Mechanical testing was structured according to a multiscale approach aimed at linking local fiber/matrix debonding phenomena to bundle-scale stress transfer and, finally, to laminate-scale delamination and crash-like opening response. For this reason, the adopted methodologies included a non-standard micro-scale Microbond test, a meso-scale Transverse fiber Bundle Tensile test (TFBT), and macro-scale laminate tests under quasi-static and dynamic conditions respectively DCB and Drop Dart impact tests. Standardised procedures were followed whenever available, whereas literature-derived methodologies were adopted for non-standard configurations developed to reproduce interface-dominated or crashworthiness-oriented failure mechanisms.

3.5.1 Micro- and Meso-Scale test: MB and Bundle test

Micro-scale fiber/matrix adhesion was investigated by means of MicroBond testing using a custom fixture mounted on an MTS loading machine equipped with a 10 N load cell. The development of the experimental setup followed two successive configurations, previously shown in Figure 3.7 in the previous Section 3.4.1. In the preliminary stage, a blade-like restraining system was adopted, in which the cured resin droplet was supported by two metal panels with sharp edges during fiber extraction. This initial configuration was useful for feasibility assessment and for defining the basic debonding sequence. However, the blade-supported arrangement revealed a pronounced sensitivity to specimen alignment and to the local interaction between the resin droplet and the restraining edges, potentially introducing local parasitic contact and friction effects during fiber pull-out action. The final campaign was therefore conducted using the needle-based configuration shown in Figure 3.7 (b), which provided a more controlled, uniform and repeatable support condition. In both cases, the test consisted in pulling a single fiber relative to a cured resin droplet while continuously recording load and displacement. To interpret the post-test morphology consistently, the present work considers two qualitative failure morphologies, namely adhesive-like and cohesive-like [97] [29] [70]. The literature show a proper qualitative interpretation of Microbond debonding curves and the aforementioned fracture distinction features, as well as the interpretation of resin remnants on the fiber surface as evidence of mixed or cohesive-like feature. A clean

or nearly clean fiber surface after pull-out is taken as evidence of a predominantly adhesive failure, in which debonding occurs mainly at the fiber/matrix interface. By contrast, the presence of visible resin remnants on the fiber surface is interpreted as a cohesive-like failure, indicating that fracture involved the resin or interphase rather than a purely interfacial separation. Since the Microbond test provides an apparent interfacial shear strength and is sensitive to specimen geometry, alignment, and frictional effects, the visual appearance of the debonded surface should be interpreted together with the mechanical response rather than used as a stand-alone indicator of interfacial quality.

MicroBond testing is used to estimate the apparent interfacial shear strength, although it is not governed by a universally accepted standard and is well known to be sensitive to specimen preparation, embedded length, droplet geometry, fixture alignment, and frictional effects. Before testing, each specimen was preliminarily inspected by optical microscopy in order to measure the fiber diameter D_f and the embedded droplet length L_e , which are the key geometric quantities required for data reduction. During the test, the fiber was loaded under displacement control at 2 mm/min until the recorded force reached a maximum value $F_{\max}$, corresponding to the onset of interface detachment. A successful test was identified by the characteristic load history typically associated with Microbond debonding, as shown in Figure 3.12, namely an initial quasi-linear increase in force, followed by a distinct peak load, a sudden post-peak drop due to unstable interfacial failure, and a residual tail associated with frictional sliding of the detached droplet along the fiber as shown by the first curve on the left. The presence of this residual frictional load was considered important because it indicated that the test ended with actual droplet separation followed by interfacial sliding, rather than fixture slippage or premature fiber fracture, as shown in Figure 3.12 with middle plot and the one on the right respectively.

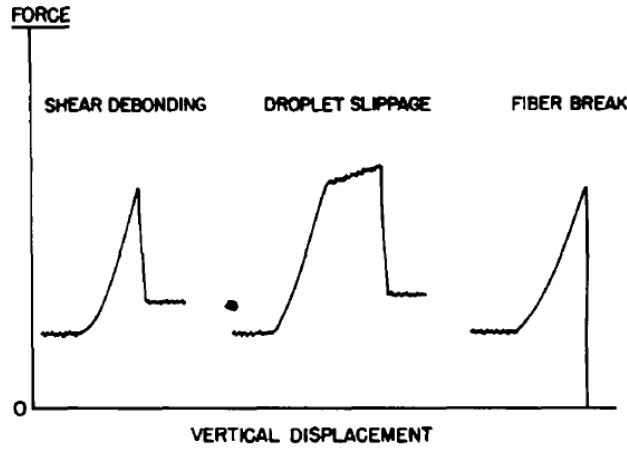


Fig. 3.12 Representative load–displacement curves for three possible results of MB test [97].

The apparent interfacial shear strength was calculated from the peak debonding force according to the classical microbond relation

$$\tau_{\text{IFSS}} = \frac{F_{\text{max}}}{\pi D_f L_e} \quad (3.3)$$

where F_{max} is the maximum recorded load, and as specified before, D_f is the fiber diameter, and L_e is the embedded length of the droplet. Since the stress state in the droplet is not perfectly uniform and the method is affected by local stress concentrations, blade contact conditions, and frictional contributions after debonding, the obtained τ_{IFSS} values were interpreted as apparent comparative parameters rather than absolute interface properties. Post-test observation of the load history and specimen morphology was therefore used as an additional validation criterion to discriminate between genuine interfacial separation and invalid tests affected by fiber rupture, excessive droplet plasticity, or unstable specimen positioning.

In methodological terms, the Microbond analysis was therefore based on four sequential steps: (i) measurement of D_f and L_e before testing, (ii) monotonic loading of the specimen up to F_{max} , (iii) verification of the characteristic post-peak force drop with residual frictional sliding, and (iv) calculation of τ_{IFSS} from the peak load. This combination of geometric control, force-history interpretation, and failure condition observation was considered essential in order to minimise artefacts, which are known from the literature to have a strong influence on apparent IFSS values.

Meso-scale interface-dominated behavior was investigated through Transverse fiber Bundle Tensile tests carried out on an Instron universal testing machine equipped with a 5 kN load cell (Figure 3.13). In this configuration, a fiber bundle embedded within a resin-rich dogbone specimen is loaded in tension so that failure is promoted in the bundle/matrix interaction region. This method does not provide a pure fracture-mechanics parameter, but it is effective for comparing the stress-transfer capability of different interface conditions and for identifying the transition from predominantly adhesive to more cohesive failure modes at the bundle scale.

The specimens were tested under displacement control at constant crosshead speed of 5 mm/min, within the quasi-static range commonly adopted in tensile and bond-strength tests (0.1–10 mm/min) [29] [98]. The applied force was continuously recorded and converted into an equivalent nominal stress by dividing the load by the resistant cross-sectional area of the specimen neck where the fiber bundle is embedded, according to

$$\sigma = \frac{P}{A} \quad (3.4)$$

where P is the applied load and A is the net resistant section. The maximum stress was taken as the main comparative parameter for each testing condition. The force-displacement response was used together with the fracture morphology to identify whether failure was abrupt and interface-dominated or accompanied by more distributed matrix cracking and progressive bundle pull-out. Literature on TFBT highlights that this kind of test is particularly informative when interpreted together with the post-fracture surface appearance, rather than only through the peak load value [29].

For this reason, the post-test analysis focused not only on the maximum stress level but also on the morphology of the fractured region. In particular, the fracture surfaces were inspected to distinguish between adhesive damage, characterized by relatively clean bundle surfaces and limited matrix retention, and cohesive damage, characterized by significant matrix residues, resin tearing, and more evident local deformation of the matrix-rich region. The relative presence of these two morphologies was used as a qualitative indicator of the quality of stress transfer across the interface. In addition, any fiber pull-out, asymmetric crack propagation, or local edge defects

was recorded because such features may influence the interpretation of the measured strength.



Fig. 3.13 Transverse Fiber Bundle Test [0°] on CF/epoxy specimen.

3.5.2 Macro Scale testing: DCB and Dynamic Impact

Macro-scale testing was performed to assess whether the interfacial modifications induced at fiber level could be translated into measurable laminate-scale improvements under opening-dominated loading conditions. The adopted configurations included standardized Mode I delamination testing by Double Cantilever Beam (DCB), together with a non-standard crashworthiness-inspired coupon tests developed to reproduce dynamic opening conditions under controlled anti-buckling constraint [96]. This combined approach enabled comparison across loading rates while preserving a coherent laminate architecture and specimen preparation route.

Mode I interlaminar fracture toughness was determined by Double Cantilever Beam testing according to ASTM D5528, using an MTS loading machine equipped with a 500 N load cell (Figure 3.14) and a high-resolution optical camera for crack monitoring. According to the standard, the DCB specimen contains a pre-implanted non-adhesive insert at the laminate mid-plane, while the opening load is introduced through bonded loading blocks, as shown in Figure 3.15. Delamination growth was monitored along the specimen edge by combining the optical recording system with the millimeter rulers applied to the coupon sides.

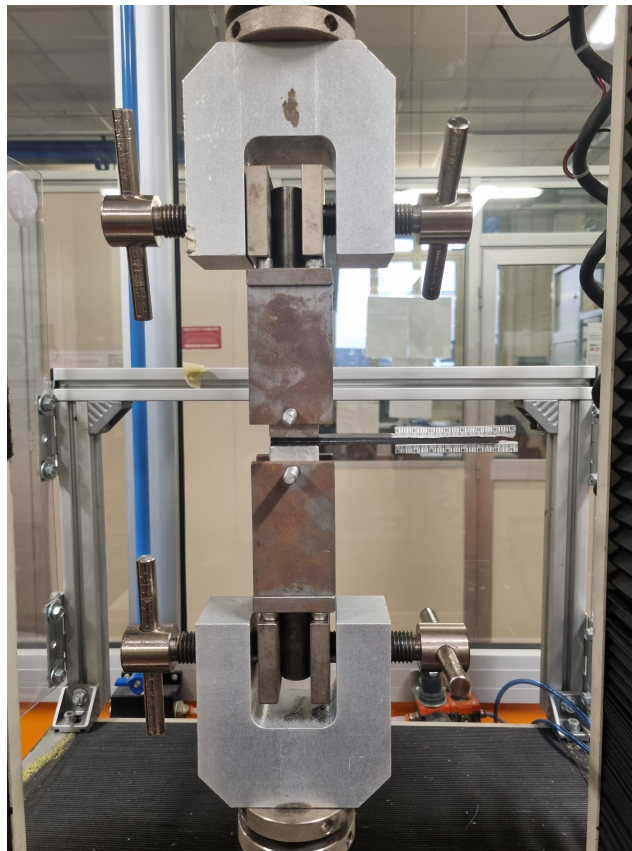


Fig. 3.14 Double Cantilever Beam CF/epoxy specimen mounted on MTS Loading machine test.

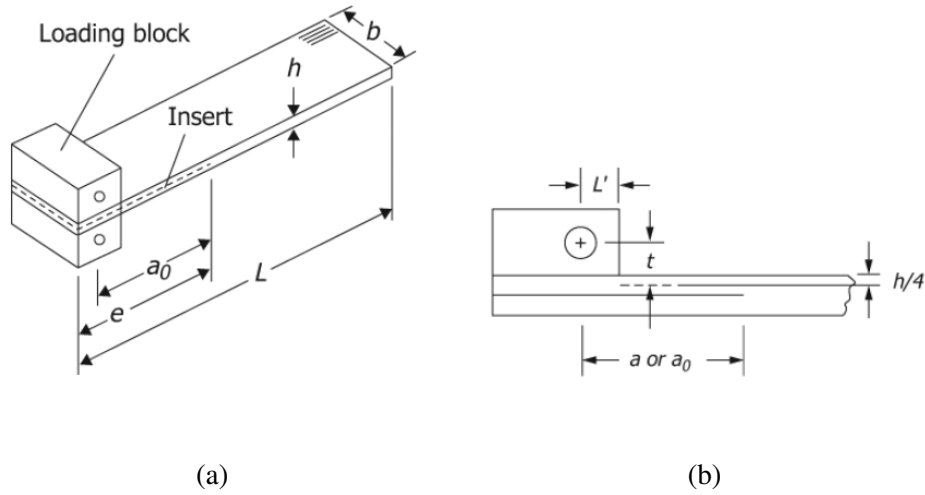


Fig. 3.15 Double Cantilever Beam specimen characteristics: (a) loading blocks to ensure load transfer by MTS Loading machine; (b) side view of final specimen [40]

Before testing, specimen width b , thickness h , initial crack length a_0 , and the geometric parameters associated with the loading blocks were measured. In particular, the ASTM data reduction for loading-block configurations requires the horizontal distance L from the loading-block pin center to the block edge and the vertical distance t from the pin center to the mid-plane of the specimen arm. During testing, force P and opening displacement δ were recorded continuously, while the crack front position was monitored visually. The initial loading stage was carried out under displacement control until the delamination propagated by a short increment beyond the insert, after which the specimen was partially unloaded and the first propagated crack length a_1 was measured. The specimen was then reloaded and the same procedure was repeated to record the subsequent propagation points a_i , thus enabling the reconstruction of the full resistance curve.

The ASTM D5528 compliance calibration method was adopted for the calculation of the Mode I interlaminar fracture toughness. For each crack length a_i , the corresponding specimen compliance was defined as

$$C_i = \frac{\delta_i}{P_i} \quad (3.5)$$

where δ_i and P_i are the opening displacement and applied load associated with the selected crack length. According to the standard, the first two compliance values

correspond to the initiation from the insert and to the first propagated crack after reloading, whereas the following points correspond to the propagation values measured at increasing crack lengths. If initial seating or fixture nonlinearity was present, the displacement values were corrected by subtracting the nonlinear contribution NL so that the linear portion of the force-displacement curve intersected the origin before applying the compliance calibration procedure.

The critical force used to calculate G_{IC} for both the non-precracked and precracked configurations was determined by the 5% compliance offset procedure prescribed by ASTM D5528. More specifically, the linear part of the force-displacement curve was identified in the 25–75% peak-load range, then a line with 5% higher compliance was constructed. The critical load P_c was taken either as the intersection with this offset line, denoted P_5 , or as the maximum load P_{max} if the intersection occurred after the peak. This procedure yields the non-precracked toughness G_{IC}^{NPC} from the initial loading curve and the precracked toughness G_{IC}^{PC} from the first reloading cycle, while the subsequent propagation values are calculated at the visually observed crack lengths a_1 .

Within the compliance calibration framework, the Mode I interlaminar fracture toughness was calculated as

$$G_{Ic} = \frac{mP_c\delta_c}{2ba}FN \quad (3.6)$$

where m is the slope of the least-squares regression of $\log(CN)$ versus $\log(a)$, b is the specimen width, a is the current crack length, P_c and δ_c are the critical force and displacement, and F and N are correction factors accounting for large displacement effects and loading-block geometry. According to ASTM D5528, the large-displacement correction factor F is given by

$$F = 1 - \frac{3}{10} \left(\frac{\delta}{a} \right)^2 - \frac{3}{2} \left(\frac{\delta t}{a^2} \right) \quad (3.7)$$

while the loading-block correction factor N is expressed as

$$N = 1 - \left(\frac{L}{a} \right)^3 - \frac{9}{8} \left[1 - \left(\frac{L}{a} \right)^2 \right] \left(\frac{\delta t}{a^2} \right) - \frac{9}{35} \left(\frac{\delta}{a} \right)^2 \quad (3.8)$$

for the geometry defined in the standard.

The DCB analysis therefore included three distinct outputs: the non-precracked initiation toughness GI_c^{NPC} , the precracked toughness GI_c^{PC} , and the propagation values $GI_c(a_i)$ used to construct the resistance curve (R curve). Since ASTM D5528 explicitly notes that fiber bridging may artificially elevate propagation values, particular attention was given to the comparison between the initiation values and the subsequent rising part of the R-curve. For this reason, the initiation parameters were considered especially important for comparing untreated and plasma-treated laminates, while propagation data were interpreted in parallel with the visual evidence of crack growth and any possibly bridging phenomena.

Dynamic impact test was performed using a custom anti-buckling fixture developed at Politecnico di Torino for crashworthiness-oriented testing of flat composite coupons. The underlying rationale of this setup, as discussed in the doctoral work of Vigna [96], is to constrain the specimen sufficiently to suppress global buckling while leaving a controlled unsupported region where progressive crushing and splaying-type failure can develop. The specimen was clamped in the fixture and loaded dynamically by means of an Instron Fractovis drop-dart impact system (Figure 3.16), whose nominal operating range spans 0.6–1800 J in energy, 2–70 kg in falling mass, and impact velocities up to 24 m/s. The specific impact mass, initial velocity, and nominal input energy used in each campaign are reported in the following chapter.

From a methodological standpoint, the dynamic procedure consisted of the following sequence. First, the specimen dimensions and mass were determined, together with the dart mass and initial impact velocity required to set the nominal machine energy. Second, the drop tower was used to acquire the raw force-time signal during the test. Third, the displacement of the striker was reconstructed through physics-based double integration of the filtered force signal by applying Newton's second law to the moving impact mass. This approach follows the procedure described in the crashworthiness literature associated with the fixture and is necessary because the direct encoder measurement may become unrepresentative after the initial crushing stage, whereas the striker dynamics provide a physically consistent estimate of the actual crushing displacement.

In the adopted formulation, the measured force signal $F(t)$ was first converted into acceleration of the dropped mass according to the dynamic equilibrium of the striker. Once acceleration was known, numerical integration yielded the instanta-

neous striker velocity $v(t)$, and a second integration provided the striker displacement $z(t)$. The resulting $F(z)$ curve was then used for the evaluation of the crushing response. This force-displacement representation is more meaningful than the raw force-time curve because it directly relates the measured load to the actual crushing progression of the specimen and allows the absorbed energy to be calculated as the area under the curve.

A dedicated MATLAB routine was developed to automate and standardize the post-processing of the dynamic tests. The code was designed to robustly import machine CSV files, handling format inconsistencies, removal of duplicated entries, and verification of the acquisition frequency. The force signal was then filtered through a multi-stage procedure aimed at removing parasitic vibrations and machine-related noise while preserving the force plateau associated with stable crushing. This filtering stage was particularly important because, as also noted in the work of Vigna, the raw drop-tower response is strongly affected by the initial impact between striker and loading plate, by load-cell structural vibrations, and by the transient associated with trigger activation.

After filtering, the code reconstructed the striker displacement and automatically identified the interval of stable crushing through two characteristic points, z_1 and z_2 , arbitrarily chosen according to specific criteria specified following. The first point, z_1 , marks the beginning of the steady crushing stage after the trigger-dominated transient, whereas the second point, z_2 , marks the end of the stable plateau before force degradation or end-of-stroke effects become dominant. The algorithm was conceived to minimise operator dependence in the choice of the integration interval and to reproduce the literature principle that only the stable crushing region should be used for the calculation of average crushing force and specific energy absorption, while the initial peak and the final deceleration zone should be excluded.

Once the interval $[z_1, z_2]$ had been identified, the mean crushing force F_{mean} was calculated over that displacement range and used as the main descriptor of the stable crash response. The absorbed energy in the same interval was obtained from the integral of the force-displacement curve,

$$E_{\text{abs}} = \int_{z_1}^{z_2} F(z) dz \quad (3.9)$$

and the specific energy absorption (SEA) was then determined following the standard crashworthiness formulation for flat coupons with constant cross-section [96],

$$\text{SEA} = \frac{F_{\text{mean}} \cdot l}{m_s} \quad (3.10)$$

where $l = z_2 - z_1$ is the effective crush length and m_s is the mass of the crushed specimen portion. This metric provides a material-intrinsic measure of energy absorption capability, normalised by mass, and aligns with established literature practices for progressive failure characterization.

The post-processing code also generated diagnostic outputs used to validate the physical consistency of each test. In particular, the comparison between reconstructed striker displacement and the machine-provided displacement signal was used as a kinematic quality check, while the filtered and unfiltered force histories were inspected to verify that the adopted signal treatment removed noise without suppressing physically meaningful oscillations related to damage progression. In this sense, the MATLAB workflow was not only a data-reduction tool, but an integral part of the methodology adopted to obtain robust and repeatable crash metrics from a non-standard dynamic test.



Fig. 3.16 Instron Fractovis drop dart machine test and High resolution and acquisition camera.

Chapter 4

Surface Characterization Analysis

4.1 Carbon Fiber Reinforcements Characterization

The surface modifications induced by the adopted N₂ APP Jet treatment on unidirectional carbon fiber textiles were systematically investigated through a comprehensive suite of complementary analytical techniques detailed in Section 3.3: Optical Emission Spectroscopy (OES) of the plasma source, micro-Raman spectroscopy for graphitic structure assessment, X-ray Photoelectron Spectroscopy (XPS) for atomic composition and functional group quantification, and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) for morphological and elemental mapping. Together, these analysis were used to identify the sequential effects of cleaning, etching, and activation on industrial-grade UD reinforcements.

The preliminary screening campaign was carried out on the 0.1 mm nominal-thickness textile variant. This thinner configuration exhibits identical single-filament properties to the 0.2 mm variant adopted for macro-scale laminate validation: Grafil 34-700 24K PAN-based carbon fiber ($\sigma_t \approx 4.8$ GPa, $E \approx 234$ GPa, $\rho \approx 1.80$ g/cm³) with equivalent sizing chemistry applied by the manufacturer. The two variants differ only in areal density and grammage, which affect plasma penetration into tow bundles but do not alter the intrinsic surface responsiveness at the filament scale. Relative to twill architectures investigated in prior work [16], UD textiles are more prone to tow shielding exhibiting higher filament packing density and unidirectional tow alignment, thus requiring finer control of flux exposure and ensuring uniform homogeneous and back-to-front activation. The following analyses can be considered

as representative of the UD carbon reinforcement systems employed throughout this study since the two UD fibers used do not present significant differences.

The characterization campaign was based on a preliminary screening of several APP Jet operating conditions, including an N₂ flow rate of 34 l/min, a nominal power of 570 W at 23 kHz excitation frequency, an 85% duty cycle corresponding to approximately 330 V and 13.5 A, two robot translation speeds, and two nozzle-to-substrate standoff distances. Here, the translation speed refers to the linear motion of the torch along the fabric surface; therefore, 320 mm/s is directly linked to a shorter plasma exposure time than 160 mm/s, which increased the residence time of the discharge on the substrate.

Among the configurations considered, the 8 mm standoff and 160 mm/s translation speed condition was retained for the final delineation campaign, as it provided the most balanced combination of surface cleaning, controlled etching, and activation. By contrast, the higher translation speed of 320 mm/s reduced the cumulative exposure time, while the 10 mm standoff lowered the plasma flux density reaching the substrate, and both conditions produced a weaker surface response.

The selected regime of 8 mm standoff and 160 mm/s scan speed was also consistent with preliminary DCB tests conducted on vacuum-infused UD/epoxy laminates, where both the 0.1 mm and 0.2 mm textile variants showed the most favorable response under this treatment window. This behavior suggested a balanced combination of cleaning, controlled etching, and activation without compromising filament integrity. The following sections therefore quantify the chemical, physical, and morphological transformations distinguishing as-received from plasma-treated surfaces, and further discuss the mechanisms of contaminant removal, controlled etching, and functional-group grafting underlying these modifications.

4.2 Cleaning, Etching, and Activation: Evidence from Characterization

In the context of N₂ APP Jet treatment of carbon fiber (CF) UD fabrics for epoxy matrix composites, OES provides critical insight into the emissive power of N₂ species, reflecting the plasma chemistry that underpins effective surface activation and fiber-matrix adhesion enhancement. Graphitisation renders CF surfaces chemi-

cally inert, with scarce polar groups leading to poor wettability ($\theta_{\text{water}} > 120^\circ$) and low surface free energy (SFE ~ 40 mN/m), inherently limiting epoxy bonding and yielding suboptimal interlaminar properties such as fracture toughness and shear strength as highlighted by Tiwari et al. [99]. The latter reference is relevant here because it agrees that there is a limited interaction between the untreated substrate and the resin. N_2 plasma sequentially ablates sizing residues, etches surface roughness to promote mechanical interlocking, and introduces nitrogen-containing functional groups such as amines and amides, thereby substantially enhancing surface polarity, free energy, and mechanical metrics like ILSS and G_{IC} .

4.2.1 OES Results and Plasma Source Characterization

OES comprehensively monitored the APP Jet N_2 source over the broad spectral range of 150 to 1100 nm, successfully resolving the characteristic vibrational-electronic band systems of molecular nitrogen that dominate the emission profile. These include:

- the first positive system, 1^+ transition from $\text{B}^3\Pi_g$ to $\text{A}^3\Sigma_u^+$, manifesting as prominent features at approximately 589, 660, and 742 nm within the extended 500–900 nm afterglow region;
- the first negative system, 1^- transition $\text{B}^3\Sigma_u^+ \rightarrow \text{A}^3\Sigma_u^+$, centered around ~ 389 nm;
- the second positive system, 2^+ transition $\text{C}^3\Pi_u \rightarrow \text{B}^3\Pi_g$ with $\Delta v = 2$ vibrational progression, yielding the diagnostically crucial sequence at $\sim 334/337$ nm (N_2^*), 354, 372, 388, and 392 nm in the high-energy 300–400 nm window.

As illustrated in Figure 4.1, the most prominent diagnostic feature in the high-energy region is the ~ 334 nm peak, associated with the N_2^* emission of the second positive system (2^+), which serves as a primary indicator of reactive species generation under the adopted plasma conditions, with supporting literature on N_2 plasma functionalization of carbon surfaces [100] [101] that support the use of these emission features as indicators of plasma activity. The shorter-wavelength 300–400 nm regime proves particularly sensitive to power-dependent ionisation processes, whereas the longer 500–900 nm manifold captures contributions from long-lived metastable

states that sustain the post-discharge nitrogen flux impinging upon the CF substrate. The optical probe was positioned in an overpressure configuration immediately at the nozzle exit to effectively exclude ambient O₂ entrainment, ensuring a pure N₂ plasma signature; observed inter-acquisition intensity variations remained limited to $\leq 10\%$, primarily attributable to minor differences in probe alignment as well as fluctuations in ambient relative humidity (40–60% RH) and laboratory temperature (22–25°C).

The OES analysis was designed to systematically isolate the effects of individual parametrisations, allowing for the rigorous deconvolution of their distinct contributions to the Power/Gas flux ratio, defined as plasma power per unit gas volume (W/(L/min)), which fundamentally governs gas ionisation extent and reactive species flux to the CF surface. The concurrent variation of voltage and flow was designed to avoid interpretative confusion, as both parametrisations influence electron density ($n_e \sim 10^{11}–10^{14} \text{ cm}^{-3}$) and collision dynamics in interconnected ways. Two focused acquisition series were implemented: first, reference voltage stepped at 70%, 85%, and 100% (modulating power through discharge peak voltage at constant flow to isolate energy effects); second, N₂ flow varied across 31, 34, 37, and 40 L/min (voltage fixed at 85% to examine dilution/flux in isolation). This targeted approach yielded the optimal configuration of 23 kHz, 85% voltage ($\sim 300 \text{ V}$, 13.5 A), and 34 L/min flow, maximizing N₂^{*} emissivity while avoiding over-etching as confirmed by SEM.

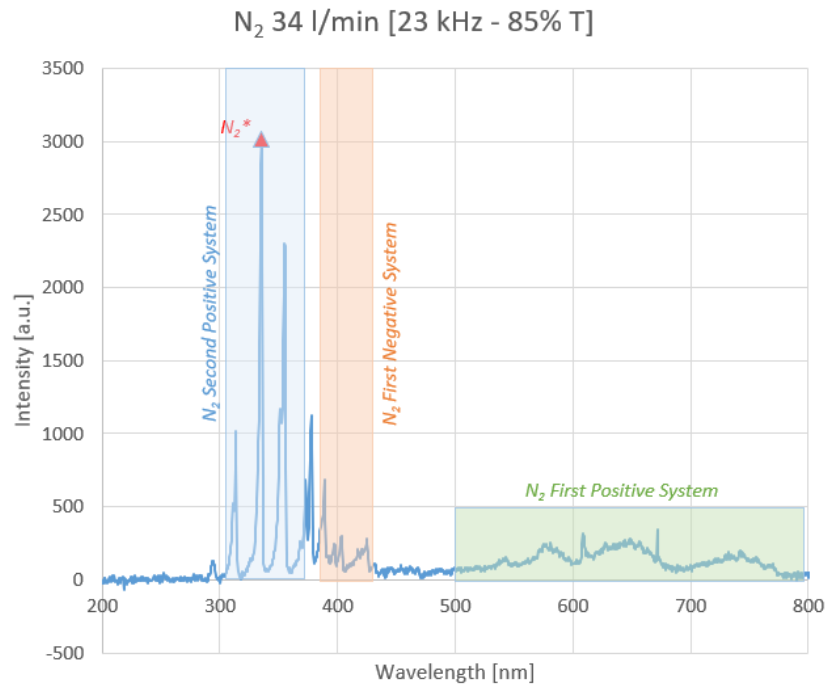
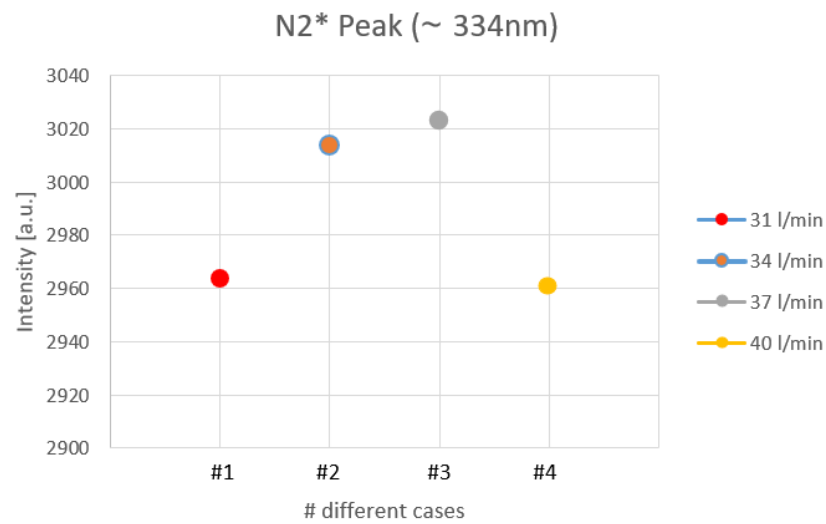
Voltage Variation (*Fixed 34 = l/min flow, $f = 23 \text{ kHz}$*) Across the voltage sweep from 70% to 100% reference, emission intensities exhibited superlinear scaling before the stabilization between 85% and 100% for both the second positive (2⁺) and first negative (1[−]) band systems, as detailed in Table 4.1. Although literature conventionally assigns the dominant N₂^{*} feature of the 2⁺ system to precisely 337 nm, the observed peak at $\sim 334 \text{ nm}$ reflects a slight downshift attributable to instrumental calibration and probe collimation effects in the Ocean Optics spectrometer configuration employed. For this trace, intensity increased by 52% from 70% to 85% (rising from 2895 to 2742 a.u.), followed by a more modest 63% increment to 100%; this pattern proved entirely consistent across the 2⁺ progression at 354, 372, and 392 nm, the 1[−] band near 388 nm, and the 424 nm high-wavelength tail. The extended first positive (1⁺) manifold in the 500–800 nm region mirrored this behavior, underscoring global ionisation saturation. Operationally, 85% reference

voltage emerged as the sweet spot, delivering near-peak reactive flux without the fiber damage (tensile degradation and excessive SEM-observed etching) encountered at 100%, thereby balancing process efficacy with substrate integrity in laboratory validations.

Table 4.1 OES peak *intensities* (a.u.) vs. reference voltage % (fixed 34 l/min N₂ flow, $f = 23$ kHz). Main observed peaks in 2⁺/1⁺ systems.

Peak (nm)	70%	85%	100%
~334 (N ₂ [*] 2 ⁺)	2894.7	2742.2	4483.8
~354 (2 ⁺)	2411.1	2584.2	3800.4
~372 (2 ⁺)	1210.9	1282.4	1753.8
~388 (1 ⁺)	687.7	819.4	1232.6
~424 (tail)	258.7	319.9	428.6

Gas Flow Variation (*Fixed 85% Voltage, $f = 23$ kHz*) Within the gas flow sweep from 31 to 40 L/min, the critical 337 nm emission reached its maximum at 37 L/min with an intensity of approximately 3060 a.u., followed by a noticeable decline to around 2500 a.u. at 40 L/min. This trend, shown in Figure 4.2, is attributable to progressive gas dilution outpacing ionisation capacity beyond the optimal throughput. Compared to the preceding voltage scan, these spectra exhibited only modest intensity shifts on the order of 5–8%, consistent with minor probe positioning and environmental influences. The 34 L/min condition was selected as the operating point, delivering near-peak performance across both N₂^{*} (2⁺) and first positive (1⁺) bands while maintaining robustness to ± 3 L/min fluctuations, thereby maximizing the Power/Gas flux ratio specifically tailored for uniform treatment of UD fabric architectures.

Fig. 4.1 OES spectra of N_2 plasma: main regions of interest.Fig. 4.2 Variation of l/min ranging from 31 to 40 l/min and relative N_2^* peak emitted intensity

4.2.2 Raman Results

Raman spectroscopy provided quantitative assessment of graphitic disorder induced by N₂ APP Jet treatment on UD carbon fiber fabrics, targeting the characteristic D₁ (disorder, $\sim 1350\text{ cm}^{-1}$, sp³ defects/edges) and G (graphitic order, $\sim 1580\text{ cm}^{-1}$, sp² tangential) bands via 532 nm excitation on a LabRAM HR Evolution spectrometer (80 $\times$ objective, 100–1700 cm⁻¹ range). The intensity ratio $R_1 = ID_1/I_G$ served as primary metric of surface modification, with plasma-induced etching elevating R_1 through preferential C–C scission at defect sites, partial sp² $\rightarrow$ sp³ hybridization, and nitrogen grafting (amines/amides), consistent with prior N₂/N₂H₂ twill studies where R_1 increased from ~ 1.43 (untreated) to 1.37–1.55 (treated).

Systematic investigation of secondary parameters was performed varying distance ($d = 6\text{--}10\text{ mm}$) and velocity ($v = 160\text{--}320\text{ mm/s}$) hence consequent exposure time, while maintaining fixed primary parameters (power 570 W, voltage $\sim 300\text{ V}$, frequency 23 kHz, gas flow 34 L/min), yielding Cases A–E (Table 4.2). Averaged over 3 measurement points per case, Case A (NT) exhibited baseline $R_1 \approx 0.89$, with modest D₁/G peaks reflecting sizing-masked graphitic order (Figure 4.3). Cases B–E showed progressive R_1 elevation (0.95–0.98) as shown in (Table 4.3). While Cases B ($d = 6\text{ mm}$, $R_1 = 0.97$) and E (320 mm/s high-speed, $R_1 = 0.95$) appeared promising from R_1 values alone, external considerations—excessive thermal stress risk at close proximity (B) and insufficient exposure/stabilization at high speed (E)—warranted their exclusion pending SEM-EDS confirmation. Cases C and D thus emerged as optimal candidates balancing flux, exposure, and fiber integrity.

Table 4.2 Plasma treatment parameters for Raman cases (fixed 570 W, 34 L/min N₂, $f = 23\text{ kHz}$).

Case	d (mm)	v (mm/s)
A	–	–
B	6	160
C	10	160
D	8	160
E	8	320

Case D proved the definitive optimum, maximizing R_1 (+25% vs. A), D₁ intensity (+48%), and surface reactivity while preserving uniformity (STD _{R_1} 2.0%). Voigt deconvolutions confirmed minimal D-band broadening ($\Delta\omega_{D_1} < 3\text{ cm}^{-1}$) versus

excessive etching risk in B/C. This configuration advanced to SEM-EDS validation and mechanical testing on 0.1/0.2 mm UD fabrics, correlating enhanced surface reactivity with improved epoxy wettability and ILSS without tensile degradation.

Table 4.3 Raman A-E cases results and statistics: $R_1(I_{D_1}/I_G)$, DevSTD % and difference ΔR_1 with respect the NT case.

Case	$R_1(I_{D_1}/I_G)$	DevSTD %	$\Delta R_1 (R_1 - R_1^{NT})$
A	0.898	0.20	–
B	0.957	0.48	0.059
C	0.995	0.94	0.097
D	0.981	1.05	0.083
E	0.987	2.52	0.089

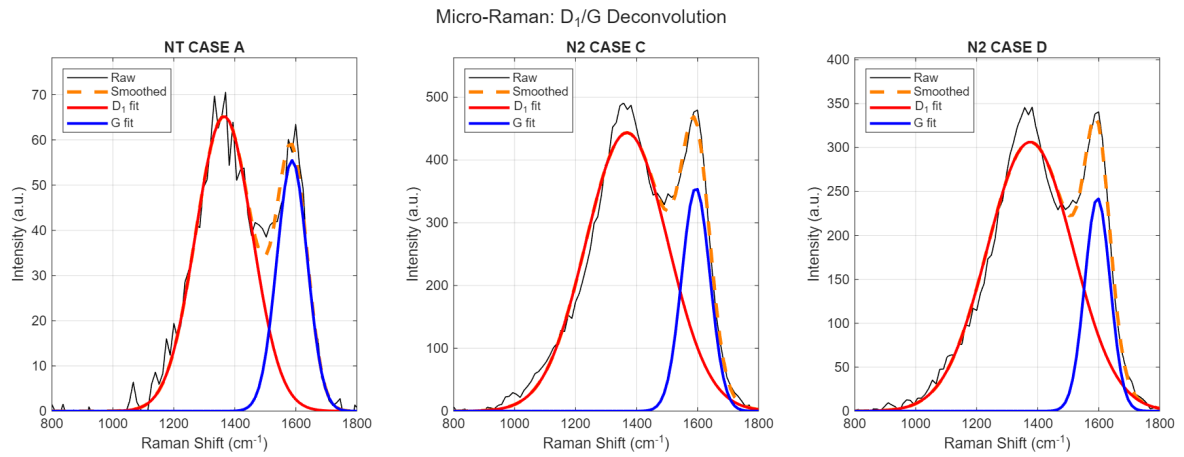


Fig. 4.3 Micro-Raman spectra examples: from left to right NT Case A1, Case C1, Case D1. Raw (black), smoothed (dotted orange) curves and deconvoluted D_1 (red), G (blue).

4.2.3 FESEM–EDS Results

Field-emission SEM analysis was carried out on N_2 treated and NT untreated samples, following the same case denomination of Raman characterization coupons shown in Table 4.2. NT (Case A) and plasma-treated fabrics for Cases C, D and E were studied to assess morphological effects and correlate them with the Raman evidence, while Case B was excluded due to the excessively short working distance, which was expected to induce detrimental thermal stress on the fibers. To avoid altering the APP Jet treatment, no conductive metallisation was applied and a

secondary-electron (SE) signal was adopted, seeking a compromise between image resolution and specimen charging. The resulting micrographs, shown in Figure 4.4, show that N₂ plasma did not induce fiber damage or aggressive transverse etching; instead, the longitudinal grooves inherited from wet spinning and sizing remain visible, but gradually smooth out in treated cases as the plasma partially removes the thermoplastic binder and surface contaminants.

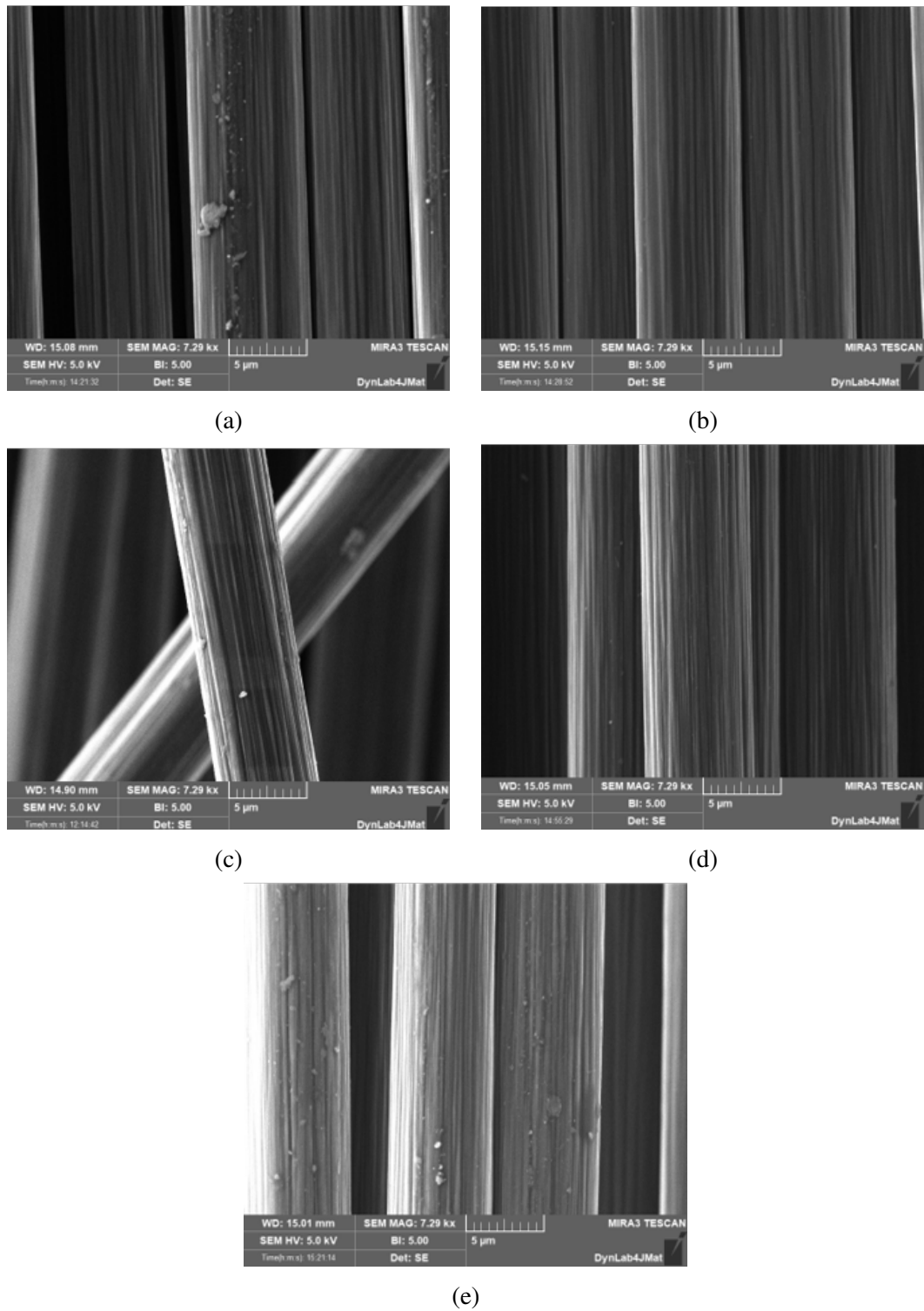


Fig. 4.4 FESEM fibre details: (a,b) Case A (untreated, NT) residues vs. clean; (c) Case C (10 mm, 160 mm/sec); (d) Case D (8 mm, 160 mm/sec); (e) Case E (8 mm, 320 m/sec). Progressive sizing ablation and grooves increase A→D.

At 10 mm working distance (Case C), the treated fibers appear more uniformly activated across the tow width, with homogeneous removal of sizing and a modest increase in surface roughness that preserves the original groove pattern. The 8 mm configurations (Cases D and E) yield more pronounced local features, including small, rounded micro-fused regions interpreted as local softening and reflow of the internal thermoplastic binder confirmed by the supplier, together with clearer evidence of sizing removal between adjacent filaments. Overall, the qualitative SEM observations support a progressive cleaning/activation sequence with increasing APP Jet exposure, without signs of over-etching or fiber fragmentation even in the closer-distance cases.

Semi-quantitative EDS measurements were performed on the same areas to estimate near-surface elemental composition (C, O and N), recognizing that the technique probes average atomic percentages over the analysed region and does not resolve specific functional groups. The results, summarised in Table 4.4, indicate that nitrogen content increases from 3.21 at.% in the NT condition (Case A) to 4.27 at.% and 4.92 at.% for Cases C and D, respectively, while oxygen decreases from 3.71 at.% (A) to 2.36 at.% (C) and 2.23 at.% (D). Consequently, N/C rises from 0.040 to 0.045 (C) and 0.053 (D), whereas O/C drops from 0.035 (A) to 0.025 (C) and 0.024 (D), revealing a progressive replacement of oxygenated species by nitrogen-containing functionalities at the fiber surface.

Table 4.4 FESEM–EDS atomic percentages and elemental ratios for selected APP Jet cases.

Case	%C	%O	%N	O/C	N/C
A (NT)	93.04	3.71	3.21	0.035	0.040
C	93.94	2.36	4.27	0.025	0.045
D	92.81	2.23	4.92	0.024	0.053
E	91.52	3.53	4.89	0.039	0.053

Case E, combining 8 mm distance with higher scan velocity (320 mm/s), exhibits comparable nitrogen uptake to Case D ($N/C \approx 0.053$) but retains higher residual oxygen ($O/C = 0.039$), indicating less effective oxygenated contaminant removal. Although Case C demonstrated promising Raman disorder metrics and SEM uniformity at extended distance, its treatment intensity was deemed potentially insufficient for robust industrial activation. Consequently, Case D (8 mm, 160 mm/s) was selected as

the optimal configuration—balancing maximal nitrogen incorporation ($N/C = 0.053$), reduced oxygen content, SEM-confirmed fiber integrity, and sufficient exposure dosage—for subsequent laminate fabrication and mechanical characterization.

4.2.4 XPS Results

X-ray photoelectron spectroscopy (XPS) provided high-resolution chemical speciation on the selected case D (8 mm, 160 mm/sec), complementing the spectroscopic analysis, using a VersaProbe II spectrometer (monochromatic Al K_{α} , 1486.6 eV). Survey scans confirmed the expected C/O/N dominance, with the NT case dominated by a C/O-rich coating signature from residual sizing/binder, which is diminished post-plasma.

High-resolution C1s spectra revealed two primary components in NT centered at ~ 286 eV (C–O, esters/ethers from sizing) and ~ 284.5 eV (sp^2 graphitic), yielding an asymmetric profile distorted by oxygenated functionalities. Post-APP Jet treatment, the 286 eV shoulder collapses substantially (but not to zero), consistent with effective sizing ablation while retaining residual C–O/C=O/COOH-like groups that enhance epoxy compatibility, in agreement with the author’s previous work on plasma-treated carbon fabrics [16]. The dominant low-binding-energy peak sharpens towards a canonical asymmetric sp^2 graphite profile (π – π^* shake-up at higher BE), confirming exposure of the inert graphitic core with minimal subsurface disruption.

The O1s region (~ 532.7 eV) exhibited a similar reduction in integrated intensity, accompanied by the emergence of a lower-BE shoulder indicative of new oxygen environments (possibly C–OH or reformed C–O–C after plasma-induced reorganization). Critically, the N1s signal (~ 400 eV), barely discernible in NT, shows a clear intensity enhancement in the N_2 -treated case as displayed in Figure 4.5, confirming successful incorporation of nitrogen-containing functionalities (amines $-NH_x$, amides) despite their low atomic fraction ($\ll 5$ at.%). These XPS signatures validate the APP Jet’s selective activation mechanism: sizing removal exposes reactive sites for N grafting, enhancing polarity and epoxy interphase formation from Case A $\rightarrow$ D, without aggressive over-oxidation.

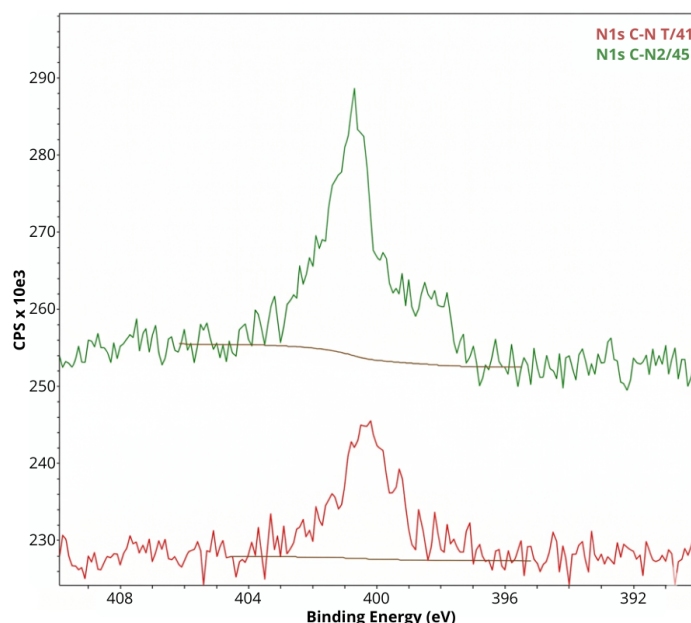


Fig. 4.5 XPS N1s region: NT (red) vs. N₂ treated (green).

4.3 Process Parameter Dependence

The systematic delineation campaign elucidated the interplay of primary (power, voltage, frequency, gas flow) and secondary (distance, velocity, passes) APP Jet parameters governing cleaning, etching, and activation on UD carbon fabrics. OES identified optimal plasma chemistry at 570 W, 85% voltage (~ 300 V), 23 kHz and 34 L/min N₂ flow, maximizing N₂^{*} emissivity without over-ionisation. Raman mapping (Cases A–E) revealed progressive graphitic disorder (R_1 : 0.90 $\rightarrow$ 0.98) with distance/velocity trade-offs, where closer proximity (6 mm) risked thermal degradation while high speeds (320 mm/s) yielded insufficient exposure.

FESEM–EDS corroborated these trends, confirming Case D (8 mm, 160 mm/s) as the optimal compromise: maximal nitrogen incorporation (N/C = 0.053), reduced oxygen (O/C = 0.024), clean sizing removal with accentuated manufacturing grooves, and no etching damage—balancing spectroscopic activation with laboratory handling constraints (fibre integrity under thermal/mechanical stress). XPS provided final chemical validation, revealing N 1s enhancement and C 1s sharpening towards sp² graphite with residual oxygenated functionality for epoxy compatibility. Case B

was excluded a priori (excessive proximity), Case E for under-treatment, and Case C—despite Raman promise—deemed marginally light for industrial robustness.

Table 4.5 summarises this optimized parameter set, adopted for UD fabric pre-treatment prior to laminate fabrication and subsequent meso/macro-scale mechanical testing in Chapter 5 and 6.

Table 4.5 APP Jet parameters chosen for CF UD surface treatment.

Parameter	Value
Frequency	23 kHz
Voltage	85% (300 V, 13.5 A)
N ₂ Flow	34 L/min
Distance	8 mm

Chapter 5

Micro- and Meso-Scale Analysis - Critical Assessment

5.1 MicroBond Tests: Results, Scatter and Key Insights

The Microbond test was conducted using the final needle-based restraining configuration detailed in Section 3.5.1. The epoxy resin droplets with characteristic dimensions $D_g \approx 100\text{--}270\ \mu\text{m}$ and embedded lengths $L_{\text{emb}} \approx 130\text{--}350\ \mu\text{m}$ were precisely deposited using a compatible glass fiber onto single glass fibers extracted from commercial twill fabrics (Section 3.1). Each specimen was then tested under displacement-controlled pull-out at 0.2 mm/min on the MTS frame equipped with 10 N load cell, ensuring consistent boundary conditions across series.

The cure protocol was selected after preliminary screening of several thermal schedules, with the aim of obtaining complete resin hardening while avoiding processing conditions that were associated with internal voids or premature embrittlement. In this context, auxiliary variables such as resin degassing and oven ventilation during the high temperature stage were also considered alongside the cure profile itself, as specified by the IB2 epoxy resin technical datasheet [2]. The selected protocol was consistent with the characteristic load-displacement profile in Figure 3.12 namely Shear Debonding case seen in Section 3.5.1., which typically featured a sharp P_{max} ($\approx 0.05\text{--}0.46\ \text{N}$), abrupt post-peak drop, and frictional tail. Geometric

control maintained $L_{\text{emb}}/D_f \approx 10\text{--}25$, in line with literature recommendations [30] [102] [103] and with the known sensitivity of Microbond IFSS to embedded length and specimen geometry. Nevertheless, droplet aspect ratio variability (0.14–0.74) remained a major source of scatter.

The apparent IFSS distributions ($\tau_{\text{app}} = P_{\text{max}}/(\pi D_f L_{\text{emb}})$) exhibited substantial dispersion ($\sigma \sim 40\text{--}60\%$, $n=10\text{--}12/\text{series}$). Untreated specimens with smaller droplets ($D_g < 0.15\text{mm}$) showed median values of approximately 13–15 MPa, whereas N₂-treated specimens reached approximately 16–21 MPa corresponding to an apparent increase of roughly 10–40%. However, the overlap between series remained significant, indicating that geometric variability and specimen-to-specimen differences still masked a fully robust statistical separation between populations. At the same time, the distinction between NT and N₂ highlights a consistent shift in the mechanical response of the two populations. Although the overlap remains substantial, the N₂ series tends to fill the higher- τ_{app} region and, in several cases, the higher-displacement region that is more tolerant to displacement, whereas NT is more frequently concentrated in the lower-strength and more brittle regime. These tendencies are visible in the three scatter diagrams in Figure 5.1 where the τ are compared with geometrical parameters belonging to resin droplet/fiber micro systems. This trend suggests that the plasma treatment does not simply increase the average strength, but alters the way the interface carries load and reaches failure.

To complement the discussion above, Tables 5.1 and 5.2 summarize the mean values and standard deviations of the main geometric and mechanical parameters for the two D_g-based clusters. In particular, they display the average shape values (fiber and droplet diameter, embedded length and D_g/L_{emb} ratio) as well as the average mechanical obtained values (maximum force and displacement at the droplet detachment, τ) for both NT and N₂ batches. A combination of these two families of parameters are expressed through the ratio between fiber embedded length and maximum displacement at the detachment onset, $L_{\text{emb}}/\text{Disp.Max}$.

Figure 5.1 further clarifies this point by displaying the dependence of τ_{app} on the main geometric descriptors. Although a general decreasing trend is visible with increasing D_g , L_{emb} and aspect ratio, the data do not collapse onto a single well defined relationship. Instead, the scatter suggests the coexistence of partially overlapping regimes, reflecting the combined influence of geometry, local wetting conditions, and failure mode. In particular, the same nominal geometry can still

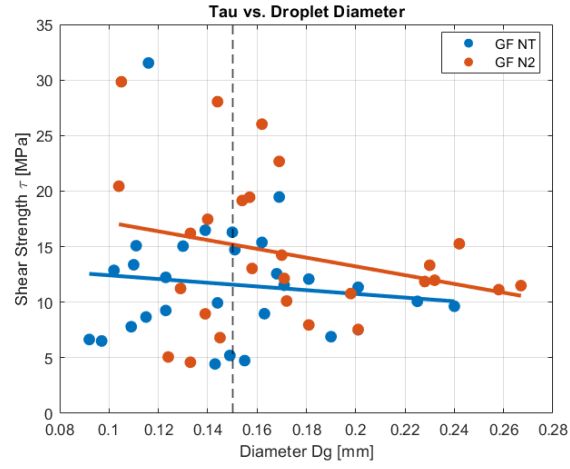
Table 5.1 NT cluster statistics for Dg-based grouping.

	D_f [mm]	L_{emb} [mm]	D_g [mm]	F_{max} [N]	Disp.Max [mm]	τ [MPa]	D_g/L_{emb} [-]	$L_{emb}/Disp.Max$ [-]
Small	0.014	0.164	0.125	0.086	0.587	11.713	0.772	0.327
Sdev	0.000	0.033	0.020	0.047	0.234	6.430	0.077	0.153
Big	0.015	0.238	0.188	0.125	0.839	11.405	0.796	0.300
Sdev	0.002	0.040	0.026	0.043	0.234	3.591	0.051	0.083

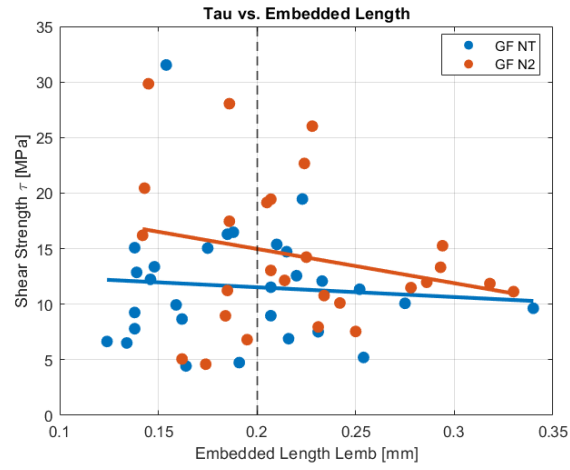
Table 5.2 N2 cluster statistics for Dg-based grouping.

	D_f [mm]	L_{emb} [mm]	D_g [mm]	F_{max} [N]	Disp.Max [mm]	τ [MPa]	D_g/L_{emb} [-]	$L_{emb}/Disp.Max$ [-]
Small	0.014	0.179	0.135	0.119	0.863	15.401	0.760	0.280
Sdev	0.000	0.024	0.017	0.062	0.436	8.089	0.057	0.200
Big	0.014	0.261	0.206	0.155	0.898	13.321	0.788	0.336
Sdev	0.001	0.038	0.036	0.051	0.302	5.157	0.065	0.186

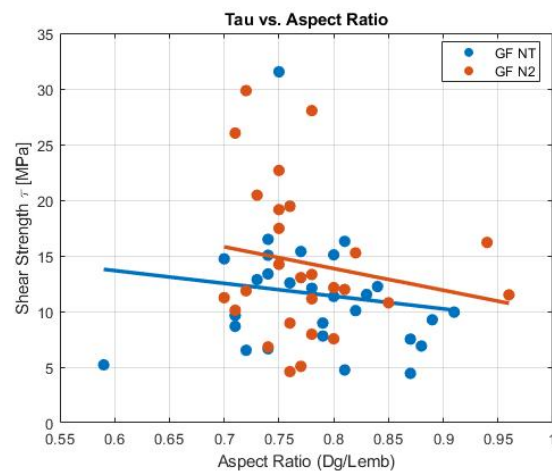
lead to markedly different responses, depending on whether failure remains abrupt and mainly adhesive or evolves into a more progressive and energy dissipative debonding process. For this reason, the three plots should be read not only as geometric correlations, but also as a first basis for distinguishing subgroups within the experimental set.



(a)



(b)



(c)

Fig. 5.1 IFSS scatter vs droplet geometry across NT/N₂ series: (a) diameter (D_g), (b) embedded length (L_{emb}), (c) aspect ratio.

To complement the qualitative trends observed in Figure 5.1, an exploratory log–log regression between apparent IFSS and droplet volume was also performed for the NT and N₂ series. The NT population yielded an almost negligible slope ($m \approx -0.014$), indicating that within the investigated range the apparent interfacial strength was only weakly dependent on droplet volume. By contrast, the N₂ series showed a more negative slope ($m \approx -0.090$), suggesting a somewhat higher sensitivity of the apparent response to volumetric scale. However, in both cases the associated p-values remained high, so this analysis should not be interpreted as evidence of a statistically robust scaling law, but rather as an exploratory indication that geometry alone does not fully explain the observed scatter. This result is consistent with the broad clouds already visible in Figure 5.1: if a dominant and unique geometric scaling law were governing the data, a clearer collapse of the points would be expected. Instead, the weak log–log dependence supports the view that the experimental variability arises from the superposition of geometry, local wetting conditions, and failure-mode-dependent effects, rather than from droplet size alone. In this sense, droplet volume can be regarded as a useful descriptive parameter, but not as a sufficient predictor of the interfacial response in the present commercial-fiber system.

More specifically, Figure 5.1 (a) indicates that droplet diameter alone is not sufficient to separate the data into clearly distinct populations. Specimens with similar D_g may still show very different τ_{app} values, which indicates that diameter acts as a scatter-amplifying parameter rather than as a unique predictor of interfacial strength. The plot suggests the presence of at least two partially overlapping sub-groups: one associated with lower apparent strength and more abrupt failure, and another associated with higher apparent strength and a more progressive response. The dashed line in (a) and (b) added a visual guide to distinguish smaller and larger droplets/embedded lengths according to the experimental campaign and literature already mentioned. Figure 5.1 (b) is more informative from a mechanical point of view because embedded length directly affects the stress-transfer length and the degree of non-uniformity along the fiber/matrix interface. A general decrease in τ_{app} with increasing L_{emb} is visible, but the scatter remains large. This trend is consistent with Microbond studies showing the apparent IFSS is strongly affected by the embedded area and by the way load is redistributed along the interface during debonding [102] [104]. In the present case, the wide dispersion indicates that similar embedded lengths may still correspond to different failure paths, depending on local geometric imperfections, meniscus shape, and actual evolution of damage during

the test. Figure 5.1 (c) combines the two previous descriptors and confirms that the aspect ratio does not remove the dispersion. Although lower aspect ratios (the ratio between droplet diameter D_g and embedded length L_{emb}) are generally associated with lower τ_{app} and higher aspect ratios with higher values, the points still form broad clouds rather than compact bands. This implies that the aspect ratio is a useful descriptor for comparison, but not a sufficient predictor of the interfacial response without appropriate morphological and surface analysis. In other words, geometry influences the test outcome, but it does not uniquely determine the debonding mode.

To further support this interpretation, Figure 5.2, reports the dependence of τ_{app} on the fragility index defined as the ratio $L_{emb}/\text{Disp.Max}$, where the Disp. Max is the maximum displacement recorded for the droplet detachment. It is worth noting that the fragility index does not derive from established fracture mechanics models or energy-based frameworks, but is rather an empirically constructed descriptor specific to this dataset. Its rationale lies in the simultaneous coupling of a geometric parameter - the embedded length, which governs the extent of the load-transfer zone - with a purely mechanical one, namely the maximum displacement recorded at detachment onset. A low value of the index therefore indicates that a relatively long interface was able to sustain a correspondingly large displacement before failure, associated with a more progressive and energy-dissipative debonding. Conversely, a high value reflects a stiffer and more brittle response, in which the interface detached early in displacement terms relative to its geometric extent. In this sense, the index should be regarded as an empirical descriptor of debonding character rather than as a physically derived quantity.

The plot is useful because it reinterprets the same scatter observed in the geometric descriptors in terms of separation at the interface stability and failure mode. In particular, a general inverse correlation is observed, with higher τ_{app} values tending to cluster at lower fragility-index values, whereas lower values of the index are associated a more unstable and abrupt response. A dashed vertical line at $L_{emb}/\text{Disp.Max} = 0.3$ is introduced as a visual threshold to distinguish two operative regimes identified in the experimental campaign. Points to the left of that threshold line correspond to specimens that can be interpreted as mechanically more tenacious: the interface is sufficiently strong that the resin droplet itself undergoes larger deformation before debonding, often leading to a more progressive and energy-dissipative failure. Points belonging to the right part of the threshold instead correspond to a more fragile response, in which detachment occurs earlier and the crack propagates along the

interface with limited resin deformation. This representation is not meant to define an absolute physical boundary, but rather to highlight a practical separation between more ductile and more brittle debonding behaviors, identified empirically on the basis of the experimental results obtained in the present campaign. In this sense, the fragility index complements the previous geometric plots by linking the apparent interfacial strength to the amount of displacement sustained before failure, thus providing a more direct indication of whether a specimen failed in a predominantly adhesive or more tenacious manner.

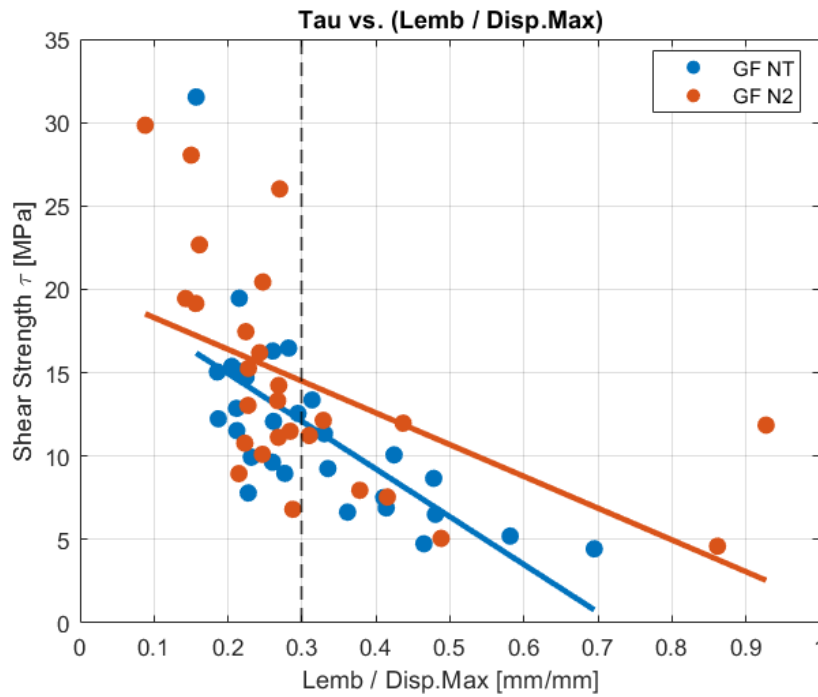


Fig. 5.2 τ_{app} versus fragility index $L_{emb}/Disp.Max$ for NT and N_2 specimens.

A broader exploratory regression screening was then carried out to identify which descriptors were more strongly associated with τ_{app} in the NT and N_2 populations. This analysis showed that purely geometric variables such as D_g , volume and L_{emb} were not the dominant predictors, whereas mechanical or mixed descriptors exhibited substantially higher explanatory power. In the NT series, the highest coefficient of determination was found for the fragility index $L_{emb}/Disp.Max$ ($R^2 \approx 0.68$), followed by F_{max} ($R^2 \approx 0.67$) and $Disp.Max$ ($R^2 \approx 0.53$). In the N_2 series, the ranking changed slightly, with F_{max} emerging as the strongest predictor ($R^2 \approx 0.76$), followed by $L_{emb}/Disp.Max$ ($R^2 \approx 0.52$) and $Disp.Max$ ($R^2 \approx 0.47$). Although these

values still reflect an exploratory rather than fully predictive analysis, they reinforce the interpretation proposed above: the apparent IFSS measured by Microbond is not governed primarily by absolute droplet dimensions, but by how the specimen deforms and redistributes stress up to debonding. The shift in the dominant predictor from NT to N₂ is also meaningful from a mechanistic point of view, because it suggests that plasma treatment may have modified not only the nominal adhesion level, but also the controlling debonding dynamics. In other words, the treatment appears to affect the way in which load, displacement and local failure stability interact during the test.

Further analysis confirmed that larger droplets ($D_g > 0.20$ mm) tend to bias τ_{app} upward by amplifying matrix plasticity and meniscus effects, while smaller droplets generally yield more consistent, albeit still scattered, results. This geometric sensitivity becomes even more critical on commercial reinforcements, where the fiber surface is not perfectly homogeneous but affected by industrial heterogeneity, including residual sizing patches, longitudinal grooves, local contamination, and fiber-to-fiber variations within the same tow. In this context, the measured IFSS is increasingly influenced by local artifacts and by the specific micro-conditions of the tested filament, rather than by the intrinsic interfacial quality alone. The issue is therefore not a single geometric threshold, but the fact that droplets outside the typical 65–110 μm recommendation progressively amplify the contribution of surface heterogeneity and meniscus-related effects to the apparent result.

Optical microscopy of NT and N₂ cases before and after debonding provided key qualitative insight into the observed scatter (Figure 5.3). However, the fracture morphologies were not fully deterministic, since both surface conditions could exhibit overlapping features and the observed appearances were not always fully repeatable from specimen to specimen. In some NT specimens, the debonded surface appeared relatively clean, while in others limited resin remnants were still visible; similarly, N₂-treated cases often showed more evident resin residues, but not in a strictly uniform manner across all samples. For this reason, the debonded morphology should not be interpreted as a direct one-to-one proxy for weak or strong adhesion. Rather, it should be considered as a qualitative indicator of the prevailing failure tendency, to be interpreted together with the mechanical response and the full distribution of results. Accordingly, fracture appearance alone does not uniquely define the actual interfacial performance, especially when the microbond data are affected by geometry-driven scatter and non-uniform surface conditions.

A fundamental methodological difficulty that emerges from the experimental dataset is the inability to fully separate material-related variability from test-induced artefacts. In the present commercial UD system, these two contributions operate simultaneously and are difficult to decouple. On the material side, residual sizing heterogeneity, tow-scale surface non-uniformity, longitudinal grooves and localised contamination introduce specimen to specimen variation that is intrinsic to the reinforcement and therefore beyond the control of the testing procedure. On the methodological side, droplet geometry, meniscus stability during curing cycle, needle alignment tolerances, and polymerisation induced residual stresses each contribute independently to the measured apparent IFSS. The observed scatter should therefore be interpreted as the combined outcome of both classes of effects, and any attempt to attribute it to a single dominant cause would risk oversimplifying the complexity of the system.

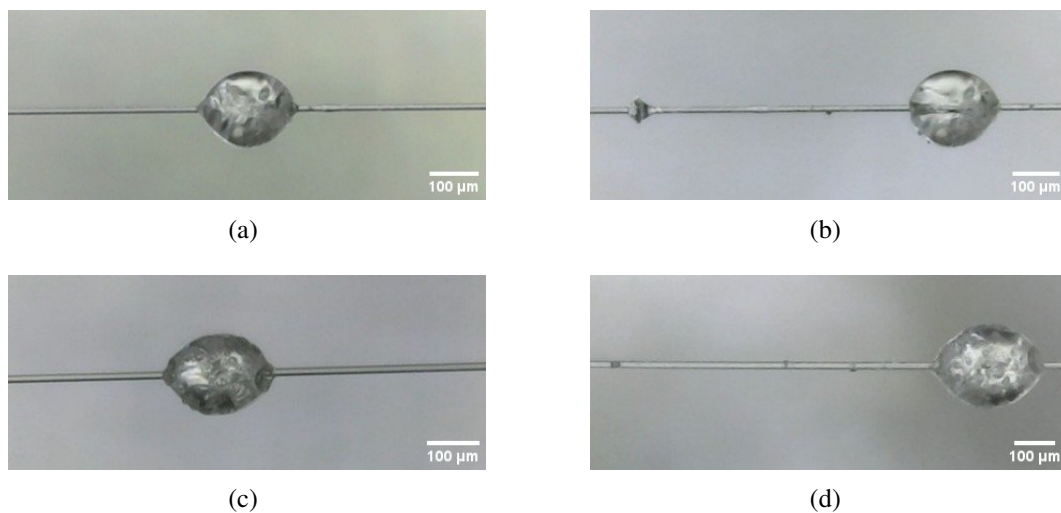
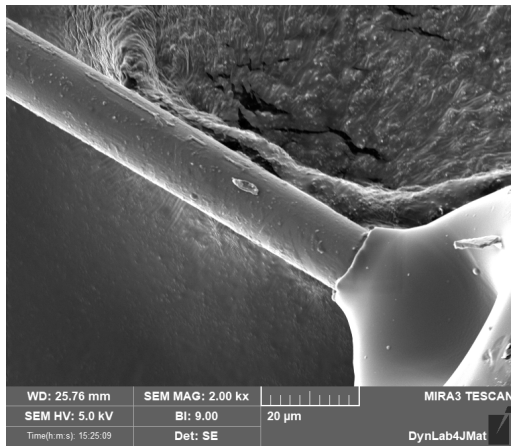


Fig. 5.3 Optical microscopy of representative cases before/after microbond debonding. NT (a,b): clean meniscus detachment with pristine fiber. N₂-treated (c,d): resin residues along fiber post-debonding.

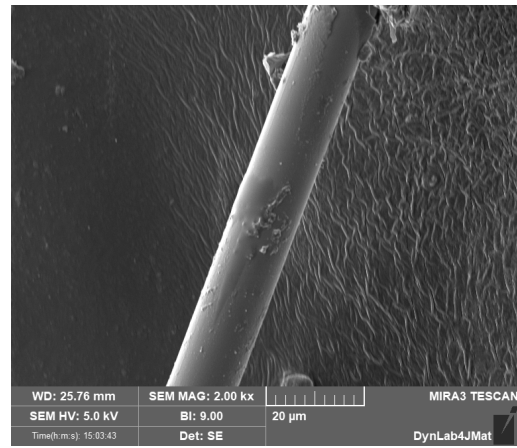
To address the extreme dispersion observed across standard NT and N₂ series and systematically isolate plasma-specific adhesion enhancement from commercial sizing heterogeneity, a complementary desized UD carbon fiber series was prepared and tested as anticipated in Section 3.4.1. The aggressive dual cleaning protocol—thermal desorption at 300°C for 1h followed by 2h acetone immersion, the same methodology adopted for TFBT meso scale specimens preparation, eliminated thermoplastic sizing variability, establishing a clean graphitic baseline to probe whether fiber surface

state alone could reduce τ_{app} scatter or improve intrinsic cohesion without plasma functionalization.

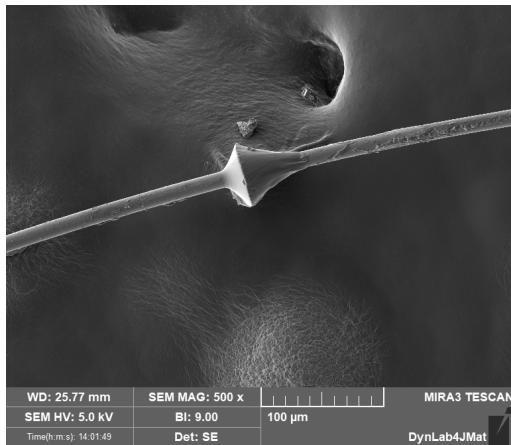
Post-debonding FESEM inspection of fracture surfaces from these desized specimens proved diagnostically invaluable, revealing the full spectrum of failure morphologies inherent to the methodology even after sizing removal (Figure 5.4). Within this single controlled series, three characteristic morphologies were systematically observed: (i) predominantly clean adhesive failure featuring pristine fiber pull-out with almost negligible resin adhesion; (ii) occasional resin bridge debris, representing limited matrix cohesion within the droplet footprint; and (iii) cohesive hackles with matrix tearing behind meniscus rapture zone.



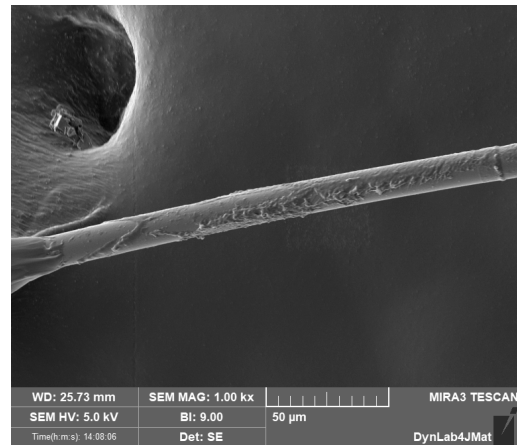
(a) Clean adhesive (IFSS = 35.2 MPa)



(b) Resin bridge (IFSS = 19.5 MPa)



(c) Meniscus view



(d) Hackles detail (IFSS = 11.0 MPa)

Fig. 5.4 High-resolution FESEM from desized series (300°C+acetone): (a) clean adhesive, (b) resin bridge, (c,d) matrix tearing/hackles at meniscus and fiber detail.

Table 5.3 summarizes the mechanical and geometric parameters for these desized specimens, grouped according to the D_g criteria previously applied to the NT and N₂ populations. Comparing these results with Tables 5.1 and 5.2, it is evident that sizing removal does not shift the interfacial strength into a higher performance regime. While the desized series shows mean IFSS values comparable to the as-received specimens (roughly 14–21 MPa), it retains a similarly high standard deviation ($\sigma \approx 45\%$). This comparison suggests that sizing removal, while effective at standardizing the chemistry, does not by itself neutralize the scatter, indicating that the experimental dispersion is linked to a broader set of variables—geometric and surface-topographical—that will be further examined in the subsequent sections of this chapter.

Table 5.3 Desized cluster statistics for D_g -based grouping.

	D_f [mm]	L_{emb} [mm]	D_g [mm]	F_{max} [N]	Disp.Max [mm]	τ [MPa]	D_g/L_{emb} [-]	$L_{emb}/\text{Disp.Max}$ [-]
Small	0.014	0.190	0.148	0.186	1.000	21.601	0.781	0.204
Sdev	0.000	0.015	0.005	0.081	0.301	9.395	0.040	0.060
Big	0.015	0.258	0.216	0.179	0.910	14.403	0.839	0.312
Sdev	0.002	0.040	0.032	0.114	0.299	7.052	0.061	0.112

An analogous exploratory analysis was also carried out for the series that counted for sizing removal. In this case, the statistical response differed from the NT and N₂ populations, since stronger correlations emerged with both geometric and mechanical descriptors. In particular, the ratio L/D showed the highest explanatory power ($R^2 \approx 0.87$, $p < 0.0001$), followed by Disp.Max ($R^2 \approx 0.79$) and F_{max} ($R^2 \approx 0.74$), while D_g also became moderately relevant ($R^2 \approx 0.40$). This indicates that, once the sizing layer is removed, the apparent response becomes more sensitive to the geometrical and mechanical structure of the test itself. At the same time, this stronger dependency should be interpreted carefully. On one hand, it may suggest that the removal of sizing reduces one source of chemical and morphological masking, allowing the underlying test mechanics to emerge more clearly. On the other hand, the desized population is still relatively limited in size and partially unbalanced in terms of small/big droplet distribution, so the observed increase in R^2 should be regarded as a meaningful trend rather than as a definitive scaling law. Nevertheless, the comparison with NT and N₂ supports the view that the as-received industrial surface state introduces an additional layer of variability that partially obscures the geometric response expected from the Microbond configuration. Table 5.4

provides a comprehensive overview of the exploratory regression analysis for all three populations (NT, N₂, and desized), allowing a direct comparison of the sensitivity of τ_{app} to the identified geometric and mechanical descriptors. As summarized in Table 5.4, the apparent IFSS exhibits no statistically significant dependence on droplet volume ($p > 0.4$). Instead, the variability is better captured by mechanical parameters such as F_{max} and the fragility index ($L_{emb}/Disp_{max}$), which show high correlation ($R^2 > 0.5$). Conversely, the desized series reveals a distinct mechanical transition: when the chemical noise of the sizing is removed, the aspect ratio (L/D) becomes the dominant predictive descriptor ($R^2 = 0.87$), indicating that the interface begins to follow deterministic geometric scaling laws. This statistical shift highlights that the ‘scatter’ in commercial specimens is primarily a consequence of interfacial chemical heterogeneity rather than test inadequacy.

Table 5.4 Summary of regression analysis for τ_{app} dependence on descriptors.

Series	Predictor	Slope (m)	R^2	p-value
NT	log(Volume)	-0.014	0.0006	0.9005
N ₂	log(Volume)	-0.090	0.0200	0.4808
NT	F_{max}	0.719	0.672	<0.0001
NT	Fragility Index	-0.978	0.676	<0.0001
N ₂	F_{max}	0.825	0.762	<0.0001
N ₂	Fragility Index	-0.691	0.524	<0.0001
Desized	Fragility Index	-1.181	0.872	<0.0001
Desized	$Disp_{max}$	1.447	0.791	<0.0001
Desized	F_{max}	0.848	0.739	<0.0001

This behavior is visually captured in Figure 5.5, which illustrates the fragility-related dependence ($L_{emb}/Disp_{max}$) across all three series. While a common inverse trend is visible, the population without sizing occupies a more defined regime, reinforcing the conclusion that the high scatter observed in commercial fibers is primarily an artifact of surface and chemical heterogeneity, rather than a lack of underlying mechanical consistency.

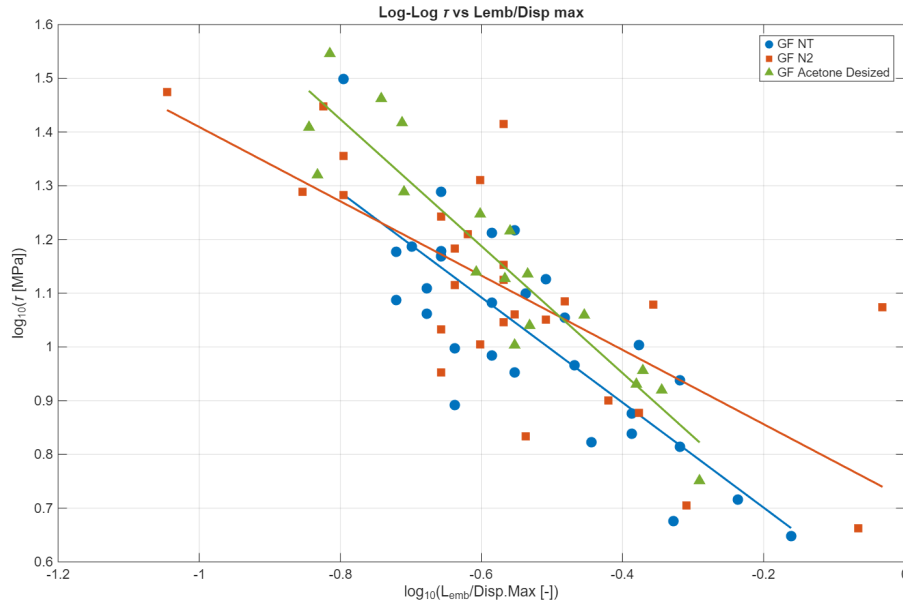


Fig. 5.5 Exploratory log–log plot of τ_{app} vs fragility-related descriptor for the three batches of specimens: NT (blue), N2 (red) and Acetone desized (green).

Regarding the fracture surfaces, a preliminary survey reveals a range of morphologies in the desized specimens, from clean adhesive debonding to localized matrix hackles (Figure 5.4). At this stage, however, the direct correlation between these specific fracture appearances and the measured IFSS values remains non-trivial; the data points appear distributed across the same range, suggesting that such morphologies may represent localized, stochastic manifestations of the test dynamics rather than distinct adhesive regimes. The desized series provided partial evidence in support of this interpretation: once the chemical noise of the sizing layer was removed, the geometric sensitivity increased substantially (R^2 rising to 0.87 for $L_{emb}/Disp.max$), suggesting that the underlying test mechanics become more visible when one source of material-level masking is eliminated. Nevertheless, even in the desized condition, significant scatter persisted, confirming that neither material heterogeneity alone nor test geometry alone is sufficient to explain the full dispersion.

At the load-displacement level, the representative curves obtained for the NT, N₂-treated and desized series provide an additional mechanical perspective on the same trends, as shown in Figure 5.6–5.8. The untreated population generally shows a sharper post-peak drop and a shorter frictional tail, compatible with a more abrupt and predominantly adhesive failure. The N₂ case more often retain load over a longer post-peak interval and exhibit a more extended tail region, suggesting a

more progressive and energy-dissipative debonding process. Lastly, the desized series occupies an intermediate position, but with noticeable specimen-to-specimen variability: some curves remain brittle, whereas others evolve more gradually after the peak. Taken together, these responses are consistent with the morphological observations and with the shift in dominant descriptors identified in the exploratory regressions, while still reflecting the substantial scatter already discussed.

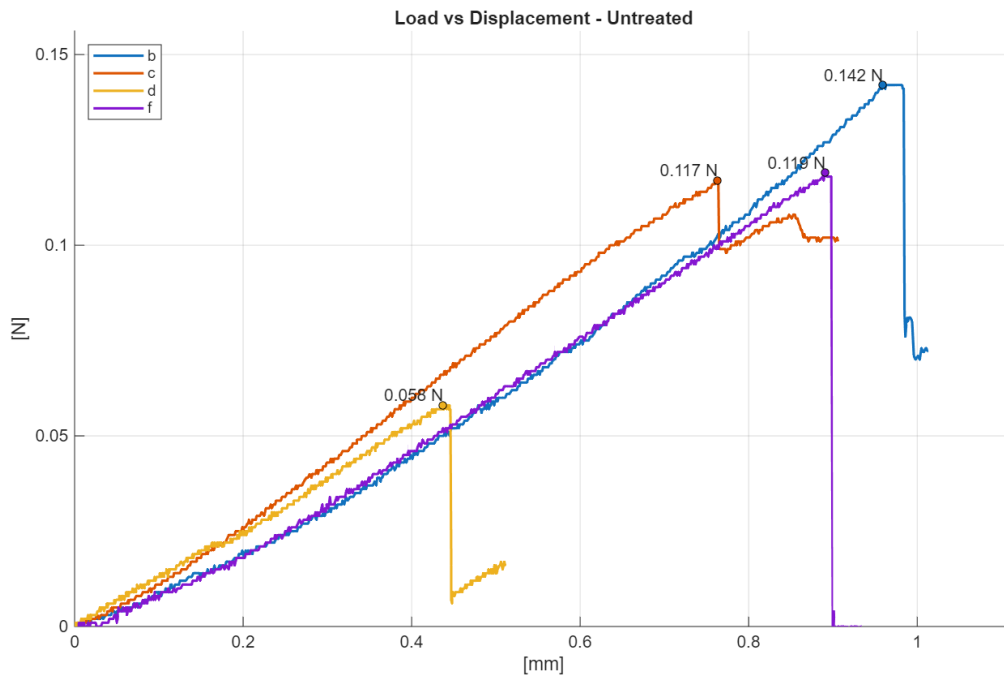


Fig. 5.6 Representative Microbond load-displacement curves for as-received (NT) specimens.

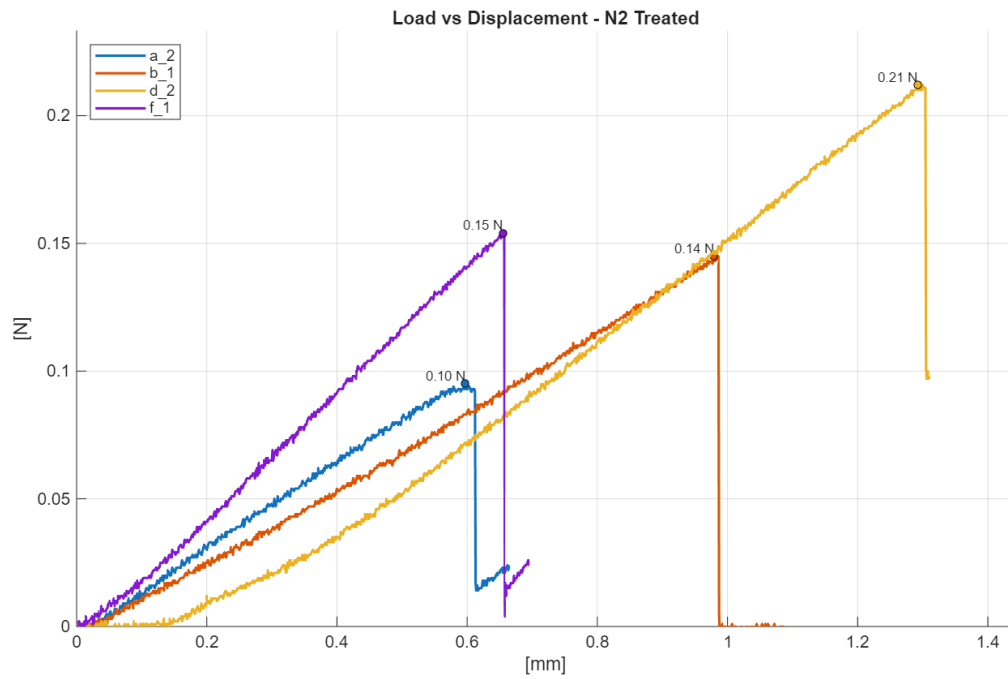


Fig. 5.7 Representative Microbond load-displacement curves for N₂ plasma-treated specimens.

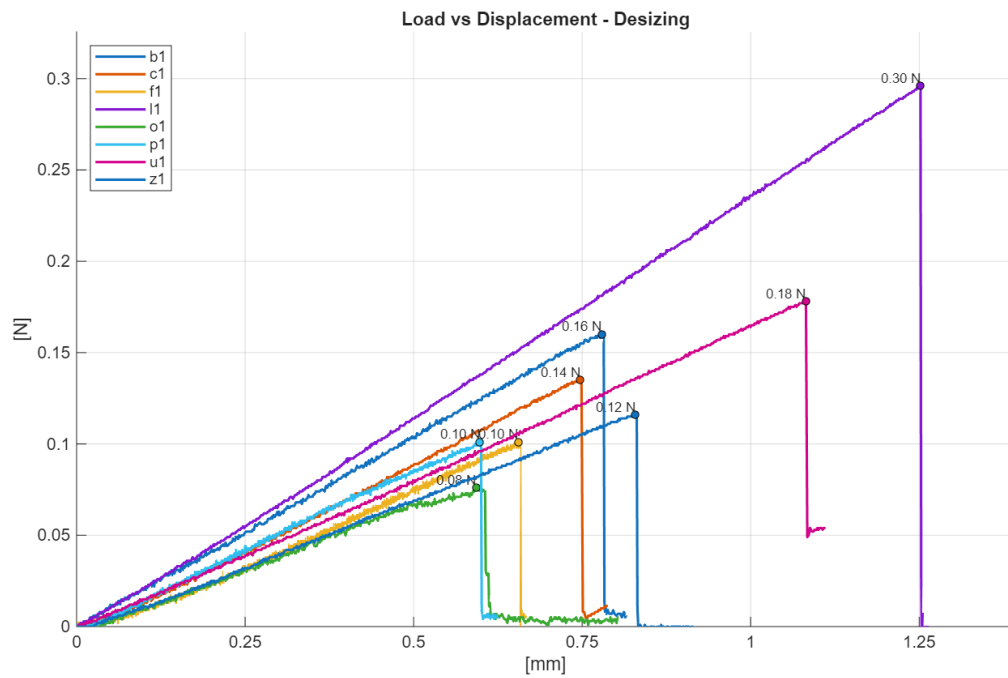


Fig. 5.8 Representative Microbond load-displacement curves for acetone-desized specimens.

The extreme experimental dispersion characterising all microbond series arises from multiple interdependent geometric and procedural factors:

- **Geometric variability:** Inconsistent droplet deposition yielding variable D_g and L_{emb} , a known source of IFSS scatter in MB testing [102];
- **Surface heterogeneities:** Local wettability gradients and fiber tow heterogeneity, including uneven sizing patches and manufacturing contaminants, which mask intrinsic interfacial strength [103];
- **Test artifacts:** Meniscus control limitations during curing and potential blade-needle misalignment tolerances ($\pm 5^\circ$), which introduce non-uniform stress distributions along the interface [104];
- **Residual stress states:** Effects of polymerization shrinkage stresses which, as discussed by Thomason et al [30], significantly bias apparent interfacial shear values in thermosetting systems.
- **Cure-state effects:** As detailed in Section 3.4.1 and Table 3.2, the cure protocol for MB specimens was selected after screening multiple thermal schedules, with the final choice of 16h pre-cure at T_{amb} followed by 8h post-cure at 80°C providing stable droplet geometry and repeatable debonding behaviour. Nevertheless, even under this controlled schedule, the thermal history of an isolated microdroplet inevitably differs from that of a bulk laminate, owing to differences in specimen mass, heat dissipation, and local oxygen exposure during curing. Such differences may locally affect the degree of crosslinking, the matrix stiffness at the fibre-matrix boundary, and the magnitude of polymerisation shrinkage stresses, all of which can influence the apparent IFSS independently of the actual adhesion quality. This represents an additional source of uncertainty to be considered when comparing MB-derived values with results obtained at meso- and macro-scale.

These compound effects reveal that absolute IFSS quantification requires rigorous geometric control; indeed, while droplets within the $65\text{--}110\ \mu\text{m}$ range yield more consistent results, deviations from these dimensions amplify the contribution of stochastic artifacts. Regarding the desized series, the data confirm that sizing removal promotes predominantly adhesive failure—as expected for the exposed graphitic surface—revealing a residual sensitivity to geometry and local fiber state. This

indicates that beneath the scatter, a deterministic mechanical response may exist, provided that dimensions are constrained and artifacts are minimized. Therefore, the observed predominance of adhesive failure after desizing demonstrates the need of plasma-induced functionalization but also suggests that the 'background noise' observed in commercial fibers is partially governed by the complex interplay between surface chemistry and local meniscus stability.

In conclusion, while the microbond test proves challenged by extreme geometric sensitivity precluding robust quantitative assessment of Case D plasma treatment efficacy, it delivers invaluable qualitative insight into failure mode transitions. The systematic observation of resin retention and cohesive features in N₂-treated specimens via optical microscopy—contrasted against persistent adhesive dominance in desized controls—validates APP Jet's unique combined ablation + nitrogen grafting mechanism as the critical differentiator.

Overall, the additional exploratory regressions confirm that the scatter observed in the present Microbond campaign cannot be interpreted as the consequence of a single geometric parameter. Rather, the apparent IFSS emerges from the interaction between specimen geometry, local interfacial state and debonding mechanics. In the NT and N₂ populations, this interaction is more strongly reflected by mechanical and mixed descriptors such as $F_{\max}$, Disp.Max and $L_{\text{emb}}/\text{Disp.Max}$, whereas in the desized series the response becomes more geometry-sensitive, especially with respect to L/D . This distinction is relevant because it suggests that the industrial fiber surface condition partially masks the underlying mechanical scaling of the test, thereby contributing to the broad experimental dispersion.

5.2 Transverse Bundle Tensile Tests (TFBT) – Meso-Scale Interface Assessment

Following the Microbond campaign, the investigation was extended to a meso-scale configuration in order to probe whether the plasma treatment could induce a more global and statistically representative change in the fiber/matrix response, beyond the highly localised single-filament debonding observed at microscale. In this sense, the Transverse Bundle Tensile Test (TFBT) methodology was not adopted simply as an alternative to Microbond, but as a means to increase the interaction volume between

fiber and matrix, involving a larger amount of resin and a broader population of filaments, so that the response of the treated interface could be assessed under a larger interaction volume, where local fluctuations are partially averaged out any treatment-induced change is more likely to emerge as a bundle level mechanical response. TFBT was therefore selected as the primary meso-scale approach, employing ASTM D638 type IV dogbone specimens with centrally embedded unidirectional carbon fiber bundles extracted from both 0.2 mm and 0.1 mm thickness UD fabrics (Section 3.1). This configuration promotes failure preferentially within the bundle-matrix interaction zone through transverse tensile loading perpendicular to the fiber axis, thereby providing a more integrated measure of load transfer than a single-fiber Microbond test and, at least in principle, a better opportunity to reveal whether the plasma treatment produces an effect that persists at a larger structural scale.

As explained in Section 3.5.1., specimens were fabricated via CF bundle hand positioning within the dogbone neck, ensuring uniform resin impregnation while minimising edge effects. Testing proceeded on an Instron universal testing machine equipped with 5 kN load cell under displacement control at 5 mm/min quasi-static rate (well within established transverse testing protocols) until bundle failure and detachment of dogbone specimen's halves. Force-displacement response was continuously recorded and converted to nominal bundle stress as presented in Chapter 3, yielding characteristic brittle failure profiles across all experimental series that proved sensitive to both surface treatment and bundle impregnation conditions.

5.2.1 TFBT 0.2 mm UD Fabric Batch

The initial TFBT analysis focused on 0.2 mm UD carbon fabric bundles in parallel with the latest macro-scale DCB test campaign, which also involved the same fabric. It investigated four distinct surface conditions: two as-received baselines with the wet chemical sizing of the manufacturer (namely AR1 and AR2), N₂ plasma-treated specimens (8 mm distance, 160 mm/s scan speed), and acetone-desized reference. Each condition comprised $n = 3\text{--}4$ replicate specimens demonstrating good experimental repeatability.

Global mechanical performance revealed average peak bundle stresses $\sigma_{\max} \approx 17\text{--}23$ MPa (Table 5.5). As-received AR1/AR2 exhibited robust performance at 23.1 ± 2.5 MPa maximum stress (at maximum loads of 521–573 N), reflecting effective

bundle-matrix stress transfer under transverse loading. N₂ plasma treatment yielded slightly reduced $\sigma_{\max} = 20.3$ MPa (460 N), consistent with plasma-induced tow opening that enhances resin penetration at the expense of slightly reduced internal bundle compactness. Critically, acetone desizing produced the lowest performance at 16.9 MPa (397 N), in agreement with with sizing removal disrupting intrinsic tow integrity and resin distribution within the bundle.

Stress-displacement curves displayed characteristic linear elastic regime terminating in abrupt bundle decohesion without significant post-peak extension, confirming transverse-dominated failure remote from machine compliance limits (Figure 5.9).

Table 5.5 TFBT 0.2 mm CF UD results.

Condition	$F_{\max}$ [N]	$\sigma_{\max}$ [MPa]
AR1	572.97 (57.13)	23.08 (2.30)
AR2	521.25 (51.38)	23.11 (2.50)
N2	459.87 (68.02)	20.27 (2.80)
Acetone	397.15 (22.39)	16.93 (0.81)

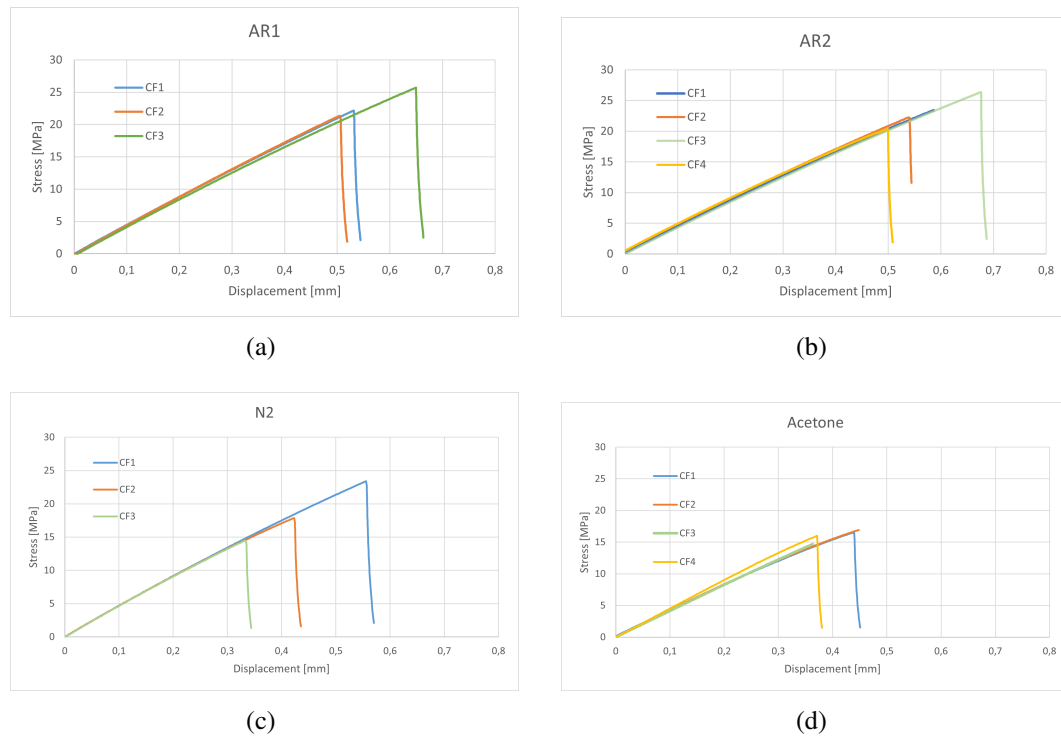


Fig. 5.9 Representative TFBT stress-displacement curves for 0.2 mm UD bundles. AR1/AR2 (a,b), N₂ plasma (c) and Acetone (d).

Post-failure optical microscopy analysis consistently revealed heterogeneous fracture morphologies across the 0.2 mm series, as shown in Figure 5.10. The red marked regions highlight zones of partial bundle opening, areas of retained resin, and regions where the fracture surface appears less compact or more irregular. In the AR1 specimen, the highlighted areas correspond to a comparatively compact fracture morphology, with one region showing a more open fiber arrangement and another indicating local resin remnants. The AR2 sample appears similarly compact overall, but the marked upper region highlights a more open and less regular bundle top surface. The N₂ specimen, although not annotated with specific circled regions, shows a generally homogeneous and densely packed fracture surface, with limited visually distinguishable local features. By contrast, the acetone-desized specimen exhibits the most evident central region of altered appearance, with less uniform morphology and a more pronounced change in local surface texture.

The AR1/AR2 specimens therefore appear relatively compact and continuous, with resin remnants still attached to a significant fraction of the filaments. This suggests that failure occurred mainly through internal bundle separation, while the

external bundle-matrix interface did not emerge as the dominant weak point under the present loading conditions. The N₂-treated bundle shows a more open and less consolidated fracture appearance, which is consistent with a modified impregnation pattern and a different local load-sharing condition relative to the as-received state. The acetone-desized specimen exhibits the most heterogeneous surface appearance, with only occasional peripheral traces that may indicate limited interface involvement, but the dominant failure mode remains bundle-centered.

Overall, the present TFBT configuration appears to be more sensitive to tow opening, resin infiltration, and bundle cohesion than to a direct ranking of interfacial adhesion among the investigated surface conditions. For this reason, the fracture morphologies should be interpreted primarily as qualitative indicators of how the surface treatment affects bundle-level impregnation and internal load redistribution, rather than as a definitive measure of surface adhesion alone.

The limited discrimination observed across the aforementioned conditions can be attributed to two alternative, non-mutually exclusive explanations that deserve explicit consideration within the multiscale framework. The first is a methodological sensitivity argument: the TFBT configuration employed here may lack sufficient sensitivity to resolve treatment effects of the magnitude induced by APP treatment under the present conditions. The second is a scale-transfer argument: the treatment effect, even if it solely affected the fibre surface, may not translate into a measureable meso-scale benefit under this specific transverse tensile loading. In this configuration, failure is predominantly governed by the weakest transverse path within the bundle rather than by the average quality of the fibre-matrix interface, and the activated stress state is not the one under which adhesion-dominated mechanisms are expected to dominate.

These two interpretations carry different implications: in the former case, a more discriminating meso-scale protocol could in principle reveal the treatment effect; in the latter case, the present test geometry may simply be poorly suited to capture a surface treatment benefit that remains localised at the finer structural scale.

A specific aspect that warrants additional discussion is the response of the N₂-treated specimens, which does not show a clear improvement in peak stress relative to the as-received condition (20.3 ± 2.8 MPa vs. 23.1 ± 2.5 MPa for AR1/AR2). This result is attributed primarily to plasma-induced tow opening: APP treatment modifies the fibre surface chemistry and partially removed the sizing layer, which

enhances resin penetration into the tow but simultaneously reduces the internal bundle compactness and fibre packing density that contribute to peak transverse load-bearing capacity. The slightly reduced peak stress therefore does not indicate a detrimental interfacial effect, but rather a modified impregnation and internal load-redistribution pattern that penalises bundle cohesion under this specimens (referred to Figure 5.10 case c), which shows a more open and less consolidated fracture surface relative to the AR1/AR2 condition, and with the observation that the acetone-desized reference –where sizing disruption is most severe – yields the lowest peak stress among all conditions (16.9 MPa). Within the multiscale framework, the N₂ response in the 0.2 mm batch therefore reflects a meso-scale architectural consequence of the treatment rather than a direct quantitative measure of interfacial adhesion quality.

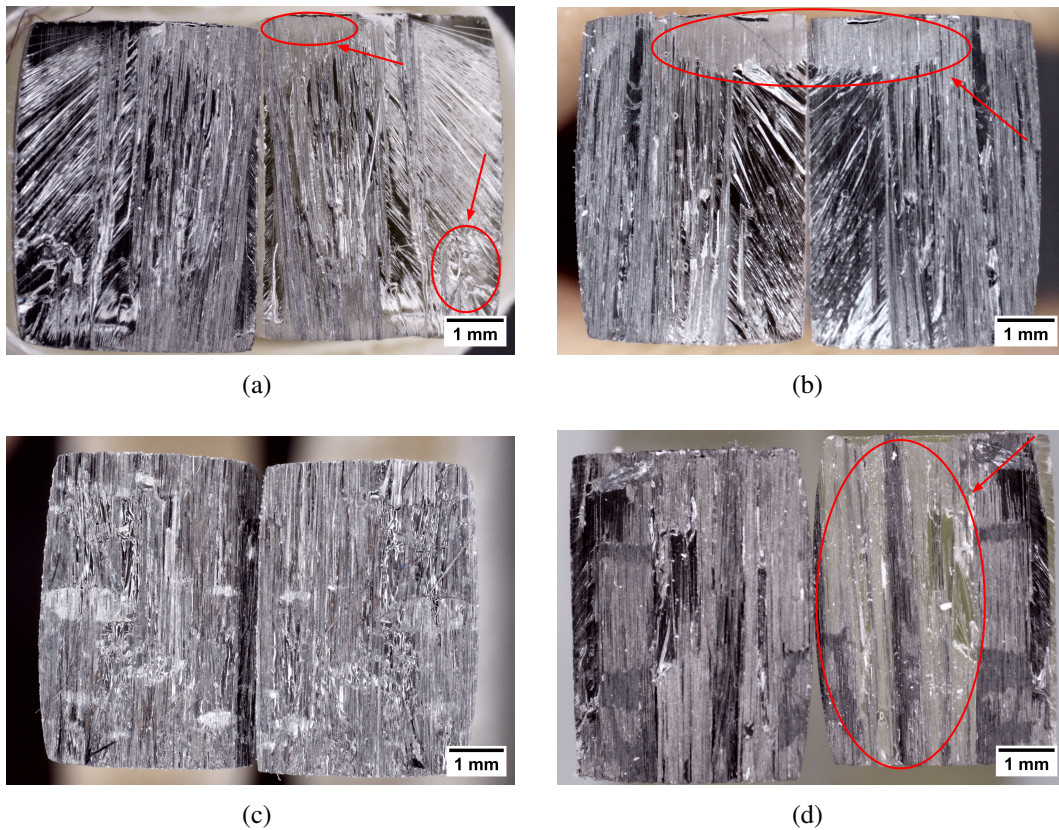


Fig. 5.10 TFBT fracture surfaces (0.2 mm UD): AR1/AR2 (a,b), N₂ (c), Acetone (d).

5.2.2 TFBT 0.1 mm UD Fabric Batch

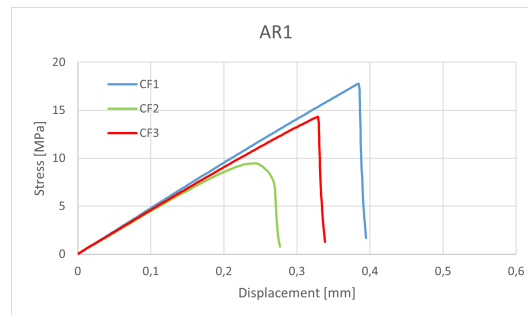
Following the 0.2 mm campaign, the 0.1 mm UD fabric configuration was investigated in order to verify whether a thinner bundle architecture could provide a more discernible bundle-level response and, at the same time, reduce the extent to which internal tow cohesion dominates the fracture process. In the present case, the emphasis is therefore placed not on a direct assessment of solely surface adhesion, but on whether changing the bundle architecture and the pre-treatment route can reveal a clearer mechanical signature in the transverse response. Three distinct batches were evaluated: the as-received AR1 reference, the N₂ plasma-treated variant, and a novel Ace + N₂ condition whereby fibers were first desized via thermal precleaning (300° C - 1h) and then immersed in acetone for 2h to extract any pre-existing sizing agents prior to plasma exposure. This additional pre-cleaning step was introduced precisely to remove any pre-existing sizing agents and to test whether plasma functionalization on a sizing-free surface could produce a more clearly identifiable change in the bundle-scale response.

The resulting stress–displacement curves are reported in Figure 5.11, while the corresponding peak values are summarised in Table 5.6. All three conditions retained the characteristic brittle response already observed in the thicker batch, but with lower absolute peak stresses attributable to the reduced bundle architecture and filament count: 13.85 ± 4.17 MPa for AR1, 14.81 ± 3.74 MPa for N₂, and 9.53 ± 3.68 MPa for Ace + N₂. The Ace + N₂ condition's reduced performance likely reflects the combined effects of (i) thinner bundle sensitivity to impregnation defects and (ii) manual resin application without vacuum bagging, which limited penetration into the desized tow—unlike the vacuum-assisted infusion employed in the DCB macro-scale tests. This highlights TFBT's sensitivity to processing conditions rather than a plasma treatment deficiency.

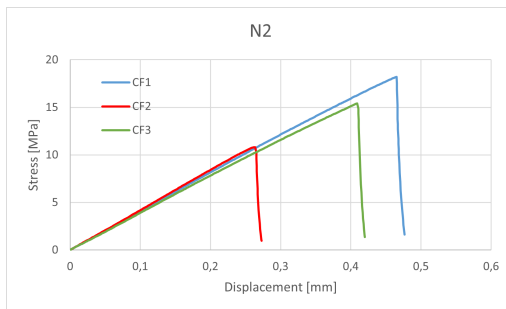
At the same time, the normalized curves suggest that the three conditions do not behave identically. The AR1 specimens show a comparatively regular linear rise followed by abrupt failure, the N₂ condition reaches the highest average peak stress among the 0.1 mm group, and the Ace + N₂ batch exhibits the lowest peak level together with a somewhat earlier loss of load-carrying capacity. These differences are visible in both the stress–displacement traces and the corresponding fracture surfaces (as displayed in detail below), but they should still be interpreted as bundle-level mechanical responses rather than as a standalone ranking of surface adhesion quality.

Table 5.6 TFBT 0.1 mm CF UD results.

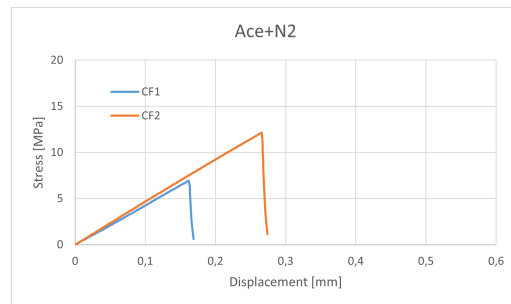
Condition	$F_{\max}$ [N]	$\sigma_{\max}$ [MPa]
AR1	299.83 (76.77)	13.85 (4.17)
N ₂	368.83 (98.47)	14.81 (3.74)
Ace + N ₂	223.35 (90.30)	9.53 (3.68)



(a)



(b)



(c)

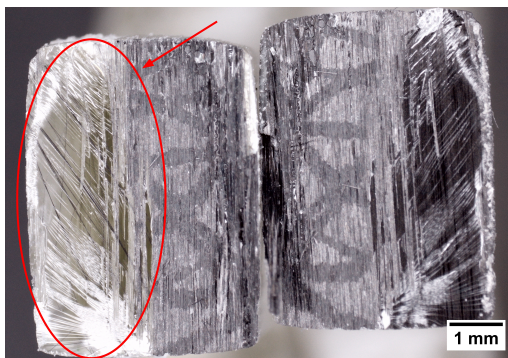
Fig. 5.11 Representative TFBT stress–displacement curves for 0.1 mm UD bundles. AR1 (a), N₂ (b), and Ace + N₂ (c).

The corresponding fracture surfaces are shown in Figure 5.12. In the AR1 specimen, the annotated region highlights a relatively compact fracture morphology, with one local zone of bundle opening and another associated with retained resin remnants. The N₂-treated specimen appears more open and less consolidated, with clearer filament separation and signs consistent with resin penetration between the fibers. The Ace + N₂ condition exhibits the most marked central region of altered appearance, where the fracture surface looks less uniform and more strongly differentiated from the surrounding bundle, suggesting a different impregnation pattern and local load redistribution during failure.

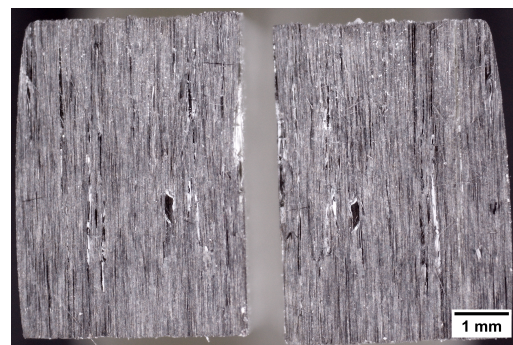
Overall, the 0.1 mm TFBT campaign indicates that reducing the bundle thickness modifies the transverse response and makes the differences among conditions more visible, but it still does not isolate a single, unambiguous surface-adhesion hierarchy. The observed contrasts likely reflect a combined effect of bundle architecture, fiber packing, resin infiltration, and pre-treatment route, all of which contribute to the measured bundle-level fracture response. In this sense, the present meso-scale test is more informative as a comparative indicator of how the investigated surface states alter load transfer within the tow than as a direct quantitative measure of interfacial adhesion.



(a)



(b)



(c)

Fig. 5.12 TFBT fracture surfaces (0.1 mm UD): AR1 (a), N₂ (b), Ace + N₂ (c).

5.3 Critical Synthesis of Bottom-Up Multiscale Approach

Considering the results obtained at micro- and meso-scale, it has emerged that these testing levels—while conceptually fundamental to a bottom-up multiscale framework—exhibit significant quantitative limitations when transferred from idealized laboratory conditions to industrial UD textiles. The original intent of the multiscale workflow was to leverage non-standard Microbond tests and transverse fiber bundle tensile tests as early, material- and time-efficient screening tools for APP Jet process optimization. In practice, however, the results obtained on the present APP Jet-treated UD reinforcements show that this bottom-up path can only be partially fulfilled.

From the micro-scale perspective, MB tests on industrial fibers revealed substantial scatter, a phenomenon widely documented in literature. Even in controlled round-robin programs [105], inter-laboratory variation remains high, frequently exceeding 25-30%. Such dispersion is driven by the extreme sensitivity to geometric parameters: as demonstrated by Zhao et al. [102] and Pandey et al. [106], variations in droplet embedded length, blade radial opening, and axial misalignment are primary sources of variability. Furthermore, the presence of the meniscus significantly alters the local stress distribution [102]. Under our industrial conditions, the measured interfacial shear strength (IFSS) reduces to an "apparent" metric (τ_{app}), the major mechanical parameter discussed in the previous sections. Experimental evidence from Qiyang Li et al. [103] reveals a pronounced size effect, where IFSS decreases with increasing embedded length, making quantitative extrapolation to laminate-scale toughness (G_{IC}) fundamentally complex. Savolainen et al. [104] suggest that while $IFSS_{app}$ can be used for comparative analysis within the same setup, it cannot serve as a basis for absolute scaling laws.

A similar, and perhaps more critical, picture emerges at the meso-scale (TFBT). This test was designed to bridge the gap between single-fiber adhesion and laminate transverse properties, but it presents significant interpretation challenges. Literature often assumes that interfacial debonding is the dominant failure mechanism in TFBT, allowing for the determination of interfacial normal strength [107]. However, the thesis' results on industrial UD bundles systematically showed failure modes dominated by matrix and bundle cohesion rather than clean interfacial debonding.

This discrepancy is supported by Wen Li et al. [108], who highlight a "remarkable discrepancy" between fiber bundle composite (FBC) tests and standard laminate tests due to the complex stress states along the heterogeneous bundle/polymer interface. In industrial reinforcements, this complexity is exacerbated by impregnation heterogeneity and local packing.

Hoecker and Karger-Kocsis [109] noted that while micro-mechanical tests (like MB) can characterize the quality of the bond, their relevance to transverse tensile response in macro-composites is often masked by the matrix's role and the presence of defects. In the proposed study, the APP Jet treatment successfully raised the interface strength above the weak links of the bundle architecture, as evidenced by the cohesive nature of the fracture surfaces. While this confirms that the treatment does not weaken the interface and indeed reinforces it, aligning with multi-scale observations on liquid resins where improved wettability correlates with better load transfer [29]. It also renders the TFBT poorly sensitive to moderate adhesion variations. As noted in literature, the gap between FBC results and laminate performance is often due to these internal stress concentrations [108], which in industrial textiles are dominated by porosity and packing flaws rather than purely by interfacial chemistry.

Overall, the results indicate that, when applied to industrial UD textiles and infusion-based laminates, MB and TFBT lose much of the quantitative predictive capability that the literature attributes to them in highly controlled, ideal working configurations. Both scales remain valuable as diagnostic tools: they verify the absence of detrimental APP Jet effects, reveal failure mechanisms, and qualitatively confirm interface strengthening. As discussed in Section 5.1, a key constraint is that material-related variability and methodological artifacts cannot be fully disentangled within the MB configuration. Sizing heterogeneity, tow-scale surface non-uniformity, and local contamination act in parallel with droplet geometry, meniscus stability, and curing-induced residual stresses, so the observed scatter reflects the combined outcome of both classes of effects. This makes a strict quantitative deconvolution of scatter sources impractical, but it also reinforces why the test should be read as a comparative probe of surface-state changes rather than as an absolute measure of interfacial strength.

However, the work clarifies that for industrial reinforcements, micro- and meso-scale tests appear more credible as mechanism-oriented probes than as a foundation for quantitative scaling laws. This intentionally shifts the focus towards macro-scale

tests (DCB, impact), as detailed in the next chapter, where the hybrid multiscale strategy uses bottom-up insights to support and interpret laminate results rather than to derive them directly.

Chapter 6

Macro-Scale Mechanical Results

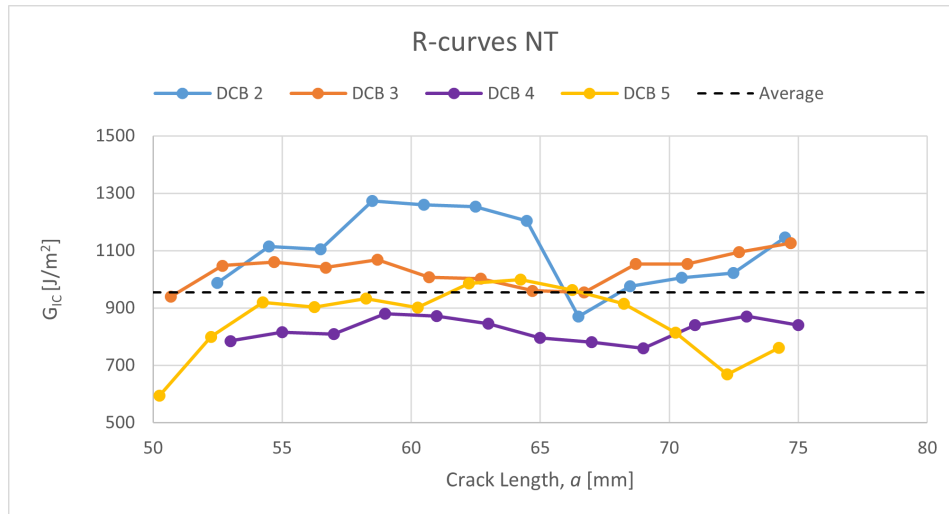
6.1 DCB MODE I Delamination Tests

Mode I interlaminar fracture toughness was assessed by DCB tests on UD CFRP laminates manufactured with 0.1 mm and 0.2 mm carbon fabrics, following ASTM D5528 and the compliance calibration (CC) method. All tests were performed following the procedure shown in Chapter 3. Initial non-linearity of the load–displacement curves was corrected whenever necessary by subtracting the δ_{NL} term so that the linear branch intersected the origin before compliance calculation; the corrected displacements were then used in all G_{IC} evaluations.

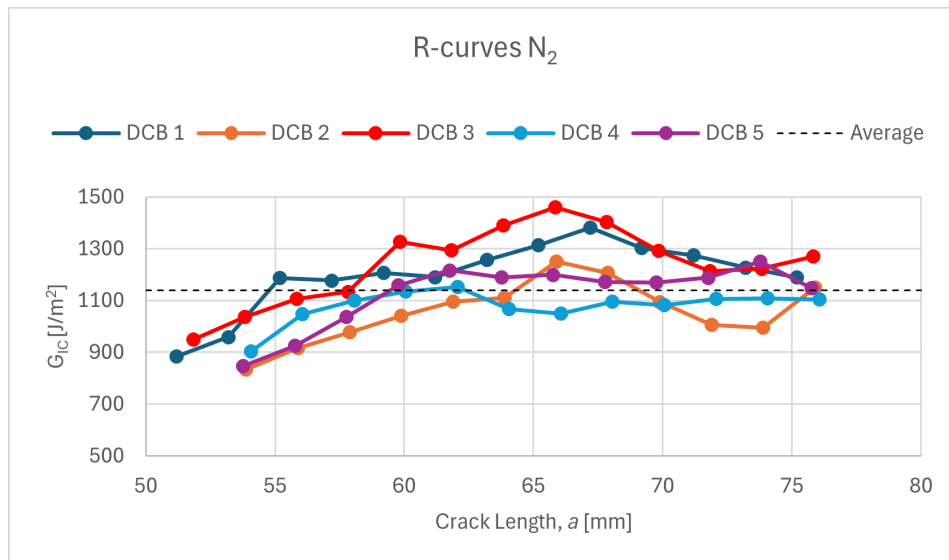
The preliminary DCB testing campaign with the 0.1 mm-thick UD fabric was primarily intended to confirm the directional benefits of the N₂ APP Jet treatment identified during surface characterization (Chapter 4) and micro-/meso-scale testing (Chapter 5). This thinner architecture, relevant for advanced industrial manufacturing processes and thin-ply applications, allowed for first process validation before committing to the 0.2 mm batches.

The characteristic resistance curves (R-curves), which provide the primary visual assessment of crack-growth stability and interlaminar toughening mechanisms, are shown for both NT and N₂ specimens in Figure 6.1. These plots highlight the transition from an irregular propagation to a more controlled crack advancement. Specifically, the NT specimens (Figure 6.1(a)) exhibit significant inter-specimen variability, with distinct and sudden drops in G_{IC} values along individual curves. This behavior is indicative of an unstable, stick-slip propagation mechanism, typical

of weak fiber-matrix interfaces where energy is suddenly released through large crack jumps. Conversely, the N_2 -treated specimens (Figure 6.1(b)) display a tighter clustering of the R-curves around the mean value. The crack progression is visibly smoother, characterized by a steady initial rise followed by a stable plateau, without the severe load drops observed in the untreated baseline.



(a)



(b)

Fig. 6.1 DCB – 0.1 mm fabric: R-curves G_{IC} – a for (a) NT and (b) N_2 specimens.

Complementing this graphical analysis, the key numerical outputs—initiation toughness at maximum load ($G_{IC,a0}$, NPC), first propagation toughness ($G_{IC,a1}$, PC), and mean subsequent propagation toughness ($G_{IC,ai}$)—are comprehensively summarised in Table 6.1, including standard deviations and N_2 /NT percentage improvements.

Table 6.1 DCB – 0.1 mm fabric: average G_{IC} values [J/m^2] (STD).

Case	$G_{IC,a0}$ (NPC)	$G_{IC,a1}$ (PC)	$G_{IC,ai}$
NT	838.59 (191.11)	1106.50 (216.53)	953.52 (133.67)
N_2	840.65 (150.88)	1282.76 (188.57)	1138.84 (76.99)
% ΔN_2 /NT	+0.3%	+15.9%	+19.4%

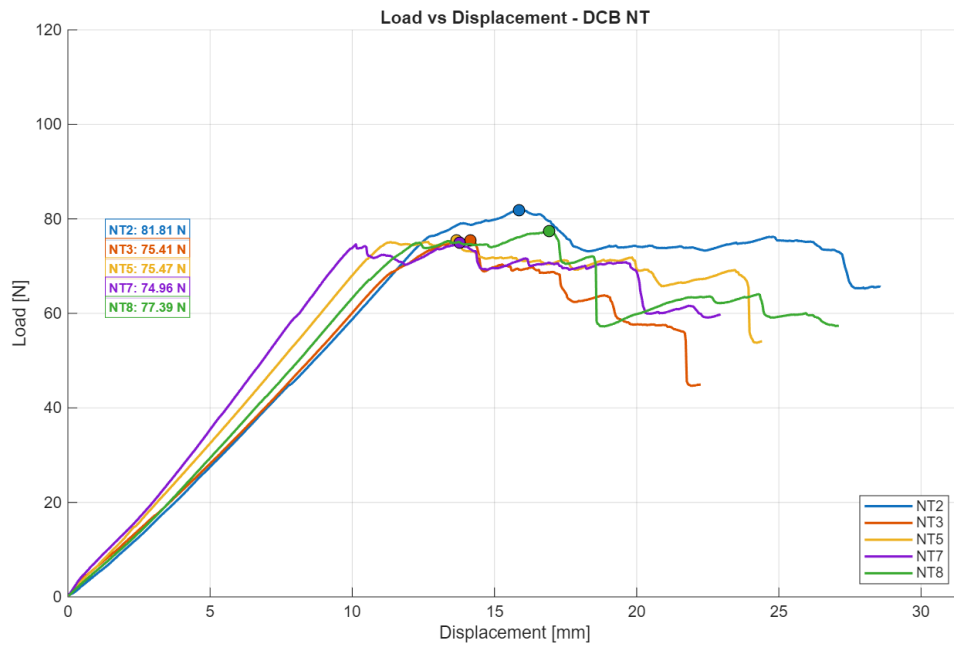
While the initiation values ($G_{IC,a0}$ and $G_{IC,a1}$) appear numerically close due to the inherent scatter and local tip effects at the insert, the effectiveness of the N_2 APP Jet treatment becomes prominently evident during the stable crack propagation phase.

The mean propagation toughness ($G_{IC,ai}$) registers a robust enhancement of +19.4% for the N_2 -treated specimens compared to the untreated baseline. The statistical significance of this improvement is confirmed by ANOVA, yielding a P-value of 0.034 ($P < 0.05$). This indicates that the engineered surface chemistry induced by plasma activation provides its most critical contribution during steady-state delamination, where the cumulative effect of improved fiber-matrix adhesion can effectively stabilize the crack growth.

This trend indicates that the primary benefit of N_2 surface activation lies in the stabilization of the failure process. This behavior is congruent with the observations reported in Chapter 5: the transition from clean adhesive debonding to a partial cohesive failure mode forces the crack to follow a more tortuous and fracture path capable of absorbing greater energy. Consequently, plasma treatment proves highly effective in increasing the delamination resistance during the propagation phase, where the fracture surface is characterized by extensive resin residues and increased roughness, leading to higher energy dissipation.

Building on the positive indications from the 0.1 mm screening, the main DCB validation focused on the 0.2 mm UD fabric under the same APP Jet parameters. This

thickness is equally representative of industrial UD preforms adopted thus provides a definitive benchmark for quasi-static Mode I performance. The representative load-displacement (P vs δ) curves for the 0.2 mm batch, which directly reveal the enhanced load-bearing capacity and propagation stability after N_2 treatment, are presented in Figure 6.2. It is observed that the N_2 treatment leads to a significant increase in the peak loads, which reach values between 100 N and 120 N, compared to the 75–80 N range typical of the NT specimens. Unlike the 0.1 mm case where NT showed marked stick-slip, the thicker 0.2 mm NT curves appear more regular. The N_2 batch, however, exhibits more frequent "saw-tooth" load fluctuations during the crack propagation. This behavior is characteristic of higher interlaminar toughness, where crack jumps occur at discrete critical lengths after accumulating higher strain energy, rather than via continuous advancement at lower loads.



(a) NT

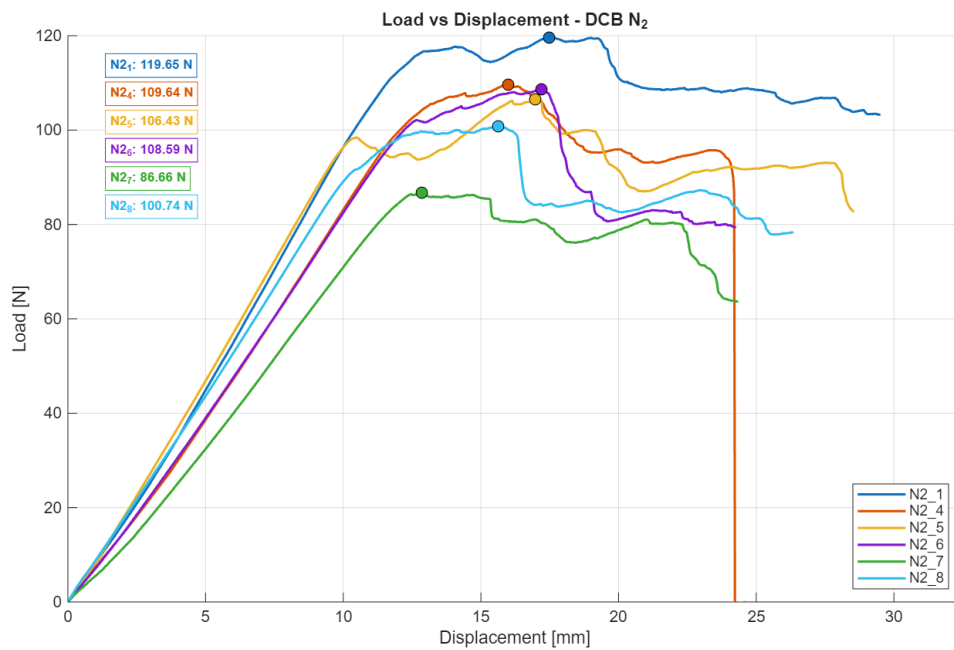
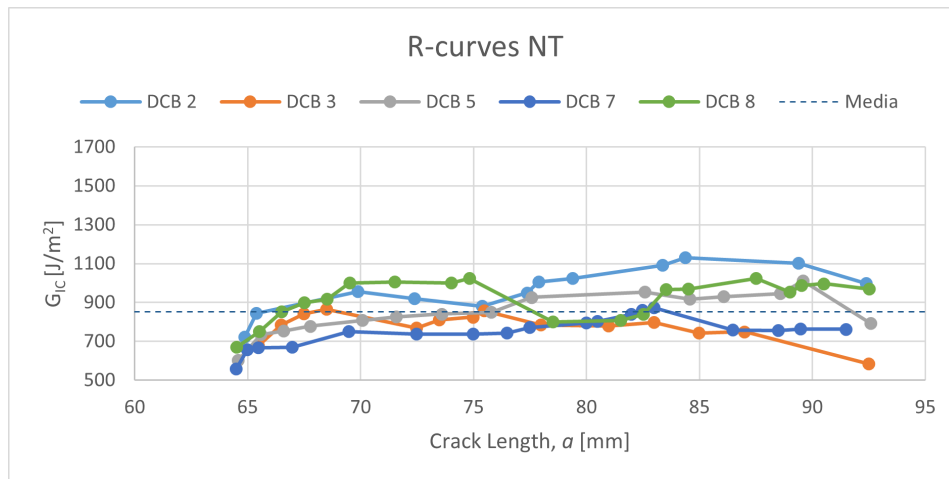
(b) N₂

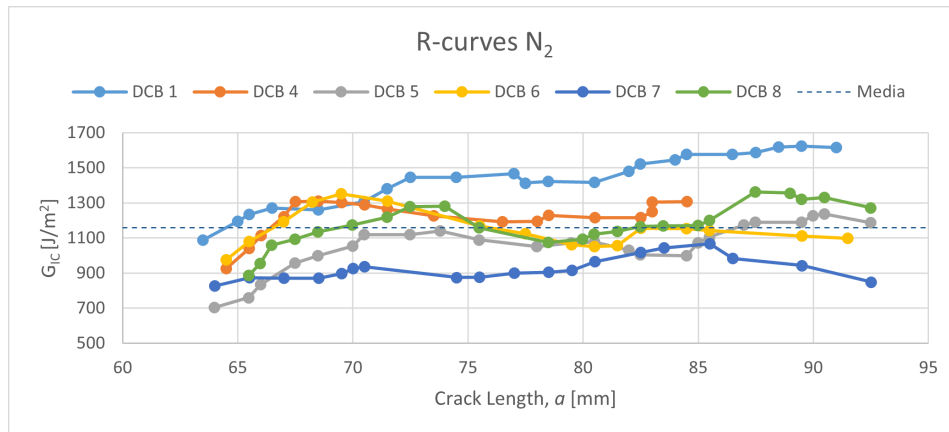
Fig. 6.2 DCB – 0.2 mm fabric: representative load-displacement curves comparing (a) as-received NT and (b) N₂-treated specimens.

The corresponding resistance curves (R-curves, G_{IC} vs a), which provide a quantitative assessment of crack-growth resistance, are shown for both NT and N₂

specimens in Figure 6.3. Graphically, the N_2 treatment results in a clear upward shift of the entire distribution of individual R-curves. Toughness values for the treated specimens reach levels as high as 1600 J/m^2 (e.g., specimen N_2 #1), while the NT references remain mostly below 1100 J/m^2 . In this configuration, the plasma treatment improves the absolute level of fracture toughness while maintaining a stable propagation plateau.



(a)



(b)

Fig. 6.3 DCB – 0.2 mm fabric: resistance curves G_{IC} – a for (a) NT and (b) N_2 specimens.

Table 6.2 DCB – 0.2 mm fabric: average G_{IC} values [J/m^2] (STD) with N_2/NT percentage increments.

Case	$G_{IC,a0}$	$G_{IC,a1}$	G_{IC,a_i}
NT	542.52 (85.51)	847.58 (44.40)	851.29 (92.45)
N_2	674.13 (107.38)	960.21 (136.82)	1158.42 (169.80)
% Δ	+24.3%	+13.3%	+36.1%

The key numerical results and the corresponding statistical significance levels are summarized in Table 6.2. The initiation toughness ($G_{IC,a0}$) shows an improvement of +24.3%, which is borderline significant with a P-value of 0.054. The most substantial benefit is found in the mean propagation toughness (G_{IC,a_i}), which registers a gain of +36.1% with a highly significant P-value of 0.058 (near to the known limit value $P < 0.05$). These results confirm that the plasma-induced surface activation is effective in increasing delamination resistance during steady-state crack growth.

A unique outlier in the N_2 series (specimen N_2 #2) displayed a prominent secondary crack ahead of the main front, inducing a characteristic force plateau and irregular propagation pattern. This phenomenon, documented in Figure 6.4, deviates from the controlled single-front growth required by the ASTM D5528 standard. Consequently, specimen N_2 #2 was excluded from the averaged statistics to ensure the toughness values remained representative of the primary interface properties.

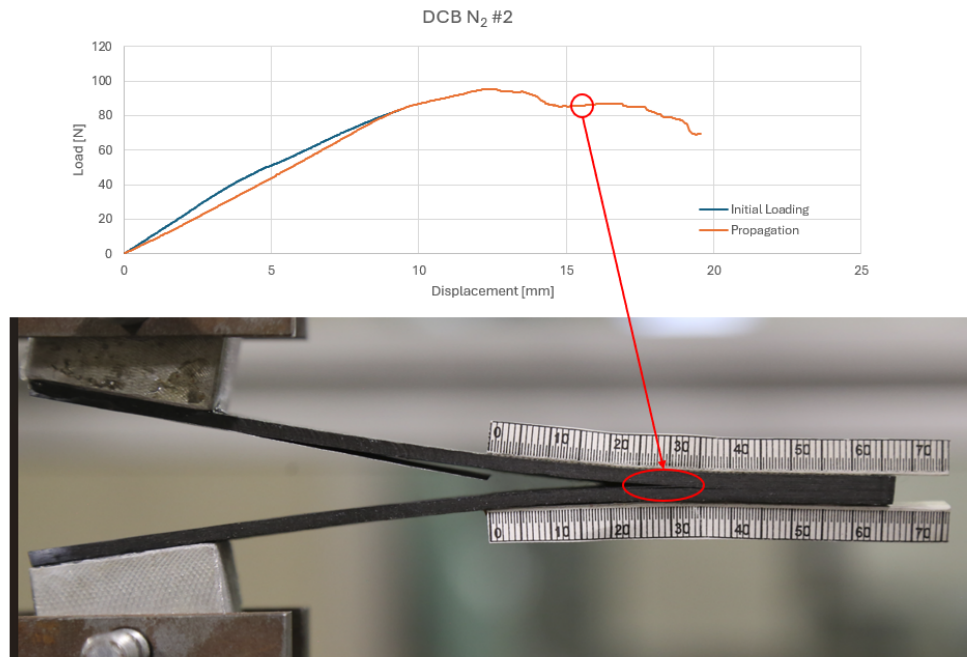


Fig. 6.4 DCB – 0.2 mm, N₂ specimen N₂ #2: load–displacement curve (top) and corresponding crack-front image (bottom) with secondary crack formation displayed.

Conversely, specimen N₂ #6, retained in the statistics as it followed a valid single-front advancement, despite a distinct load drop tied to a sudden advance of approximately 4–5 mm, followed by a stable plateau (Figure 6.5). This behavior, shown in Figure 6.5, reflects the ability of the reinforced interface to store higher strain energy before crack initiation, characteristic of the enhanced interlaminar toughness achieved via plasma treatment.

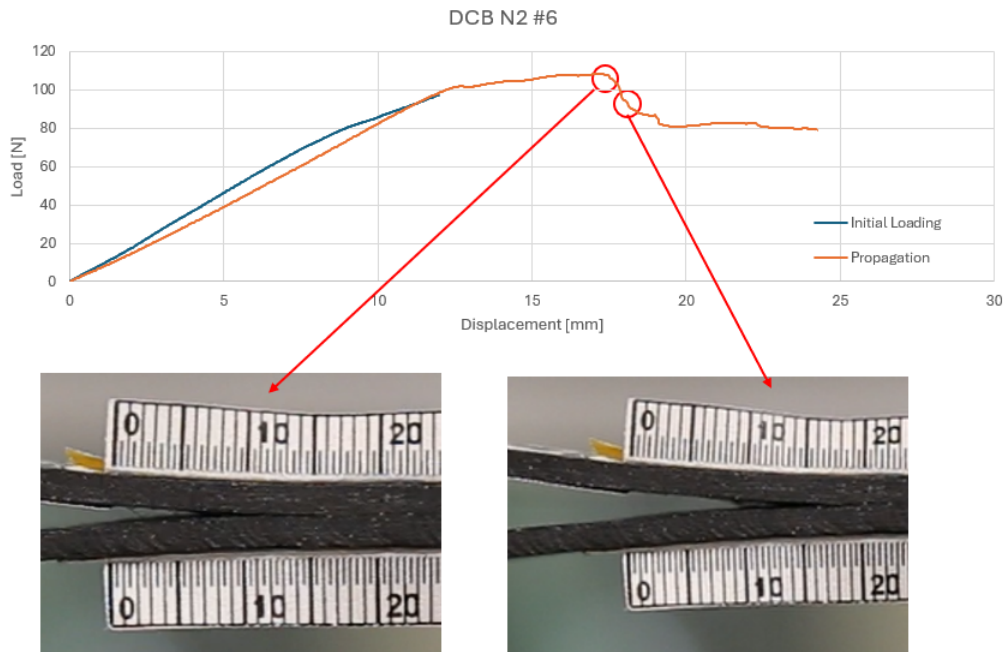


Fig. 6.5 DCB – 0.2 mm, N_2 specimen N_2 #6: load–displacement curve (top) with a characteristic load drop and corresponding crack-front images (bottom).

Outliers were also identified in the untreated NT batch, such as specimen NT #6 (Figure 6.6), where premature failure and rapid crack propagation occurred at only $\sim 60\%$ of the batch maximum load. This abrupt loss of stiffness highlight the inherent variability and localized weaknesses of untreated industrial interfaces. The N_2 treatment effectively mitigates these issues by homogenizing the surface chemistry, leading to a more consistent performance across the series.

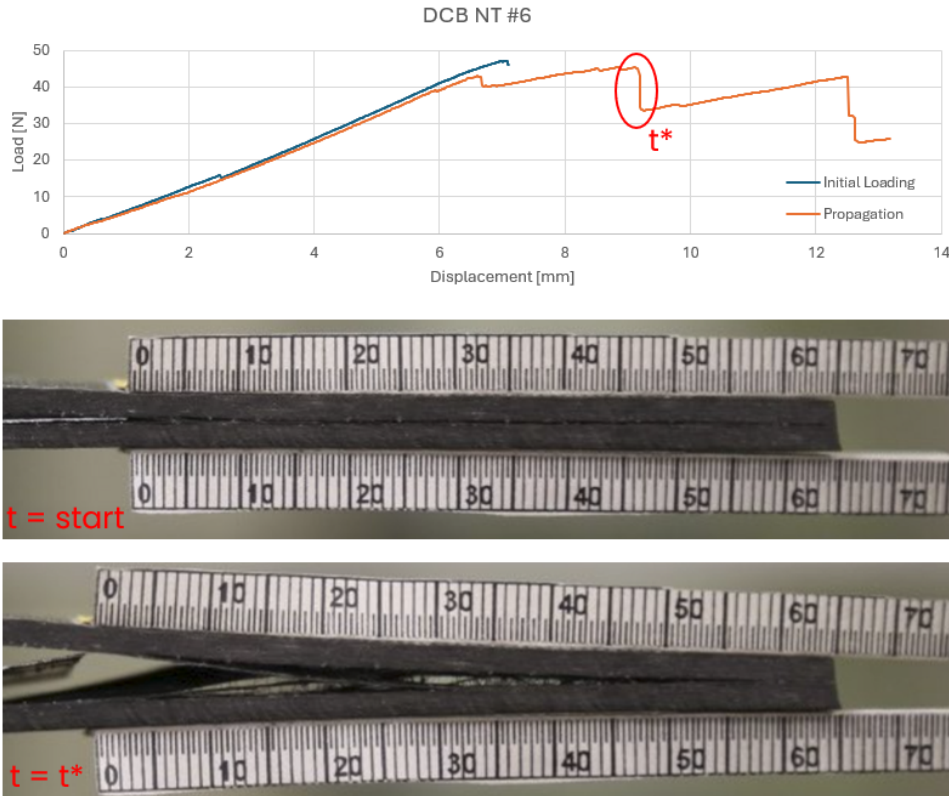


Fig. 6.6 DCB – 0.2 mm, NT_6 outlier: premature failure with rapid crack propagation (top), with corresponding crack-front images (bottom).

To provide a unified visual comparison of the toughness results across both fabric architectures, the mean G_{IC} values with standard deviations and the full data distributions for all conditions tested are summarised in Figure 6.7 and Figure 6.8, respectively. In the 0.1 mm batch, the initiation toughness $G_{IC,a0}$ shows virtually identical mean values between NT and N_2 specimens, while clear upward shift becomes apparent for the propagation descriptors $G_{IC,a1}$ and $G_{IC,ai}$, consistently with the crack-stabilisation role attributed to the plasma treatment.

In the 0.2 mm batch, the N_2 treatment produces a systematic increase across all three toughness descriptors, with the most pronounced gain observed for $G_{IC,ai}$, as presented previously (+36.1%). The relatively wide interquartile ranges visible in the boxplots reflect the inherent scatter typical of interlaminar fracture toughness measurements in industrial UD laminates, and are consistent with the moderate P-values obtained from the ANOVA analysis. Despite this scatter, the N_2 -treated series displays a systematic shift of the entire distribution toward higher toughness

values, confirming that the observed improvements reflect a genuine treatment effect rather than statistical noise.

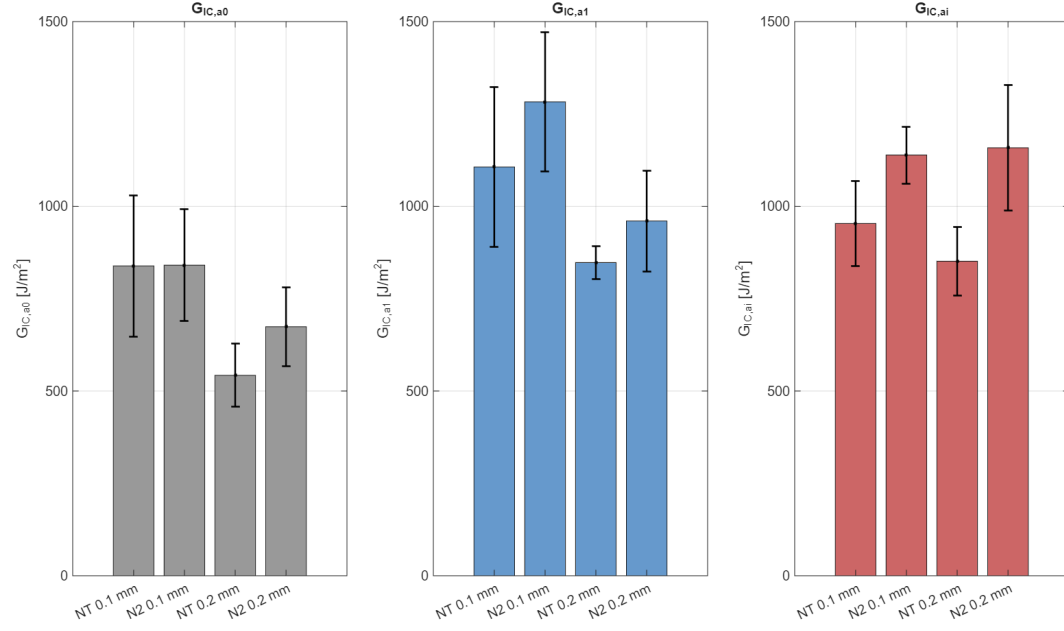


Fig. 6.7 Mean G_{IC} values with standard deviation for NT and N₂ specimens across 0.1 mm and 0.2 mm fabric batches.

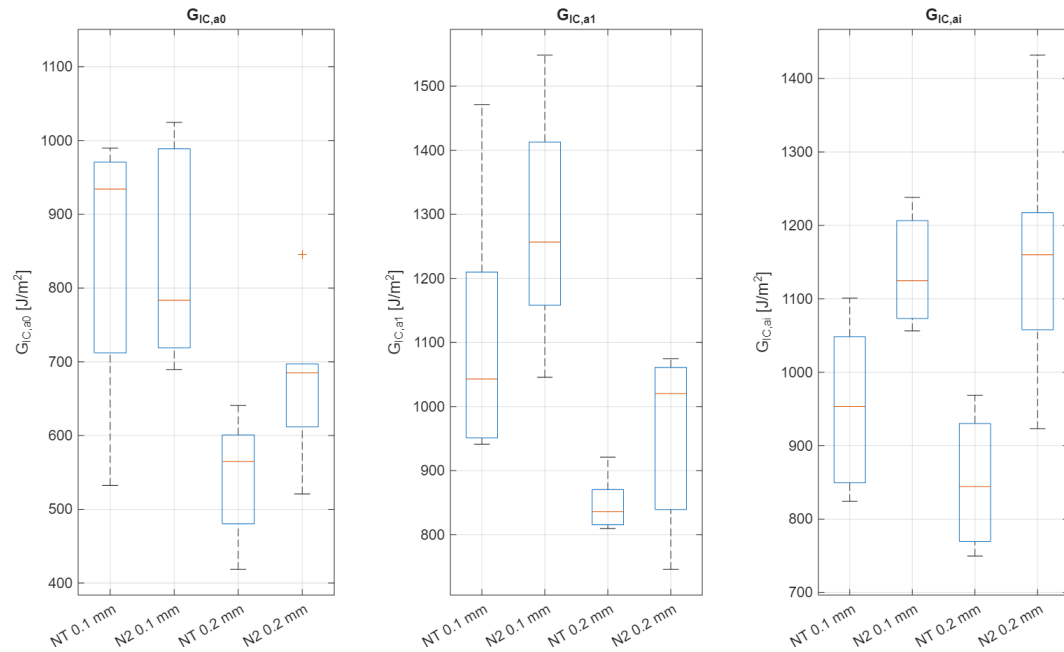
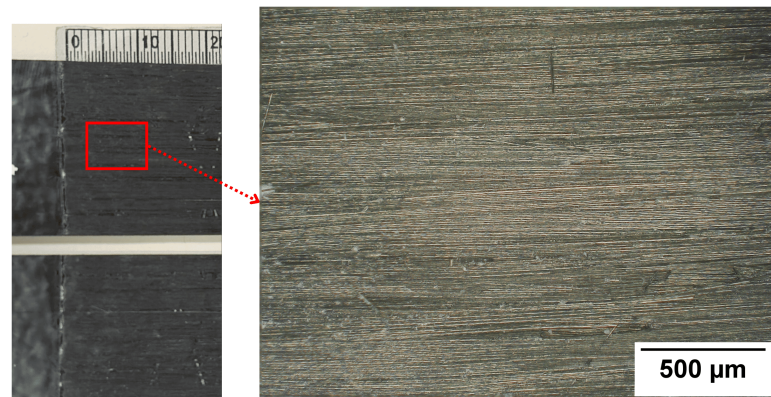
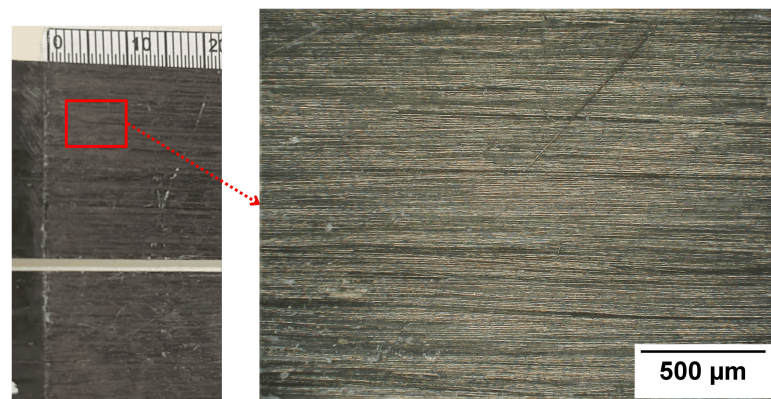


Fig. 6.8 Distribution of $G_{IC,a0}$, $G_{IC,a1}$ and $G_{IC,ai}$ for NT and N₂ specimens across 0.1 mm and 0.2 mm fabric batches.

The post-fracture morphology in the initial delamination region was also examined by optical microscopy, in order to complement the mechanical response with a qualitative observation of the crack path and of the local damage state. A couple of representative images are reported in Figure 6.9 and Figure 6.10 respectively for laminates fabricated with 0.1 mm and 0.2 mm fabrics, comparing NT and N₂ specimens. In all cases, the observed fracture surfaces appear broadly similar, with only limited local resin remnants and no pronounced qualitative differences between untreated and plasma-treated samples at the examined length scale. This suggests that, while the N₂ APP Jet treatment affects the delamination resistance in terms of measured G_{IC} , its effect is not necessarily reflected in a strongly distinctive macroscopic fracture appearance in the early propagation zone. The fracture morphology therefore remains consistent with a predominantly interlaminar separation process, whereas the treatment-related changes are more effectively captured by the toughness values and resistance curves than by optical appearance alone.



(a)



(b)

Fig. 6.9 Representative optical micrographs of the fracture surfaces in the initial (0-15 mm) delamination region after DCB testing: NT#3 (a) and N₂#1 (b) of 0.1 mm fabric batch.

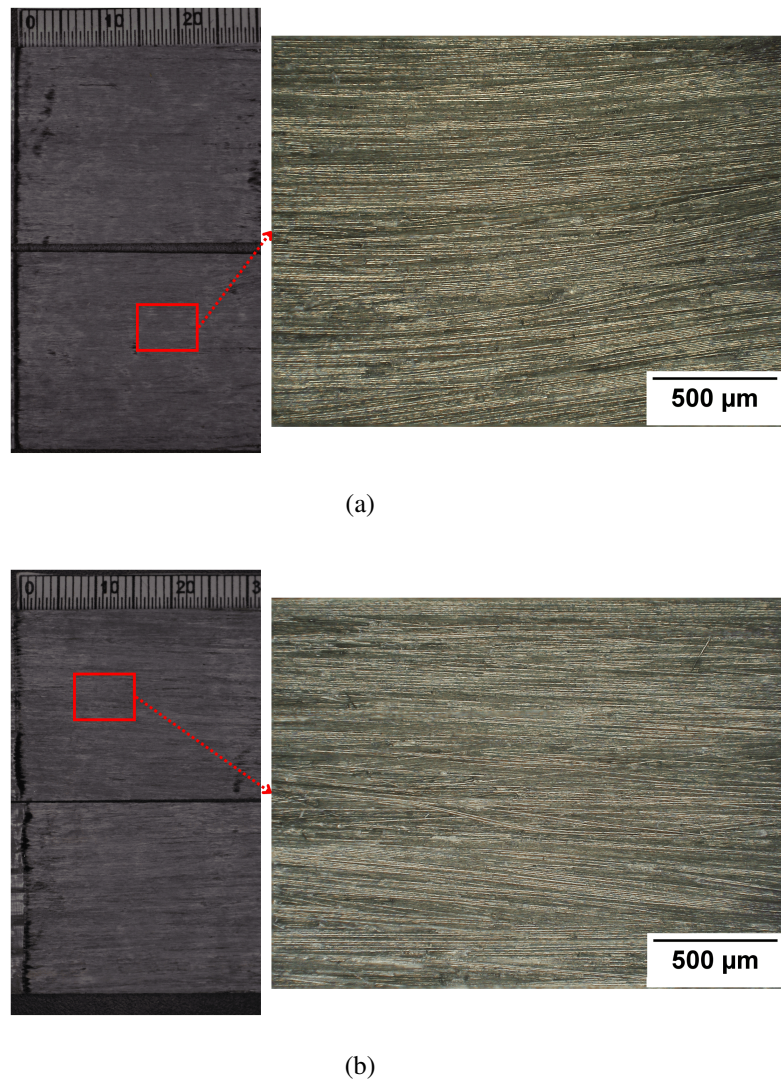


Fig. 6.10 Representative optical micrographs of the fracture surfaces in the initial (0-15 mm) delamination region after DCB testing: NT#2 (a) and N₂#8 (b) of 0.2 mm fabric batch.

In summary, the Mode I characterization across both fabric architectures provides a consistent validation of the N₂ APP Jet treatment. While the 0.1 mm series served as a successful preliminary screening, the 0.2 mm campaign delivered the quantitative proof of the process effectiveness, with a statistically significant gain of +36.1% in mean propagation toughness. The convergence of results from both thicknesses indicates that the primary role of the plasma activation is the strengthening of the fiber-matrix interface. By promoting a partial cohesive failure mode, the treatment

forces the crack front to follow a more energy-absorbing fracture path, effectively suppressing the unstable stick-slip behavior observed in the untreated baseline.

These quasi-static findings establish that the optimised parameters are effective under low-rate opening modes. However, to provide a comprehensive evaluation of the reinforced interface, it is necessary to assess the material response under high-rate loading conditions. Consequently, the performance of these laminates during dynamic impact is investigated in the following sections.

6.2 Impact Opening Test

Dynamic impact tests were conducted to evaluate the crashworthiness response of vacuum-infused UD carbon/epoxy laminates under high strain-rate conditions, extending the multiscale assessment of N₂ APP Jet surface treatment effects beyond quasi-static delamination (Section 6.1) to loadings which are relevant for aerospace and automotive impact scenarios. Following the specimen fabrication and methodological framework established in Section 3.5.2, coupons of nominal dimensions 150×50×3.5 mm were waterjet-cut from 0.2 mm textile-based panels and tested within a custom anti-buckling fixture originally developed for progressive failure analysis. This setup effectively suppressed global buckling while permitting controlled splaying and crushing in the unsupported gauge region, mirroring crashworthiness-inspired boundary conditions validated in prior Politecnico di Torino investigations. The Instron Fractovis drop-dart system delivered impact energies via 15–20 kg masses dropped at velocities approximating 5.5 m/s, with nominal inputs calibrated to achieve stable progressive damage without catastrophic specimen expulsion or fixture interaction.

Raw force-time signals acquired during impact were post-processed through the dedicated MATLAB pipeline that first applied multi-stage filtering to mitigate load-cell ringing, trigger transients, and high-frequency noise (common artifacts in drop-tower testing) while rigorously preserving the characteristic low-frequency oscillations associated with ply splaying and stable crushing. Figure 6.11 shows a representative Force vs Time history before and after filtering, highlighting the suppression of parasitic oscillations without loss of the physically meaningful crushing trend. Figure 6.12 further details the stable crushing region used for the extraction

of the mean crushing force F_{mean} , evidencing the filtered plateau response together with the raw signal retained in the selected interval for diagnostic comparison.

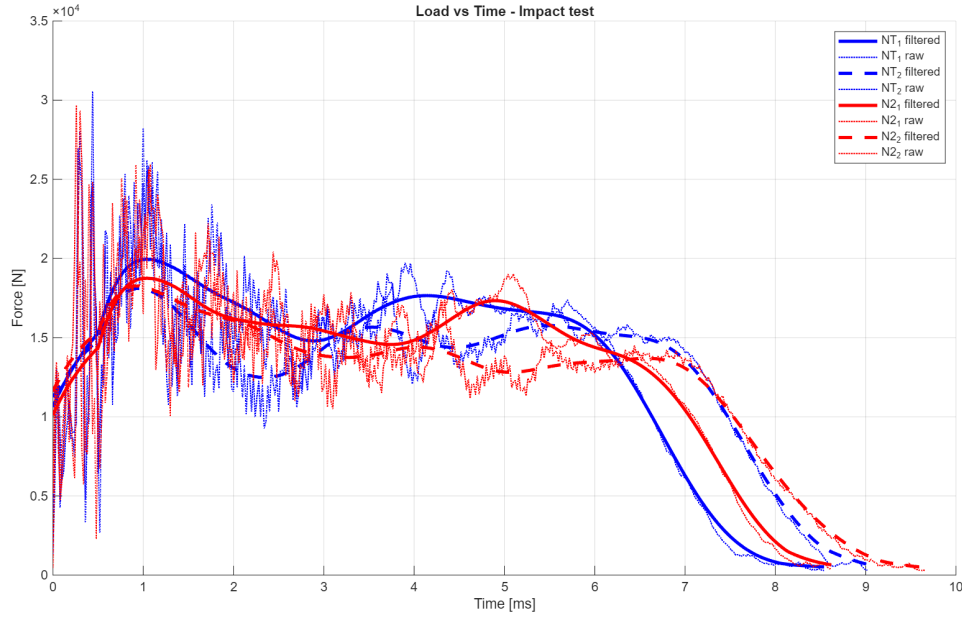


Fig. 6.11 Representative impact force-time signal (raw and filtered) for NT and N₂ specimens.

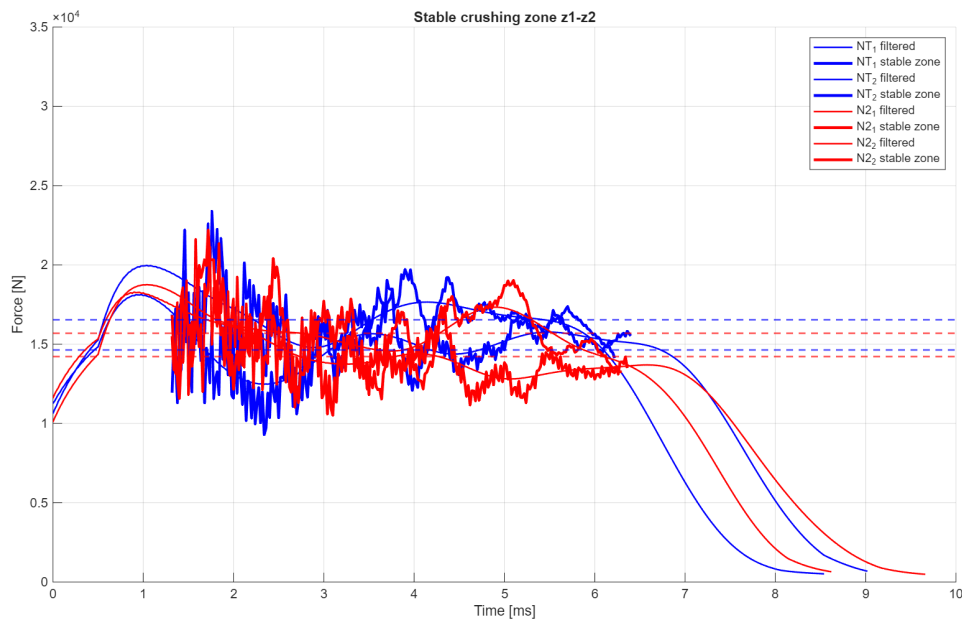


Fig. 6.12 Representative impact force-time response in the stable crushing region: raw signal, filtered signal and the corresponding mean crushing force F_{mean} .

Striker displacement $z(t)$ was then reconstructed via physics-based double integration of the filtered acceleration $a(t) = F(t)/m$, yielding velocity $v(t)$ and absolute displacement from dynamic equilibrium of the impactor mass. This approach, aligned with established crashworthiness protocols, overcomes limitations of direct encoder measurements post-initial contact, providing physically consistent force-displacement (F - z) representations for energy partitioning analysis.

The resulting F - z curves for both as-received and plasma-treated N₂ configurations exhibited the canonical progression typical of progressive failure in UD composites: an initial sharp peak (20–25 kN) from striker-plate contact and trigger activation, followed by partial load relief during elastic settling, and subsequent stabilization into a sustained plateau at mean crushing forces $F_{\text{mean}} \approx 14 \text{ kN}$. This plateau, delimited by algorithmically identified points z_1 (post-trigger steady-state onset) and z_2 (pre-degradation/end-of-stroke), represented the core region of energy dissipation through stable mechanisms, with specific energy absorption (SEA) normalized per standard flat-coupon formulation.

Quantitative comparison across the four valid specimens revealed tightly clustered performance with no systematic plasma influence (Table 6.3). Batch averaging yielded NT: $F_{\text{mean}} = 15.6 \pm 1.3 \text{ kN}$, $\text{SEA} = 67.6 \pm 5.8 \text{ kJ/kg}$; N2: $F_{\text{mean}} = 14.96 \pm 1.04 \text{ kN}$, $\text{SEA} = 62.0 \pm 4.9 \text{ kJ/kg}$. Given the limited number of specimens tested, these impact results should be interpreted with appropriate statistical caution. The absence of a measurable treatment effect under the present dynamic loading conditions does not necessarily imply that no effect exists, but rather that any potential difference was smaller than the sensitivity of the available dataset. These results show high consistency with the existing literature for thin unidirectional carbon fiber laminates. While typical values for flat UD coupons tested in anti-buckling configurations range between 50 and 80 kJ/kg, the measured SEA values (62–68 kJ/kg) occupy a performance regime significantly higher than twill-weave CFRP equivalents. This difference may be partly associated with the more regular fiber alignment of UD laminates, whereas woven architectures introduce interlacing regions and local resin-rich pockets that increase fiber spacing and may reduce the specific energy absorbed per unit mass. For instance, Vigna [96] reported SEA values of 45–46 kJ/kg for twill CFRP tested within the same fixture geometry, and Meredith et al. [110] documented a range of 35–60 kJ/kg for various prepreg layups, with the maximum performance (60.25 kJ/kg) achieved by 8 plies of 200 gsm twill fabric.

The performance advantage of the unidirectional architecture is further corroborated by Troiani et al. [111], who reported that UD tape specimens can reach specific energy absorption levels of up to 100 kJ/kg, outperforming fabric-based specimens by more than 30%. This substantial discrepancy is physically consistent with the transition from fabric to unidirectional architecture, as the absence of fiber crimp in UD systems enhances the efficiency of splaying and fragmentation mechanisms.

Table 6.3 Dynamic impact metrics extracted from the stable crushing plateau.

Specimen	F_{mean} (kN)	SEA (kJ/kg)
NT1	16.54	71.71
NT2	14.63	63.49
N ₂ 1	15.69	65.36
N ₂ 2	14.22	58.59

Post-test visual inspection of the specimens, complemented by high-speed acquisition during testing, corroborated the quantitative equivalence in mechanical metrics. Both macroscopic crush morphologies and dynamic response sequences appeared consistently similar across NT and N₂ configurations (Figures 6.13, 6.14 and 6.15). High-resolution impact frames captured indistinguishable initial striker engagement and early damage localization for all four specimens, while post-test views revealed a complex combination of progressive failure signatures. The crushing process is dominated by characteristic extensive splaying of surface plies, fiber kinking/pull-out, and matrix fragmentation [112] [113] [96].

Specifically, a prominent splaying and fragmentation effect was observed, as shown in Figure 6.14 and Figure 6.15. The outer layers peel away from the central axis to form external fronds, a phenomenon clearly detailed in the close-up view of the crush zone (Figure 6.15), where the unidirectional plies separate along multiple interlaminar planes. This architectural breakdown is coupled with extensive matrix pulverization and debris formation at the impact interface—labeled as delamination and fragmentation in Figure 6.15—indicating severe crushing of the epoxy phase. In particular, the images show that a secondary delamination of the outer plies that is present in both NT and N₂ specimens, confirming that the plasma treatment does not suppress the outer-layer delamination mechanism under impact. This suggests that, for the thicker coupons tested here, a thickness effect remains dominant and

the treatment is not sufficient to overcome the tendency of the external layers to delaminate under dynamic loading.

Furthermore, the flattened and compact appearance of the specimen base confirms the continuous sliding of the delaminated material against the steel crash plate. This mechanism, identified as "splaying and sliding" in the annotated morphology, contributes significantly to the sustained crush force measured during the stable plateau. Longitudinal views provide additional evidence of fiber bundles beaking through shear and compression instability in the regions forced directly against the crash surface.

These macroscopic features, including equivalent crushing extents ($\sim 20\text{--}25$ mm) and debris accumulation patterns, show no plasma-attributable distinctions. The findings align with the morphologies reported by Vigna [96], confirming that under high strain loading, the crashworthiness response is dictated by these volumetric failure modes rather than by localized interfacial enhancements.

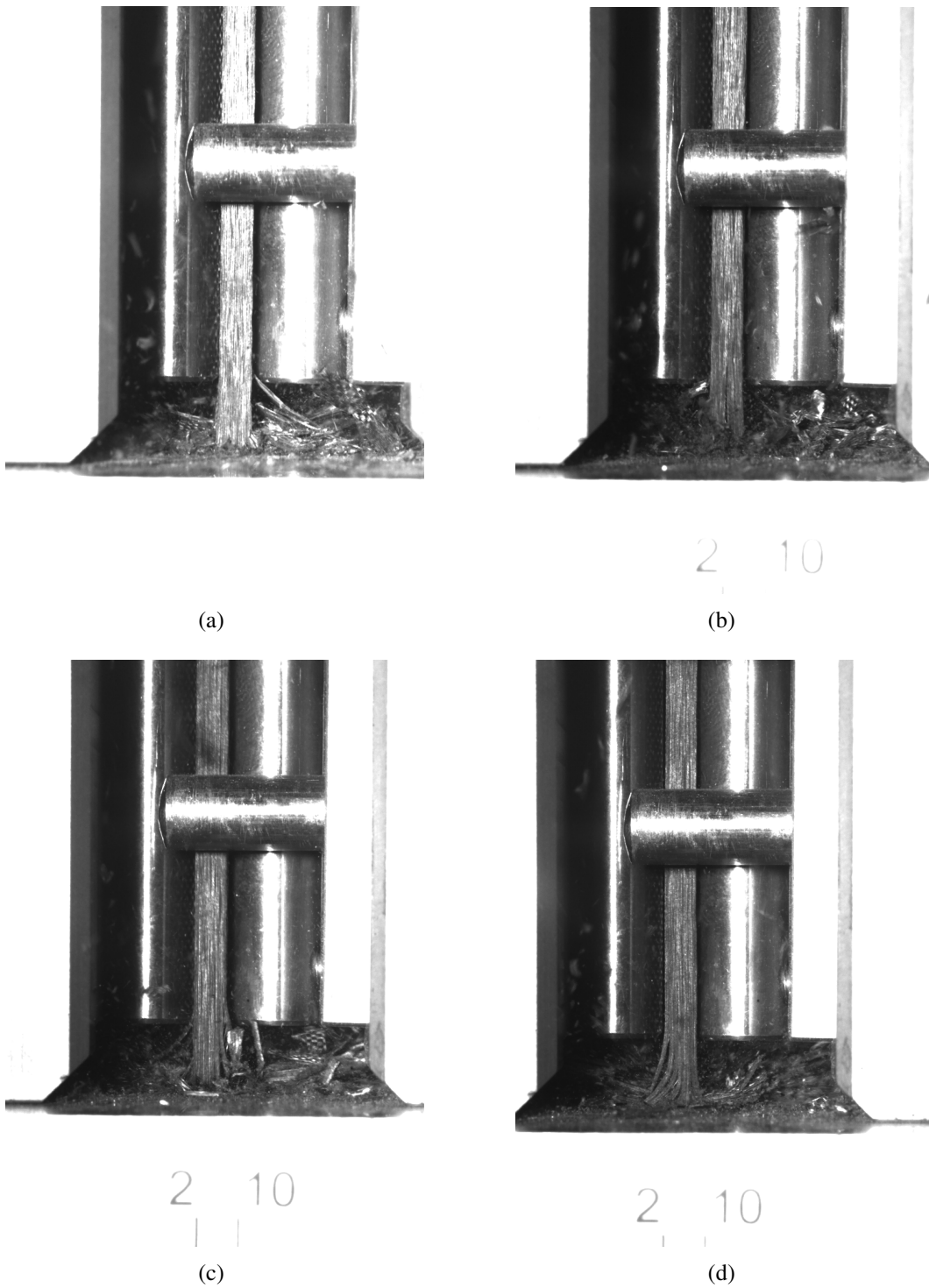


Fig. 6.13 High-speed acquisition images during impact: (a) NT1, (b) NT2, (c) N₂1, (d) N₂2.

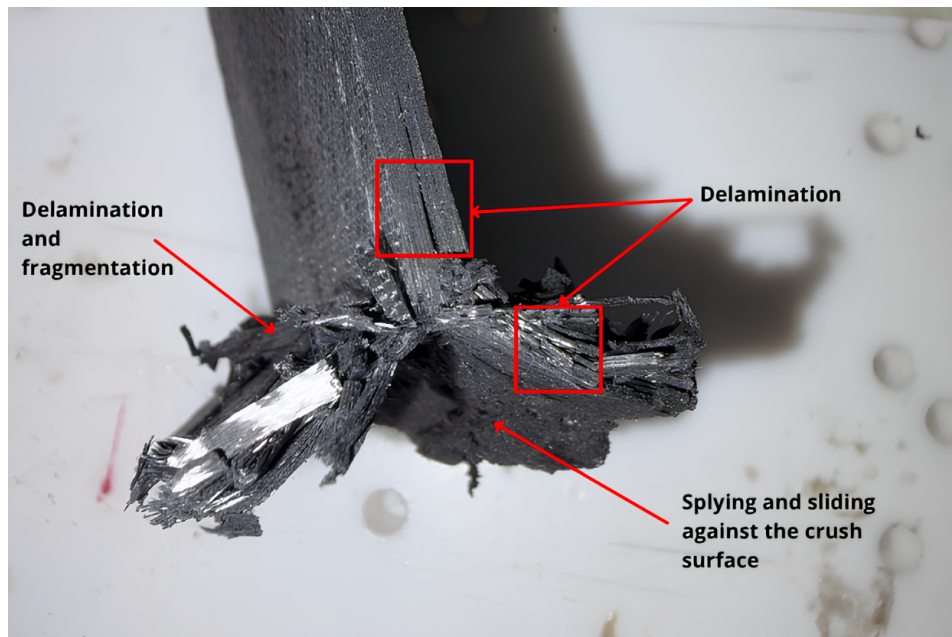


Fig. 6.14 Post-impact macroscopic morphology (N_2): evidence of delamination, fragmentation, and sliding.



Fig. 6.15 Detail of the splaying mechanism and frond formation in the crush zone.

The observed equivalence under dynamic conditions represents a critical contrast to the pronounced Mode I delamination enhancements documented in Section 6.1 (up to 36% G_{IC} propagation gain for 0.2 mm N_2 laminates). At high strain rates (for example $\dot{\epsilon} > 10^2 \text{ s}^{-1}$), failure transitions from interface-dominated clean crack

growth to a complex, volume-distributed cascade where multiple energy dissipation pathways—transverse matrix cracking, saturation delamination via secondary cracks, shear plugging, and fiber instability—overwhelm localized interfacial contributions. The modest adhesion improvements from N₂ APP Jet (20–30% micro/meso-scale indications from Chapter 5) thus become negligible against bulk laminate mechanisms that dictate overall SEA, explaining the lack of differentiation despite unequivocal surface activation (Chapter 4).

At dynamic rates, plasma-enhanced cohesive strength—which excels under quasi-static loading—degrades due to increased matrix brittleness and rate-sensitive interfacial decohesion, rendering adhesion gains ineffective against distributed damage. These findings delineate clear regime boundaries for APP Jet efficacy: pronounced benefits in quasi-static delamination where interface governs propagation, diminishing to null effect under impact where volume mechanisms prevail.

Chapter 7

Integrated Discussion and Multiscale Correlations

7.1 From Surface Modification to Mechanical Response

The central question addressed in this chapter is whether the effects of N₂ APP Jet treatment can be interpreted as a direct and systematic transfer from surface modification to composite-scale mechanical improvement. The experimental evidence collected in the previous chapters suggests a more nuanced picture. The treatment clearly modifies the fiber surface, as shown by the spectroscopic and morphological analyses, but the mechanical consequences are not equally visible at all length scales. In particular, the response is strong and statistically significant at the laminate scale under quasi-static delamination, whereas it remains much less clear at the micro- and meso-scale. This means that the treatment should not be described as a uniformly strengthening intervention, but rather as a surface engineering strategy whose effectiveness depends on the governing failure mechanism and on the scale at which the material is interrogated.

This distinction is important because the thesis does not simply seek to show that plasma treatment "improves adhesion". It aims instead to clarify how a specific surface modification, applied to industrial UD carbon fabrics, interacts with different experimental scales and failure modes. The analysis therefore has to move from the local observations on fiber surfaces to the broader laminate response, while keeping in mind that the transfer from one scale to another is neither linear nor guaranteed. In

this sense, the discussion below follows the chronological sequence already adopted in the thesis, namely surface characterisation, micro-scale testing, meso-scale testing, and finally macro-scale validation.

7.2 Surface Evidence and Interpretation

The surface analysis presented in Chapter 4 identified an optimal treatment window in which plasma activation, cleaning, and etching were simultaneously achieved without evident fiber damage. The selected condition, based on the combined interpretation of OES, Raman, SEM-EDS, and XPS, corresponded to the case that maximised nitrogen incorporation while preserving fiber integrity and limiting excessive roughening. In practical terms, the plasma removed part of the surface contamination and sizing-related layer, exposed the graphitic core more clearly, and introduced chemically active sites that are plausibly more favourable to epoxy interaction.

The surface results, however, should not be read as proof of a fully established adhesion mechanism. They provide strong evidence of a modified interphase precursor, but the actual mechanical role of these changes has to be inferred indirectly. As found by the XPS analysis in this work, the untreated surface was still dominated by a CO-rich signature related to residual sizing, whereas the plasma-treated surface displayed a reduction of that contribution and the appearance of nitrogen-related functionalities. At the same time, the Raman data indicated a controlled increase in structural disorder, and the SEM observations documented the formation of grooves and the removal of weak outer layers without catastrophic erosion. Taken together, these findings support the idea that the plasma treatment does not simply "coat" the fiber with polar groups, but rather reorganises the outer surface into a more reactive and mechanically textured state.

At the same time, the literature makes clear that surface activation alone is not sufficient to guarantee laminate-scale performance improvements. As found by Bonandini et al. [26], atmospheric-pressure plasma can improve wettability and hydrophilicity, but the magnitude of the effect remains dependent on the specific substrate and processing window. In a similar way, Fu et al. [21] reported the plasma-treated carbon fibers can improve interfacial adhesion without fiber damage, with the benefit linked to the presence of polar groups such as OH and COOH. The

present work fits within this broader framework: it confirms that a controlled N₂ APP Jet treatment can generate a favorable surface state, but it also shows that the resulting mechanical benefit is scale dependent.

7.3 Micro-Scale Response and its Limits

The Microbond results provide the first mechanical indication of the effect of the plasma treatment, but they also reveal the limitations of using a highly local test on industrial UD fibers. The main features of the aforementioned methodological test are summarized in the Table 7.1. As found by Zhao et al. [102] and Pandey et al. [106], the apparent IFSS in Microbond testing is highly sensitive to droplet geometry, embedded length, blade alignment, and local meniscus conditions. This is directly relevant here because the apparent interfacial shear strength ranged roughly between 13 and 27 MPa, with a very high standard deviation and substantial overlap between the untreated and plasma-treated populations. On a purely statistical basis, this prevents the Microbond data from being treated as a robust quantitative proof of interfacial strengthening.

At the same time, the present results also expose a limitations of some of the literature studies when interpreted in view of industrial UD fibers. For example, Thomason et al. [30] show that Microbond outcomes can be strongly influenced by sample preparation artefacts, especially curing completeness and mounting-adhesive effects, to the point that the measured IFSS may reflect preparation details as much as the true interface. This is highly relevant for the present work because it means that part of the scatter and part of the absolute IFSS level may derive from test artefacts rather than from the plasma treatment alone. Conversely, it is also found the limitation with respect to those studies because it does not isolate all possible preparation pieces with the same level of control, so the comparison must remain primarily qualitative.

Nevertheless, the Microbond campaign is not inconclusive. It provides an important qualitative indication that the failure mode changes after treatment. Untreated specimens tend to detach in a cleaner adhesive manner, whereas plasma-treated fibers more frequently retain resin remnants, hackles, or partial cohesive features. This transition is important because it suggests that the surface modification has altered the local failure path, even if the measured IFSS values do not separate cleanly

enough to support a strong numerical ranking. In other words, the test does not provide a stable absolute measure of adhesion, but it does reveal that the treated interface behaves differently from the untreated one.

This result is consistent with the discussion developed in Chapter 5, where the role of droplet geometry and the fragility index was analysed in detail. According to Savolainen et al. [104], Microbond values should be used for comparative purposes within the same setup, but not as basis for absolute scaling laws. The present interpretation is therefore that the Microbond test is useful as a diagnostic tool, but it is not sufficiently predictive for industrial UD systems unless droplet geometry and local surface variability are much more strictly controlled. The present thesis has a different limitation with respect the latter literature reference considering that the Microbond campaign here is based on the industrial UF fibers with a more pronounced intrinsic heterogeneity, which increases scatter and makes a strict quantitative ranking more difficult. Nevertheless, the additional desized series confirms that removing the sizing layers does not eliminate the scatter, indicating that the response is governed not only by the sizing contribution but also by the intrinsic variability of the reinforcement and the limitations of the test itself.

From a methodological point of view, this is an important outcome. It means that the micro-scale test can confirm whether the plasma treatment is damaging the fiber or shifting the failure behavior, but it should not be used alone to infer the magnitude of the laminate-scale benefit. The most defensible interpretation is therefore that the Microbond test provides local qualitative evidence of interfacial activation, while the large scatter prevents it from acting as a direct quantitative bridge to the DCB results.

7.4 Meso-Scale Response and Failure Saturation

The meso-scale TFBT results add a second layer of interpretation. Unlike the Microbond test, the bundle test interrogates a larger material volume and therefore has the potential to average out some of the local noise observed at the single-fiber level. In practice, however, the results show that this higher representative volume comes with another limitation: the failure often localises within the bundle itself rather than at a clean bundle-matrix interface. Li et al. [108] proved the divergence between fiber bundle tests and standard laminate tests. This divergence is related to the complexity and heterogeneity of stress state in the bundle-matrix region. The

present results are consistent with that observation, but they also indicated that, for industrial UD fabrics, this divergence is not only a matter of stress-state complexity; it also becomes a practical saturation limit, beyond which the test loses sensitivity to moderate interfacial changes.

It is worth clarifying that the limited discrimination observed at meso-scale may reflect either a methodological sensitivity ceiling or a genuine absence of scale transfer, and these two interpretations have different implications for the proposed framework. If the primary limitation is test sensitivity, the TFBT under the present specimen preparation and loading conditions may not resolve the magnitude of adhesion change induced by APP treatment; in this case, the meso-scale level remains conceptually valid as a screening step, but would require a more discriminating experimental configuration to fulfill its intended role. If, conversely, the interfacial improvement does not translate into a measurable meso-scale benefit under transverse tensile loading, this would indicate a more fundamental limitation in the bottom-up hierarchy, since the fibre-matrix interaction volume and stress state in the TFBT configuration may not be representative of the conditions under which the treatment is effective at laminate scale. The two interpretations are not mutually exclusive, and the present data do not allow a definitive separation, as already mentioned in Section 5.2.1.

For the 0.2 mm and 0.1 mm UD fabric batches, the measured peak stresses are clustered within a relatively narrow interval, with the thicker configuration showing values roughly around 20–23 MPa. In parallel, the fracture morphologies of the plasma-treated specimens appear consistent with a modified bundle-level failure response, characterized more by internal redistribution and impregnation-related differences than by a clear and isolated interfacial ranking. This is a useful indication, because it suggests that the treatment modifies the bundle-level failure response, moving it away from a purely local adhesive interpretation and toward a more distributed fracture process influenced by bundle cohesion and resin infiltration. In this respect, the present work adds an explicit limitations that is only partly addressed in the literature: unlike idealized bundle studies, the UD architecture makes the TFBT response sensitive to tow packing, impregnation heterogeneity and internal fiber redistribution, and specimen preparation route. As a result, the measured differences cannot be read as a direct hierarchy of interfacial adhesion alone, particularly when bundle thickness and resin penetration conditions vary between batches.

This behavior should not be interpreted as a weakness of the thesis; rather, it is an important methodological result. It shows that the meso-scale test becomes increasingly governed by bundle cohesion, impregnation state, and internal architecture, making the extraction of a clean interfacial ranking progressively more difficult. As noted by Hoecker and Karger-Kocsis [109], micro mechanical tests can characterize bond quality, yet their relevance to transverse tensile response in macro-composites is often masked by the matrix role and by defects. The present work confirms that this limitation is particularly relevant for industrial UD textiles.

The TFBT results therefore occupy an intermediate position in the multiscale logic of the thesis. They do not provide the same degree of local mechanistic detail as Microbond, and they do not yet reach the laminate-level relevance of DCB, but they indicate that the plasma treatment can modify the bundle-level load-transfer response in a meaningful, though not unambiguously rankable, way. The key point is that this change is visible mainly as a shift in failure mode rather than as a large and clean numerical improvement. That distinction is essential for a rigorous interpretation.

Table 7.1 Representative literature on plasma-assisted interphase engineering at micro- and meso-scale.

Reference, year	Material / architecture	Main work	Main test(s)	Key outcome and comparison
[104], 2025	CF / epoxy	Microbond data analysis	Microbond	IFSS extraction methods compared; methodological benchmark rather than a treatment study, useful to frame the scatter observed in this thesis.
[114], 2023	CF / polymers	Interface characterization review	Microbond, SFFT, push-out	Reduction models and test sensitivities critically compared; broad methodological reference.
[38], 2022	CF / epoxy	Fiber surface chemistry and sizing reactivity	Push-out, wettability	Sizing chemistry strongly affected IFSS; relevant for surface-reactivity discussion, but on a different test logic and specimen architecture.
[30], 2022	GF / vinylester	Microbond benchmark	Microbond analysis	Apparent IFSS increased with full sizing; strong benchmark for artefact sensitivity, but on GF/vinylester.
[51], 2022	PAN-based CF / epoxy	Rapid atmospheric plasma modification	IFSS-related surface-chemistry analysis	ILSS increased from 64.9 to 80.0 MPa; confirms plasma-assisted strengthening, but on a different plasma route and response scale.
[33], 2021	CF, GF / thermoplastics	Reinforcement comparison at matched diameter	Microbond	Matched-diameter comparison isolated material effects; useful as a material benchmark.
[70], 2016	CF / epoxy	Electrochemical oxidation	Microbond	IFSS increased from 25.1 to 35.8 MPa; similar adhesion gain, but via analogous surface treatment.
[107], 2014	CF / epoxy bundle	Fiber-bundle interfacial evaluation	TFBT / multiscale model	Bundle-scale interfacial response characterized; different architecture and modeling framework.
This thesis, 2026	UD carbon/epoxy	N₂ APP Jet on GFs and Carbon bundles	Microbond, TFBT, stats	Industrial UD case; scatter and meso discrimination limits identified, providing multiscale diagnostic value rather than direct macro prediction.

7.5 Macro-Scale Validation Under Quasi-Static Loading

The DCB results provide the clearest evidence that the N₂ APP Jet treatment is effective when the failure mechanism is controlled by interlaminar delamination. As summarized in Table 7.2, the macro-scale literature generally reports improved delamination resistance after plasma-assisted interphase engineering, but the reported gains are strongly dependent on reinforcement architecture, treatment configuration and loading regime. Compared with those studies, the present work is more specific in showing how this improvement develops in an industrial UD carbon/epoxy system, where the role of the treatment window can be assessed directly on the laminate response rather than only on a bonded-joint or idealized laminate configuration.

For the 0.1 mm fabric, the average propagation toughness increased by about 19.4%, while for the 0.2 mm fabric the increase reached about 36.1%, with statistically significant improvement in the propagation regime. The resistance curves also show a more stable crack-growth response for the plasma-treated laminates, whereas the untreated specimens tend to exhibit more irregular and unstable crack propagation.

This is the most convincing part of the thesis because the DCB test interrogates the same structural level at which delamination is a meaningful engineering problem. In contrast to Microbond and TFBT, the laminate-scale test integrates the cumulative effect of the modified interphase over a larger and more representative volume. According to the ASTM standard [40] and by the quasi-static delamination literature discussed in the thesis, the propagation regime is the most sensitive to interphase quality when the crack path is interface-dominated. The improvement should therefore be interpreted as a genuine laminate-scale benefit rather than as a simple artefact of local surface measurements.

The fracture behavior also supports the interpretation developed earlier. The plasma-treated specimens show signs of a more energy-consuming crack path, with greater resistance to steady crack propagation and a stronger tendency toward partial cohesive features on the fracture surfaces. This is consistent with the notion that the plasma treatment created an interphase that is more capable of sustaining load transfer and delaying crack advance. At the same time, the fact that the improvement is most evident in propagation rather than initiation suggests that the treatment is

more effective once the crack is already developing along the interface and the modified interphase can contribute to crack-tracking resistance.

The literature provides a useful frame for this outcome. Several examples are summarized in Table 7.2 and some of these studies agree that plasma-assisted interphase engineering often produces improvements in Mode I delamination resistance, but the magnitude of the effect is strongly dependent on the architecture of the reinforcement and on the balance between surface chemistry and fiber integrity. The present results fit this trend well: the chosen N₂ treatment window appears to have achieved a favorable compromise between activation and damage avoidance, allowing the interphase to become more effective without compromising the fiber reinforcement.

7.6 Impact Response and Regime Dependence

The impact tests complete the picture by showing that the plasma effect is not universal across loading regimes. Under dynamic impact, the treated and untreated laminates do not show a meaningful difference in mean crushing force or specific energy absorption. This result is not contradictory to the DCB data; rather, it indicates that the governing failure mechanisms are different. In impact, damage evolves through a combination of crushing, splaying, delamination, fiber fracture, and matrix fragmentation, so the contribution of the interphase is progressively diluted by bulk failure modes [96] [112] [113] [20]. Compared to these studies, the present work therefore adds an explicit limitation: even when the interphase is strengthened enough to improve quasi-static delamination resistance, that benefit does not necessarily translate into improved crash performance.

This regime dependence is a critical conclusion of the thesis. It means that the N₂ APP Jet treatment is effective when the mechanical response is dominated by interfacial or near-interfacial delamination, but much less influential when the structure responds through a more distributed and rate-sensitive damage process. The lack of improvement in impact should therefore not be interpreted as a failure of the plasma treatment, but as a boundary condition on its effectiveness. In practical terms, the treatment targets quasi-static delamination resistance more than crashworthiness [96] [112]. The comparison between DCB and impact is especially important because it prevents over-generalisation. A shallow reading of the results might

suggest that if the treatment improves one mechanical property it should improve all of them. The thesis shows instead that the interphase modification has a selective effect: it becomes visible when the fracture process is interface-controlled and much less so when the failure mechanism is dominated by distributed structural dissipation. This distinction is scientifically valuable because it defines the actual operational window of the treatment.

Table 7.2 Representative literature on plasma-assisted interphase engineering at macro-scale.

Reference, year	Material / architecture	Main work	Main test(s)	Key outcome and comparison
[9], 2024	Composites / review	Delamination mitigation review	Review of macro-scale damage strategies	Comprehensive overview of delamination mechanisms and mitigation routes; contextual reference rather than a direct comparison.
[67], 2024	CFRP laminates	Plasma jet arrays on laminates	DCB, Mode I	Peak load increased by 19.49% and G_{IC} by 29.94%; closest DCB analogue, but on a different architecture and plasma configuration.
[48], 2024	CF/epoxy CFRP	Carbon fiber surface oxidation	Tensile test on laminates	Macroscale tensile resistance improved after oxidation; similar laminate-level benefit, but not delamination-focused and not APP Jet-based.
[68], 2023	CF/PEKK bonded joints	Atmospheric plasma treatment on bonded joints	Mode I, Mode II fracture toughness	Fracture toughness improved in bonded joints; strong toughening analogue, though on bonded joints and a different matrix system.
[96], 2023	UD CFRP / epoxy	Multiscale crashworthiness study	Impact, SEA	Defined multiscale limits and reported strong crashworthiness trends; useful for regime dependence, while this thesis adds a direct DCB vs impact contrast.
[73], 2022	CF/epoxy	Surface oxidation optimization	Macroscale tensile testing	Mechanical performance increased up to about 26%; demonstrates interfacial benefit, but through oxidation and tensile loading rather than delamination.
[28], 2020	CFRP / adhesive	APP treatment on CFRP surfaces	Interlaminar bonding validation	Bonding response improved and depended on gas choice; relevant bonding analogue, but less direct than laminate delamination in UD laminates.
[61], 2019	CFRP / adhesive	APP process parameter study	DCB, bonding-related testing	Nozzle distance and exposure time controlled bond performance; process-window study, whereas this thesis extends the comparison to industrial UD laminates and impact.
[110], 2015	CFRP structures	Impact / cost trade-off	Impact, SEA	Specific energy absorption compared for design; useful impact benchmark, but not plasma-assisted interphase engineering.
This thesis, 2026	UD carbon/epoxy	N₂ APP Jet on CF UD fabrics	DCB, impact SAE	DCB G_{IC} increased by 36%, whereas impact/SEA showed no plasma distinction; defines an operational window rather than a universal strengthening effect.

7.7 Multiscale Correlations and Methodological Meaning

One of the main contributions of this thesis is not only the identification of a positive plasma effect on delamination resistance, but also the clarification of how the different test scales should be interpreted relative to one another. The data show that the surface analyses are necessary to demonstrate that the treatment has altered the fibers in a controlled way, but they are not sufficient to predict the final structural performance. The micro- and meso-scale tests are useful because they reveal how the interface begins to respond, but their quantitative power is limited by geometry, heterogeneity, and failure saturation. The DCB test remains the decisive scale for validating a structural benefit.

This means that the multiscale framework is best understood as a hierarchy of functions rather than as a simple chain of numerical prediction. Surface characterization answers the question of whether the treatment worked chemically and morphologically. Micro-scale testing asks whether the local interface response changed and whether the failure mode shifted. Meso-scale testing checks whether the bundle-level response is measurably altered by the surface state, while also revealing when the interpretation becomes dominated by bundle cohesion, impregnation pathways, and architectural constraints. Macro-scale testing finally establishes whether these changes are relevant for delamination resistance in a laminate. The value of the thesis lies precisely in showing that these four levels are complementary but not interchangeable.

Although the curing cycle was kept constant across the different specimen types, the three testing scales are not directly equivalent in terms of representativeness. The amount of resin used, the number of fibres included and the local geometrical constraints differ substantially between MB, TFBT and laminate-scale specimens. Therefore, the multiscale analysis should be interpreted as a comparison of scale-dependent responses, rather than as a direct quantitative mapping between absolute values. This limitation should be considered when interpreting the correlations, since part of the observed divergence may arise from representativeness effects rather than from interfacial chemistry alone.

The literature supports this methodological reading. As defined by Wen Li et al. [108], the gap between fiber-bundle tests and laminate performance is often caused

by internal stress concentrations and heterogeneous interphase states rather than by a simple lack of adhesion. This is particularly true for industrial UD reinforcements, where tow packing, residual sizing, impregnation pathways, and local geometry can all blur the relationship between a local adhesion signal and a structural response. The present work therefore adds an important practical conclusion: the most informative use of Microbond and TFBT is not as absolute predictors, but as diagnostic probes that help interpret the macro-scale results.

7.8 Concluding Interpretation

Overall, the thesis demonstrates that N₂ APP Jet treatment can produce a measurable and useful improvement in quasi-static delamination resistance for industrial UD carbon/epoxy laminates, provided that the process parameters are kept within a window that balances cleaning, etching, and activation without damaging the fiber. The improvement is real, but it is selective: it appears clearly in DCB, is suggested qualitatively at the micro- and meso-scale, and does not translate into dynamic impact enhancement under the tested conditions.

The work also clarifies the methodological role of each scale. Surface analysis identifies the modified chemistry and morphology; Microbond reveals local failure-mode changes but remains strongly affected by scatter; TFBT indicates that the treatment can alter the bundle-level failure response, but does not offer a robust ranking for moderate adhesion changes because the measured behaviour is strongly affected by bundle cohesion, impregnation conditions, and architectural heterogeneity; DCB provides the most reliable evidence of the actual structural benefit. This hierarchy is one of the central outcomes of the thesis because it defines both the strengths and the limitations of the multiscale approach.

From an industrial perspective, the results support the use of N₂ APP Jet as a dry and potentially scalable surface modification route for delamination-sensitive applications. From a scientific perspective, they also show that the path from surface chemistry to structural performance is mediated by architecture, failure mode, and loading regime. The thesis therefore contributes not only a positive treatment result, but also a more critical understanding of how multiscale evidence should be interpreted in industrial composite systems.

Chapter 8

Conclusions and Future Perspectives

8.1 Summary of Main Results, Original Contributions and Future Developments

This doctoral work has shown that a nitrogen-based Atmospheric Pressure Plasma Jet (N_2 APP Jet), applied to industrial unidirectional carbon/epoxy reinforcements within a suitable process window, can improve quasi-static Mode I delamination resistance without producing measurable damage to the fibers or to the laminate manufacturing route. Surface analyses indicated effective removal of sizing and peel-ply residues, together with an increase in surface reactivity and the introduction of nitrogen-containing functional groups, while preserving the overall graphitic structure of the reinforcement. These results support the view that the treatment modifies the fiber surface in a favorable way, but also show that the mechanical consequences of such modification are not identical across all testing scales.

At the micro-scale, the Microbond tests provided qualitative evidence of a change in failure mode, since plasma-treated fibers more often showed resin residues and mixed or cohesive-like fracture features. At the same time, the strong scatter associated with droplet geometry, meniscus shape, and local debonding conditions limited the quantitative value of the apparent interfacial shear strength as a predictor for industrial UD systems. The meso-scale transverse fiber bundle tensile tests suggested that the treated interface can affect bundle-level failure, but they also showed that the response is strongly influenced by bundle cohesion, impregnation conditions,

and heterogeneity, which reduces the sensitivity of the test to moderate adhesion changes. In this sense, micro- and meso-scale testing are therefore best interpreted as probes of bundle-level and local interfacial response, rather than as direct predictors of laminate-scale performance.

The laminate-scale results gave the clearest evidence of treatment effectiveness. In quasi-static DCB tests, the plasma-treated laminates showed a meaningful increase in propagation fracture toughness and a more stable crack-growth response than the untreated ones. By contrast, dynamic impact tests did not reveal a significant distinction between treated and untreated specimens, indicating that the benefit of the treatment is regime-dependent and most evident when delamination is the dominant failure mechanism. This distinction is important because it suggests that the plasma treatment is not a universally strengthening intervention, but a surface modification strategy whose effectiveness depends on the loading regime and on the governing failure mode. Even when applied on both sides of the fabric, the treatment may remain partially non-uniform within industrial UD textiles because filament packing and residual binder can shield the inner tow regions from full plasma exposure.

The main original contribution of this thesis lies in the combined use of a dry, solvent-free N₂ APP Jet treatment on industrial UD fabrics and in the critical multiscale interpretation of its effects. The work does not only show that the treatment can improve quasi-static delamination resistance, but also clarifies where micro- and meso-scale tests remain informative. A further contribution is methodological: the thesis provides a structured comparison between surface chemistry, local interphase response, bundle-scale behavior, and laminate-scale performance, showing that these levels are complementary but not interchangeable.

The main limitations identified in the micro- and meso-scale tests also define the most relevant future developments. In particular, the finite element modeling activity already underway on the Microbond configuration should be directed toward reproducing the non-ideal features actually observed in the experiments, rather than idealized droplet geometries only. Previous studies (Table 7.1) have shown that Microbond-type FEM models can be useful for separating the role of geometry from the apparent IFSS [102, 103, 106]. More recently, comparative Microbond data analysis has also confirmed that the extraction method itself can affect the estimated interfacial strength [104]. However, these approaches remain only partially transferable to the present campaign, because they do not directly resolve specimen-

specific irregularities such as droplet asymmetry, non-standard debonding paths and residual friction. A model calibrated on the present data could help separate true interfacial effects from geometric artefacts and improve the robustness of future micro-scale assessments.

The meso-scale tests would likewise benefit from alternative configurations that preserve sensitivity to interfacial changes while reducing the influence of bundle cohesion and impregnation heterogeneity, and specimen-preparation route. More generally, future studies should aim to reconcile the local mechanics captured by Microbond-type simulations with the numerical and experimental frameworks that address the same physical limitations. Beyond the mechanical characterization, further work may explore whether plasma activation and functionalization combined with tougher matrix formulation or modified interlayers can extend the benefit also to dynamic loading, together with a broader industrial and environmental assessment, including a well-designed life cycle assessment (LCA) to compare the treatment route with alternative solutions.

References

- [1] Sun C., Min J., Lin J., and Wan H. Effect of atmospheric pressure plasma treatment on adhesive bonding of carbon fiber reinforced polymer. *Polymers*, 11(1), 2019.
- [2] Easy Composites. Easy composites UK Ltd, 2026. Accessed: 05 March 2026.
- [3] Rajak D.K., Pagar D.D., Menezes P.L., and Linul E. Fiber-reinforced polymer composites: Manufacturing, properties, and applications. *Polymers*, 11(10), 2019.
- [4] Kelly J.C., Sullivan J.L., Burnham A., and Elgowainy A. Impacts of vehicle weight reduction via material substitution on life-cycle greenhouse gas emissions. *Environmental Science & Technology*, 49(20):12535–12542, 2015.
- [5] Sharma H., Kumar A., Rana S., Sahoo N.G, Jamil M., Kumar R., Sharma S., Li C., Kumar A., Eldin S.M., and Abbas M. Critical review on advancements on the fiber-reinforced composites: Role of fiber/matrix modification on the performance of the fibrous composites. *Journal of Materials Research and Technology*, 26:2975–3002, 2023.
- [6] Mahesh B., Tasneem Khan K.H., Kiran D., B. Vijay Krishna, Sreekanth S., H.K. Eftikhaar, H. Pal Thethi, and Nakul G. Review of composite materials and applications. *Materials Today: Proceedings*, 2023.
- [7] Choi J.Y., Jeon J.H., and Lyu J.H. Current applications and development of composite manufacturing processes for future mobility. *Int. J. of Precis. Eng. and Manuf.-Green Tech.*, 10:269–291, 2023.
- [8] Simões S. High-performance advanced composites in multifunctional material design: State of the art, challenges, and future directions. *Materials*, 17(23), 2024.
- [9] de Castro Saiki L.E. and Ferreira Gomes G. Understanding and mitigating delamination in composite materials: A comprehensive review. *Mechanics of Advanced Materials and Structures*, 31(30):13147–13167, 2024.
- [10] ASTM International. Standard Test Method for Compressive Residual Strength Properties of Damaged Polymer Matrix Composite Plates. Technical

- Report D7137/D7137M-17, ASTM International, West Conshohocken, PA, 2017.
- [11] Zobeiry N., Forghani A., Li C., Gordnian K., Thorpe R., Vaziri R., Fernlund G., and Poursartip A. Multiscale characterization and representation of composite materials during processing. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 374(2071):20150278, 07 2016.
- [12] Radjef R., Jarvis K.L., Fox B.L., and McArthur S.L. Comparing the properties of commercially treated and air plasma treated carbon fibers. *Surface and Coatings Technology*, 408:126751, 2021.
- [13] Asmatulu R., Erukala K.S., Shinde M., Alarifi I.M., and Rahimi Gorji M. Investigating the effects of surface treatments on adhesion properties of protective coatings on carbon fiber-reinforced composite laminates. *Surface and Coatings Technology*, 380:125006, 2019.
- [14] Marques A.C., Mocanu A., Tomić N.Z., Balos S., Stammen E., Lundevall A., Abrahami S.T., Günther R., de Kok J.M.M., and Teixeira de Freitas S. Review on adhesives and surface treatments for structural applications: Recent developments on sustainability and implementation for metal and composite substrates. *Materials*, 13(24), 2020.
- [15] Sampino S. Mechanical effects of the plasma surface treatment on carbon fabrics used in composite materials. Master's thesis, Politecnico di Torino, Turin, 2022.
- [16] Sampino S., Ciardiello R., D'Angelo D., Cagna L., and Paolino D.S. Effect of the atmospheric plasma treatment parameters on the surface and mechanical properties of carbon fabric. *Materials*, 17(11), 2024.
- [17] Wisnom M. R. The role of delamination in failure of fibre-reinforced composites. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 370(1965):1850–1870, 04 2012.
- [18] Talreja R. and Singh C. V. *Damage and Failure of Composite Materials*. Cambridge University Press: Cambridge, 2012.
- [19] Abrate S. *Impact on Composite Structures*. Cambridge University Press: Cambridge, 1998.
- [20] Sato Y., Miura K., Kashiwagi M., Suhara M., Nonaka Y., and Esaki K. Progressive failure analysis for impact damage and compressive strength of composite laminates. *European Journal of Emergency Medicine*, 4:16–00710–16–00710, 2017.
- [21] Fu Y.F., Xu K., Li J., Sun Z.Y., Zhang F.Q., and De Min Chen. The influence of plasma surface treatment of carbon fibers on the interfacial adhesion properties of UHMWPE composite. *Polymer-Plastics Technology and Engineering*, 51(3):273–276, 2012.

- [22] Soutis C. Fibre reinforced composites in aircraft construction. *Progress in Aerospace Sciences*, 41(2):143–151, 2005.
- [23] Dilsiz N. Plasma surface modification of carbon fibers: a review. *Journal of Adhesion Science and Technology*, 14(7):975–987, 2000.
- [24] Qiu J., Li J., Yuan Z., Zeng H., and Chen X. Surface modification of carbon fibres for interface improvement in textile composites. *Applied Composite Materials*, 25, 08 2018.
- [25] Peng X., Wu Y., and Wei Z. Research progress on the surface modification of carbon fiber. *RSC Advances*, 14:4043–4064, 01 2024.
- [26] Bonandini L., Barbero N., Costabello K., Pavan C., Parisi F., and Viscardi G. Roll-to-roll atmospheric plasma treatment: a green and efficient process to improve the hydrophilicity of a PET surface. *ChemSusChem*, 3 5:591–6, 2010.
- [27] Liu G., Chen C., Xia Y., Zhang T., Shang K., and Liu D. Numerical study on the effect of shielding gas on atmospheric pressure plasma jet interacting with target surface. *Physica Scripta*, 100, 2025.
- [28] Lin J., Sun C., Min J., Wan H., and Wang S. Effect of atmospheric pressure plasma treatment on surface physicochemical properties of carbon fiber reinforced polymer and its interfacial bonding strength with adhesive. *Composites Part B: Engineering*, 199:108237, 2020.
- [29] Kaybal H.B., Ulus H., Cacik F., Eskizeybek V., and Avci A. Multi-scale mechanical behavior of liquid Elium® based thermoplastic matrix composites reinforced with different fiber types: Insights from fiber–matrix adhesion interactions. *Fibers Polym*, 25:4935–4950, 2024.
- [30] Thomason J.L., Jenkins P.G., and Xypolias G. Microbond testing of the interface in glass fibre vinylester composites. *Composite Interfaces*, 29(6):695–709, 2022.
- [31] Toray - Innovation by Chemistry. Toray - carbon fiber composite materials, 2026. Accessed: 13 April 2026.
- [32] Kim S.G., Heo S.J., Kim S., Kim J., Kim S.O., Lee D., Lee S., Kim J., You N-H., Kim M., Kim H.C., Chae H.G., and Ku B-C. Ultrahigh strength and modulus of polyimide-carbon nanotube based carbon and graphitic fibers with superior electrical and thermal conductivities for advanced composite applications. *Composites Part B: Engineering*, 247:110342, 2022.
- [33] Chu P.F., Iwasawa S., Schell P.L., and Lin C-Y. Carbon fiber versus glass fiber reinforcements: A novel, true comparison in thermoplastics. *Polymer Composites*, 42(11):6173–6181, 2021.

- [34] Obukuro M., Takahashi Y., and Shimizu H. Effect of diameter of glass fibers on flexural properties of fiber-reinforced composites. *Dental Materials Journal*, 27(4):541–548, 2008.
- [35] Prashanth S., Subbaya K.M., Nithin K., and Sachhidananda S. Fiber reinforced composites - a review. *J Material Sci Eng*, 6(3), 2017.
- [36] Nunna S., Creighton C., Fox B.L., Naebe M., Maghe M., Tobin M.J., Bambery K., Vongsvivut J., and Hameed N. The effect of thermally induced chemical transformations on the structure and properties of carbon fibre precursors. *J. Mater. Chem. A*, 5:7372–7382, 2017.
- [37] Tang L-G. and Kardos J-L. A review of methods for improving the interfacial adhesion between carbon fiber and polymer matrix. *Polymer Composites*, 18:100–113, 1997.
- [38] Laukmanis E., Janowski M., Horn S., and Moosburger-Will J. Effect of the interplay between fiber surface chemistry and sizing reactivity on fiber matrix interaction in carbon fiber reinforced epoxy resin. *Composite Interfaces*, 29(12):1325–1355, 2022.
- [39] Kiss P., Glinz J., Stadlbauer W., Burgstaller C., and Archodoulaki V.M. The effect of thermally desized carbon fibre reinforcement on the flexural and impact properties of PA6, PPS and PEEK composite laminates: A comparative study. *Composites Part B: Engineering*, 215:108844, 2021.
- [40] ASTM International. Standard Test Method for Mode I Interlaminar Fracture Toughness of Unidirectional Polymer Matrix Composite. Technical Report D5528/D5538M-21, ASTM International, West Conshohocken, PA, 2021.
- [41] ASTM International. Standard test method for determination of the mode II interlaminar fracture toughness of unidirectional fiber-reinforced polymer matrix composites. Technical Report D7905/D7905M-19, ASTM International, West Conshohocken, PA, 2019.
- [42] Das T., Ghosh P., and Das N. Preparation, development, outcomes, and application versatility of carbon fiber-based polymer composites: a review. *Advanced Composites and Hybrid Materials*, 2, 06 2019.
- [43] Newcomb B.A. Processing, structure, and properties of carbon fibers. *Composites Part A: Applied Science and Manufacturing*, 91:262–282, 2016.
- [44] Pitto M., Fiedler H., Kim N.K., Verbeek C.J.R., Allen T.D., and Bickerton S. Carbon fibre surface modification by plasma for enhanced polymeric composite performance: A review. *Composites Part A: Applied Science and Manufacturing*, 180:108087, 2024.
- [45] Ansari M., S., Zafar S., and Pathak H. A comprehensive review of surface modification techniques for carbon fibers for enhanced performance of resulting composites. *Results in Surfaces and Interfaces*, 12:100141, 2023.

- [46] Kim K., Kim M., Kim G., and Kim D. The effect of chemical and thermal treatment for desizing on the properties and chemical functional groups of carbon fiber. *Materials*, 16(20), 2023.
- [47] Dilsiz N. and Wightman J.P. Effect of acid–base properties of unsized and sized carbon fibers on fiber/epoxy matrix adhesion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 164(2):325–336, 2000.
- [48] Roseno S., Ammarullah M.I., Rohman S., Kurniawati F., Wahyudi T., War-gadipura A.H.S., Masmui M., Budiyanto D., Effendi M.D., Wahyudin W., Kalembang E., Hernawan H., Subari S., Habibie S., Simanjuntak T.P.H., Santoso H., Ahmad A., and Juwono A.L. The effects of carbon fiber sur-face treatment by oxidation process for enhanced mechanical properties of carbon fiber/epoxy composites for biomedical application. *AIP Advances*, 14(1):015044, 2024.
- [49] Wu Z., Pittman C.U., and Gardner S.D. Nitric acid oxidation of carbon fibers and the effects of subsequent treatment in refluxing aqueous NaOH. *Carbon*, 33(5):597–605, 1995.
- [50] Harder S. *Near-infrared laser surface treatment of milled CFRP aircraft structures for bonded repair applications*. PhD thesis, TUH, 2020.
- [51] Xiao J., Zhang X., Zhao Z., Liu J., Chen Q., and Wang X. Rapid and continuous atmospheric plasma surface modification of PAN-based carbon fibers. *ACS Omega*, 7(13):10963–10969, 2022.
- [52] Kusano Y., Andersen T.L., and Michelsen P.K. Atmospheric pressure plasma surface modification of carbon fibres. *Journal of Physics: Conference Series*, 100(1):012002, mar 2008.
- [53] Wen L., Xu X., and Qin L. Effect of low-temperature plasma surface treat-ment on bonding properties of single-lap joint of thermosetting composites. *Polymers*, 15(7):1631, mar 2023.
- [54] Wang Z., Huang X., Xian G., and Li H. Effects of surface treatment of carbon fiber: Tensile property, surface characteristics, and bonding to epoxy. *Polymer Composites*, 37:2921–2932, 2016.
- [55] Botana-Galvín M., Blanco G., González-Rovira L., Rodríguez M.A., and Botana F.J. Adhesive behaviour of carbon fibre reinforced plastic panels man-ufactured using woven and unidirectional tape after ultraviolet laser surface treatment. *Journal of Composite Materials*, 52:853 – 865, 2018.
- [56] Hartwig A., Vitr G., Dieckhoff S., and Hennemann O-D. Surface treatment of an epoxy resin by CO₂ laser irradiation. *Die Angewandte Makromolekulare Chemie*, 238:177 – 189, 03 2003.
- [57] Kusano Y. Atmospheric pressure plasma processing for polymer adhesion: A review. *The Journal of Adhesion*, 90(9):755–777, 2014.

- [58] Fathi B., Esfandeh M., Khalifeh Soltani A., and Taghavian H. Effect of corona discharge treatment on dynamic mechanical properties of unsaturated polyester/carbon fiber pultruded composites. *Polymer-Plastics Technology and Engineering*, 53(2):162–166, 2014.
- [59] Kong L., Wang X., Zheng W., Tian S., Qi Y., Xue Y., and Wang B. Effects of plasma treatment on properties of carbon fiber and its reinforced resin composites. *Materials Research Express*, 7(6):065304, jun 2020.
- [60] Hsu A.R., Chien H.-H, Liao C.-Y., Lee C.-C., Tsai J.-H., Hsu C.-C., Cheng I.-C., and Chen J.-Z. Scan-mode atmospheric-pressure plasma jet processed reduced graphene oxides for quasi-solid-state gel-electrolyte supercapacitors. *Coatings*, 8(2), 2018.
- [61] Yoozbashizadeh M., Chartosias M., Victorino C., and Decker D. Investigation on the effect of process parameters in atmospheric pressure plasma treatment on carbon fiber reinforced polymer surfaces for bonding. *Materials and Manufacturing Processes*, 34(6):660–669, 2019.
- [62] Park J., Henins I., Herrmann G.S. H.W., Selwyn, and Hicks R.F. Discharge phenomena of an atmospheric pressure radio-frequency capacitive plasma source. *Journal of Applied Physics*, 89(1):20–28, 01 2001.
- [63] Ricard A., Zerrouki H., and Sarrette J. Determination of N and O-atoms, of $N_2(A)$ and $N_2(X, v > 13)$ metastable molecules and N_2^+ ion densities in the afterglows of Ar- N_2 microwave discharges. *Journal of Analytical Sciences, Methods and Instrumentation*, 5(4):59–65, 2015.
- [64] Barrie C., Kim I.K., Marques D., and Zaldivar R.J. Investigations on the effect of plasma treatment on the adhesive bonding behavior of ultra high modulus K13C2U/cyanate ester fiber composites. *Journal of Adhesion Science and Technology*, 35(12):1263–1283, 2021.
- [65] Chen Z., Dai X.J., Lamb P.R., du Plessis J., de Celis Leal D.R., Magniez K., Fox B.L., and Wang X. Coating and functionalization of carbon fibres using a three-step plasma treatment. *Plasma Processes and Polymers*, 10:1100–1109, 2013.
- [66] Gravis D., Moisan S., and Poncin-Epaillard F. Surface characterization of plasma-modified carbon fiber: Correlation between surface chemistry and morphology of the single strand. *Surfaces and Interfaces*, 21:100731, 2020.
- [67] Anyu Wang, Shuran Li, Shuo Zhang, Shihao Zhang, Zhen Liu, and Keping Yan. Enhancing CFRP laminates with plasma jet arrays: A study of inter-laminar mechanical properties. *Polymer Composites*, 45(11):10190–10203, 2024.
- [68] Yildirim C., Ulus H., Beylergil B., Al-Nadhari A., Topal S., and Yildiz M. Effect of atmospheric plasma treatment on Mode-I and Mode-II fracture

- toughness properties of adhesively bonded carbon fiber/PEKK composite joints. *Engineering Fracture Mechanics*, 289:109463, 2023.
- [69] Xypolias G. *The environmental resistance of glass fibre vinyl ester composites and their interface for use in structural applications*. PhD thesis, University of Strathclyde, Glasgow, Scotland (UK), 2022.
- [70] Dong-Kyu Kim, Kay-Hyeok An, Yun Hyuk Bang, Lee-Ku Kwac, Sang-Yub Oh, and Byung-Joo Kim. Effects of electrochemical oxidation of carbon fibers on interfacial shear strength using a micro-bond method. *Carbon letters*, 19:32–39, 2016.
- [71] Yi Zhao, Chuyang Zhang, Xin Shao, Youjiang Wang, and Yiping Qiu. Effect of atmospheric plasma treatment on carbon fiber/epoxy interfacial adhesion. *Journal of Adhesion Science and Technology*, 25(20):2897–2908, 2011.
- [72] Stojceveski F., Hendlmeier A., Randall J.D., Arnold C.L., Stanfield M.K., Eyckens D.J., Alexander R., and Henderson L.C. Effect of tow size and interface interaction on interfacial shear strength determined by Iosipescu (V-notch) testing in epoxy resin. *Materials*, 11(9), 2018.
- [73] Guimarães B.S.S., de Carvalho L.E., and Cairo C.A.A. Otimização da adesão interfacial do compósito fibra de carbono/epóxi utilizando tratamento superficial oxidativo. *Tecnol Metal Mater Min.*, 19, 2022.
- [74] Calvimontes A., Hasan M., and Dutschk V. Effects of topographic structure on wettability of woven fabrics. *Textile Research Journal - TEXT RES J*, 78, 08 2010.
- [75] M.A Kabachi, L. Stettler, S. Arreguin, and P. Ermanni. Concurrent characterization of through-thickness permeability and compaction of fiber reinforcements. *Composites Part A: Applied Science and Manufacturing*, 141:106203, 2021.
- [76] Grafil Inc. Grafil 34-700 carbon fiber: Technical data sheet. Technical Report CF_34-700, Grafil Inc., 5900 88th Street, Sacramento, CA 95828, USA, 2023. Technical datasheet, accessed 5 March 2026.
- [77] Neunkirchen S., Bender M., and Schledjewski R. Effect of binder activation on in-plane capillary flow in multilayer stacks of carbon fiber fabrics. *Applied Composite Materials*, 31:709–719, 2024.
- [78] Yoo H.M., Lee J.W., Kim J.S., and Um M.K. Influence of non-reactive epoxy binder on the permeability and friction coefficient of twill-woven carbon fabric in the liquid composite molding process. *Applied Sciences*, 10(20), 2020.
- [79] Portela R.M., Schäfer B., Kärger L., Rocha de Faria A., and Montesano J. Effect of loading rate, viscosity, and binder activation on the bending response of an infiltrated UD-NCF. *Composites Part A: Applied Science and Manufacturing*, 200:109347, 2026.

- [80] Ramon E., Sguazzo C., and Moreira P.M.G.P. A review of recent research on bio-based epoxy systems for engineering applications and potentialities in the aviation sector. *Aerospace*, 5(4), 2018.
- [81] Quirino R.L., Garrison T.F., and Kessler M.R. Matrices from vegetable oils, cashew nut shell liquid, and other relevant systems for biocomposite applications. *Green Chem.*, 16:1700–1715, 2014.
- [82] Boursier Niutta C., Ciardiello R., Tridello A., and Paolino D.S. Epoxy and bio-based epoxy carbon fiber twill composites: Comparison of the quasi-static properties. *Materials*, 16(4), 2023.
- [83] Ge M., Liang G., and Gu A. Structural design strategy of biobased propargyl ether-functionalized epoxy monomer to access low viscosity resin with excellent heat resistance and mechanical properties for advanced composite via vartm. *Chemical Engineering Journal*, 475:146269, 2023.
- [84] Jokinen V., Suvanto P., and Franssila S. Oxygen and nitrogen plasma hydrophilization and hydrophobic recovery of polymers. *Biomicrofluidics*, 6(1):016501, 01 2012.
- [85] Mendez-Linan J.I., Ortiz-Ortega E., Jimenez-Moreno M.F., Mendivil-Palma M.I., Martínez-Guerra E., Aguirre-Tostado F.S., Martinez-Chapa S.O., Hosseini S., and Madou M.J. Aging effect of plasma-treated carbon surfaces: An overlooked phenomenon. *Carbon*, 169:32–44, 2020.
- [86] Plasmatreat. Openair-plasma(r) jets, 2023. Accessed: 20 March 2026.
- [87] Castro A.H.R., Kostov K.G., and Prysiashnyi V. Influence of nozzle shape on the performance of low-power Ar plasma jet. *IEEE Transactions on Plasma Science*, 43:3228–3233, 2015.
- [88] Plasmatreat. Openair-plasma(r) plasma systems, 2023. Accessed: 20 March 2026.
- [89] TESCAN. Mira3 field emission scanning electron microscope, 2023. Accessed: 16 March 2026.
- [90] Andrea Orlando, Filippo Franceschini, Cristian Muscas, Solomiya Pidkova, Mattia Bartoli, Massimo Rovere, and Alberto Tagliaferro. A comprehensive review on raman spectroscopy applications. *Chemosensors*, 9(9), 2021.
- [91] Li Z., Deng L., Kinloch I.A., and Young R.J. Raman spectroscopy of carbon materials and their composites: Graphene, nanotubes and fibres. *Progress in Materials Science*, 135:101089, 2023.
- [92] Qayyum A., Zeb S., Naveed M.A., Ghauri S.A., Zakaullah M., and Waheed A. Diagnostics of nitrogen plasma by trace rare-gas–optical emission spectroscopy. *Journal of Applied Physics*, 98(10):103303, 11 2005.

- [93] ASTM International. Standard Test Method for In-Plane Shear Response of Polymer Matrix Composite Materials by Tensile Test of a $\pm 45^\circ$ Laminate. Technical Report D3518/D3518M18, ASTM International, West Conshohocken, PA, 2025.
- [94] Norolem S.R.L. Norolem S.R.L. IT, 2026. Accessed: 09 March 2026.
- [95] ASTM International. Standard Test Method for Tensile Properties of Plastics. Technical Report D638-22, ASTM International, West Conshohocken, PA, 2022.
- [96] Vigna L. *Development of an innovative procedure to assess the crashworthiness of composite materials*. PhD thesis, Politecnico di Torino, Turin, 2023.
- [97] Bernard Miller, Pierre Muri, and Ludwig Rebenfeld. A microbond method for determination of the shear strength of a fiber/resin interface. *Composites Science and Technology*, 28(1):17–32, 1987.
- [98] B. Das, S.K. Sahu, and B.C. Ray. Effects of loading speed on the failure behaviour of FRP composites. *Aircraft Engineering and Aerospace Technology*, 79(1):45–52, 01 2007.
- [99] Tiwari S., Sharma M., Panier S., Mutel B., Mitschang P., and Bijwe J. Influence of cold remote nitrogen oxygen plasma treatment on carbon fabric and its composites with specialty polymers. *JOURNAL OF MATERIALS SCIENCE*, 46(4):964–974, FEB 2011.
- [100] Saloum S., Naddaf M., and Alkhaled B. Diagnostics of N₂–Ar plasma mixture excited in a 13.56 MHz hollow cathode discharge system: application to remote plasma treatment of polyamide surface. *Journal of Physics D: Applied Physics*, 41(4):045205, feb 2008.
- [101] E. Abdel-Fattah, D. Ogawa, and K. Nakamura. Nitrogen functionalization of MWCNTs in Ar-N₂ dielectric barrier discharge – gas ratio effect. *Materials Science and Engineering: B*, 261:114680, 2020.
- [102] Zhao Q., Qian C.C., Harper L.T., and Warrior N. Finite element study of the microdroplet test for interfacial shear strength: Effects of geometric parameters for a carbon fibre/epoxy system. *Journal of Composite Materials*, 52:2163 – 2177, 2018.
- [103] Li Q., Nian G., Tao W., and Qu S. Size effect on microbond testing interfacial shear strength of fiber-reinforced composites. *Journal of Applied Mechanics*, 2019.
- [104] Savolainen J.A. and Sarlin E.L. Microbond data analysis: comparative assessment of different approaches to determine IFSS. *IOP Conference Series: Materials Science and Engineering*, 1338:012021, 10 2025.

- [105] Pitkethly M.J., Favre J.P., Gaur U., Jakubowski J., Mudrich S.F., Caldwell D.L., Drzal L.T., Nardin M., Wagner H.D., Di Landro L., Hampe A., Armistead J.P., Desaegeer M., and Verpoest I. A round-robin programme on interfacial test methods. *Composites Science and Technology*, 48(1):205–214, 1993. Special Issue Microphenomena in Advanced Composites.
- [106] Pandey G., Kareliya C.H., and Singh R.P. A study of the effect of experimental test parameters on data scatter in microbond testing. *Journal of Composite Materials*, 46:275 – 284, 2012.
- [107] Qi G., Du S., Zhang B., Tang Z., and Yu Y. Evaluation of carbon fiber/epoxy interfacial strength in transverse fiber bundle composite: Experiment and multiscale failure modeling. *Composites Science and Technology*, 105:1–8, 2014.
- [108] Li W., Chen W., . Tang L, Jiang Z., and Huang P. A general strength model for fiber bundle composites under transverse tension or interlaminar shear. *Composites Part A: Applied Science and Manufacturing*, 121:45–55, 2019.
- [109] Hoecker F. and Karger-Kocsis J. Effects of the interface on the mechanical response of CF/EP microcomposites and macrocomposites. *Composites*, 25(7):729–738, 1994. Third International Conference on Interfacial Phenomena in Composite Materials.
- [110] Meredith J., Bilson E., Powe R., Collings E., and Kirwan K. A performance versus cost analysis of prepreg carbon fibre epoxy energy absorption structures. *Composite Structures*, 124:206–213, 2015.
- [111] Troiani E., Donati L., Molinari G., and Di Sante R. Influence of plying strategies and trigger type on crashworthiness properties of carbon fiber laminates cured through autoclave processing. *Strojniški vestnik - Journal of Mechanical Engineering*, 60(6), 2014.
- [112] D. Hull. A unified approach to progressive crushing of fibre-reinforced composite tubes. *Composites Science and Technology*, 40(4):377–421, 1991.
- [113] Damien Guillon, Samuel Rivallant, Jean-Jacques Barrau, Caroline Petiot, Pascal Thévenet, and Benoît Malherbe. Experimental and numerical study of the splaying mode crush of cfrp laminates. *ICCM International Conferences on Composite Materials*, 01 2009.
- [114] AhmadvashAghbash S., Verpoest I., Swolfs Y., and Mehdikhani M. Methods and models for fibre–matrix interface characterisation in fibre-reinforced polymers: a review. *International Materials Reviews*, 68(8):1245–1319, 2023.