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Evaluation of grit-blasting as a pre-treatment for carbon-fibre thermoplastic composite to aluminium bonded joints tested at static and dynamic loading rates

Karthik Ramaswamy, Ronan M O’Higgins*, Ajay Kumar Kadiyala, Michael A McCarthy, Conor T McCarthy
CONFIRM centre and Bernal Institute, University of Limerick
*Corresponding Author: ronan.ohiggins@ul.ie

ABSTRACT

Light-weighting of transportation structures necessitates multi-material design employing composites and aluminium, with thermoplastic composites being of increasing interest to the industry. Adhesive bonding is a viable solution for joining dissimilar materials, but joint performance can be considerably affected by surface preparation. In this paper, alumina grit-blasting is investigated as a surface preparation technique for thermoplastic-matrix composites to be bonded to aluminium alloys. Grit-blasting is performed on composite adherends for varying durations, and the resulting chemical and morphological modifications are analysed using goniometry, profilometry, scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. Adhesively-bonded single-lap joints are tested at quasi-static and dynamic (0.5 m/s) loading rates, and fractography analysis is performed at macro and micro scales. It is found that high lap shear strength and work-to-failure can be achieved through optimisation of the grit-blasting parameters. The optimised process produces a composite surface with plasticised matrix, minimal fibre exposure, and favourable surface chemistry for adhesive bonding. Grit-blasting can thus be a simple, yet effective surface preparation technique for composites to be bonded to aluminium.

Keywords: E. Joints/joining, B. Adhesion, E. Surface treatment, metal to thermoplastic composite bonding.

1. INTRODUCTION

In the transportation industry, there is an increasing demand for lightweight, energy-absorbing structures due to requirements on fuel efficiency, emissions and crashworthiness. Carbon fibre reinforced polymer (CFRP) composites offer excellent specific mechanical properties, making them ideal for such applications. While more than 75% of CFRPs are manufactured using a thermoset matrix [1], the automotive and aerospace industries are increasingly showing interest in thermoplastic composites due to their short processing cycles, high fracture toughness, unlimited shelf-life, good solvent resistance, and inherent recyclability [2–4]. Fully composite structures are considered too costly and slow-to-produce for general automotive applications, but multi-material designs offer a viable option. This, however, poses a challenge for joining technologies. Conventional mechanical fastening, like bolting or riveting, is widely used to join dissimilar materials, but introduces stress concentrations, potential for galvanic corrosion, and a significant weight penalty. Adhesive joining offers a lower-weight solution with a more uniform stress distribution, better corrosion resistance, and superior acoustic and vibration insulation. However, obtaining a reliable bond requires surface pre-treatment of the adherends.

Surface pre-treatment of thermoset CFRPs for adhesive bonding is a highly active research area with several recent studies on mechanical and chemical surface treatment techniques such as sanding [5], grit-blasting [6], chemical etching [7], laser [8–12], plasma [13,14], flame [15] and peel-ply based treatments [6,16,17], as well as novel techniques such as the soft-layer method [18,19] and laser-based surface patterning [20,21]. Use of nanocomposite adhesives produced by adding nanostructures like graphene, carbon nanotube, SiO₂, fullerene,
organoclay to the adhesive polymer is reported to improve the mechanical properties of the bulk adhesive and the joint [22–27]. References [25–27] evaluate the effect of doping different nanostructures in rigid and toughened adhesives and reports that the type of nanostructure and its quantity, adhesive type, and adherend material significantly influence the joint performance and this technique significantly reduces the loss in joint strength due to thermal cycling. Overall, the literature [7–10,14,15,21] indicates that, while more advanced methods have their advantages, sanding followed by solvent cleaning offers a simple yet effective surface treatment for CFRP/epoxy composites.

In comparison, there have been relatively few studies on surface pre-treatment methods for thermoplastic matrix composites. Kodokian et al. [28] performed Mode I fracture toughness tests on a range of thermoplastic composites bonded with epoxy adhesive and found weak adhesion when employing abrasion/solvent wipe treatment, but obtained better results with corona discharge treatment. Wade et al. [29] studied the effect of Ar, O₂, N₂ and NH₃ plasmas on glass-fibre/Nylon-66 substrates for adhesive bonding using particle-reinforced epoxy adhesive and concluded that O₂ plasma was the most effective. Iqbal et al. [30] performed atmospheric plasma treatment on CF/PEEK, CF/PPS and GF/PPS, which led to the introduction of polar functional groups (FG) and increased roughness. This changed the failure mode from interfacial to cohesive (adherend) failure, resulting in a 3–4 times improvement in lap shear strength. Recently, Genna et al. [31] optimised Q-switched Yb:YAG laser parameters and scanning direction to improve the adhesion of satin-weave GF/PPS composites.

To date, there has been a lack of detailed studies on grit-blasting as a surface preparation technique for bonding thermoplastic matrix composites. In addition, there have been very few studies on the effects of surface treatment on composites to be bonded to metal [19,32], and the influence of strain rate on joint performance following surface treatment. In the present work, an investigation is performed on the effectiveness of aluminium oxide grit-blasting as a surface pre-treatment for a polyamide matrix composite, prior to bonding to an aluminium alloy. Morphology and chemistry of the treated surfaces are examined, and the composite and aluminium adherends are bonded in a single-lap joint (SLJ) configuration, using a crash-durable epoxy adhesive. Joints are tested at quasi-static and dynamic loading rates and post-failure analysis is performed at macro and micro scales. Relationships between the degree of surface treatment, morphological and chemical modifications, lap shear strength, energy absorption, and failure mechanisms are assessed.

2. MATERIALS AND METHODS

2.1 Materials

The selected composite material is a 2/2 twill weave fabric prepreg, in which the fibres, consisting of carbon fibre cores, co-wrapped with Polyamide12 (PA12), are stretch-broken for high drapability (Schappe Techniques, France). This material was chosen, as the present work is part of a larger study on through-thickness-reinforced hybrid metal-composite joints, for which high drapability is an essential requirement [33]. The CF/PA12 fabric has an aerial weight of 375 g/m² and nominal consolidated ply thickness of 0.27 mm. The chosen metal is an Al-Mg alloy, AA5754-H111 (Aalco Metals Ltd), which is used in the automotive industry as a recycled material, and offers excellent formability and corrosion resistance, with high specific strength and toughness. A one-component structural epoxy adhesive, Betamate 1496V (Dow Automotive, USA), used in the automotive industry to bond body panels, is employed here due to its crash durability and high stiffness. The basic
mechanical properties of the composite material and aluminium alloy as provided by their respective manufacturer are summarised in Table 1

Table 1: Basic mechanical properties of adherend materials

|                  | AA5754-H111 | CF/PA12 |
|------------------|-------------|---------|
| Tensile modulus  | 68          | 688     |
| (GPa)            |             | Shear strength (MPa) 113 |
| Tensile yield strength (MPa) | 115          | Tensile modulus – Warp (GPa) 56 |
| Ultimate tensile strength (MPa) | 299.6        | Shear modulus (GPa) 5.5 |
| Strength co-efficient (MPa) | 469.4        | Tensile strength - Weft (MPa) 365.7 |
| Strain hardening exponent | 0.3          | Flexural strength (MPa) 636 |

2.2 Adherend Manufacture

Composite panels, containing 8 plies, with dimensions 600 mm × 600 mm × 2.16 mm, were consolidated in an autoclave at 240°C and 600 kPa for 40 minutes [34]. The SLJ configuration is illustrated in Figure 1(a).

Composite adherends, 25 mm wide and 132.5 mm long, were cut from the panels, and similar-sized metallic adherends were cut from 2 mm thick aluminium plates. A water-lubricated precision sawing operation was employed for composite adherend manufacturing to ensure defect-free cutting edges, as recommended by ASTM D 3039 [29]. Moreover, edge charring was not observed under magnification, as recommended by ASTM D 5687 [30]. The overlap length is 25 mm in accordance with ASTM D 5868 [35], and a grip-to-grip length of 150 mm was chosen to account for the slack mechanism in the dynamic testing machine that controls the actuator acceleration [33]. To minimise the secondary bending that occurs within single-lap joints due to the eccentricity of the applied tensile loads, 2 mm aluminium spacers are added, as shown in Figure 1(a). In addition, to enhance gripping and minimise specimen damage, particularly during the high-speed tests, 0.25 mm aluminium tabs are added. These are kept as thin as possible to minimise secondary bending.

2.3 Surface pre-treatment and characterisation

The flowchart in Figure 2, summarises the course of treated and untreated aluminium and composite adherends through different characterisation techniques. A total of 49 metal adherends and 52 composite adherends were manufactured. In Figure 2, the “standard” process followed for the adherends involved in the 39
SLJs is illustrated by the grey shaded boxes. For these adherends, the metallic adherends were degreased with acetone and ultrasonically etched in a 0.5 M sodium hydroxide (NaOH) solution for 30 minutes. The specimens were then ultrasonically rinsed twice in de-ionised water (DIW) for five minutes and dried in an oven at 80°C for 16 hours, before bonding. In [36], a similar treatment on aluminium alloy AA6061 resulted in a successful bond with cohesive failure which was attributed to the removal of the native oxide layer and formation of a stable oxide layer, together with an increase in surface roughness. Therefore, this simple, safe, and reproducible surface treatment was chosen here, among several mechanical, chemical and electro-chemical surface treatment methods that have been reported for aluminium substrates [37]. The composite adherends were grit-blasted in a heavy-duty blast cabinet (Clarke power products, UK) using ultra-pure (99.81%) aluminium oxide (Al₂O₃) blast media having an angular grain shape, a mean particle size of 220 µm (# 70 mesh) and measuring nine on a Mohs hardness scale (Guyson International Limited, UK). Grit-blasting was performed at an air pressure of 1.72 bar, through a 4 mm diameter spray nozzle. The nozzle was held perpendicular to the surface at a distance of approximately 300 mm and moved back and forth along the loading direction. Treatment times of 10, 20 and 40 seconds were used, and the corresponding specimens are labelled T10, T20, and T40 respectively. Grit-blasted specimens were cleaned with acetone, and ultrasonically rinsed in a DIW bath for five minutes to remove alumina particles deposited during grit-blasting.

Table 2 summarises the number of adherends that were subjected to different surface characterisation techniques. Thirteen composite adherends were not bonded. Five, which were not grit-blasted (denoted T0), were used for baseline measurements of contact angle and roughness, and two each were either not grit-blasted or grit-blasted for 10, 20 or 40 seconds and used for EDX/SEM and XPS analyses. Ten metallic adherends were not bonded in SLJs. As shown in Figure 2, five followed the standard pre-treatment above, with the other five undergoing acetone degreasing only, to examine the effect of etching on contact angle and surface roughness. Finally, 39 surface-treated aluminium and grit-blasted composite adherends were bonded as single-lap joints for testing.

Figure 2. Flowchart summarising sequence of treatments and surface characterisation techniques. Shaded boxes indicate “standard” process for adherends which were bonded in SLJs. Unshaded boxes indicate processes applied to adherends used for surface characterisation only, i.e. not bonded in SLJs.
Table 2: Number of adherends subjected to different characterisation techniques

| Material | Surface treatment          | Contact angle and surface roughness | EDX/SEM* | XPS* | Number of adherends bonded as SLJ | Total number of specimens |
|----------|----------------------------|-------------------------------------|----------|------|----------------------------------|--------------------------|
|          | Non-grit blasted (T0)      | 5                                   | 1        | 1    | 0                                | 7                        |
| Composite| Grit blasted (T10)          | 13                                  | 1        | 1    | 13                               | 15                       |
|          | Grit blasted (T20)          | 13                                  | 1        | 1    | 13                               | 15                       |
|          | Grit blasted (T40)          | 13                                  | 1        | 1    | 13                               | 15                       |
| Metal    | Surface treated            | 5*                                  | 0        | 0    | 39                               | 44                       |
|          | “Only” Acetone degreased   | 5*                                  | 0        | 0    | 0                                | 5                        |

* Not bonded as single-lap joints

2.3.1 Contact angle and surface energy

Contact angle measurements were performed using the sessile drop method with a contact angle and surface tension meter (KSV Limited) at ambient pressure and temperature. The analysis was performed on a series of images (at least 20) after the drop stabilised using CAM200 software provided by the equipment manufacturer. Two liquids, de-ionised water (DIW) and ethylene glycol (EG), were selected for surface energy computation, using the Owens, Wendt, Rabel and Kaelble (OWRK) method [38]. The polar and dispersive surface tension components are 51 mJ/m² and 21.8 mJ/m² respectively for DIW, and 19 mJ/m² and 29 mJ/m² for EG. At least five contact angle measurements were made on the overlap area of each adherend.

2.3.2 Surface roughness

Surface roughness was measured using contact profilometry (Hommel Tester T500, Hommel Werke, Germany) with a standard tracing length of 4.8 mm and a cut-off wavelength of 0.8 mm. Three measurements parallel to the loading direction and two measurements perpendicular to the loading direction were performed. The arithmetic average roughness (Ra) was extracted from the obtained profiles.

2.3.3 Scanning electron microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX)

Surface topography of 10 mm × 25 mm specimens extracted from the composite adherends was studied using a Hitachi SU-70 high-resolution scanning electron microscope (SEM), and elemental constituents were analysed using an EDX attachment (Oxford Instruments) on the SEM. Prior to SEM/EDX, specimens were acetone-wiped and ultrasonically cleaned in DIW, and then dried in the oven at 80°C for 16 hours. Fractography of selected failed SLJ specimens was also performed on a JEOL Carry Scope JCM-5700.

2.3.4 X-ray photoelectron spectroscopy (XPS)

Surface chemistry of treated and untreated composite specimens was analysed using a Kratos Ultra XPS instrument. Specimens were prepared in the same way as for SEM/EDX and stored in a desiccator before XPS measurements. Results were analysed using CasaXPS software.

2.4 Joint specimen preparation

Surface-prepared adherends were bonded in a mould to minimise joint misalignment [39]. Bondline thickness was controlled by adding 250-micron glass microbeads. Bonding was carried out in an oven at 180°C for 60 minutes, which allows 30 minutes for the mould to heat up and 30 minutes at the curing temperature.
recommended for the BM1496V adhesive. As illustrated in Figure 1(a), the adhesive spew was allowed to take an unconstrained “oval” shape at the free end of the aluminium adherend, while a flat adhesive spew was enforced by the use of a shim at the free end of the composite. Such adhesive spew shapes yielded good repeatability in joint performance in a separate unpublished study.

2.5 Mechanical testing

Table 3 presents the SLJ test matrix. Quasi-static tests were conducted at 1 mm/min, on a Tinius-Olsen universal tensile test machine with a 25 kN load-cell. Dynamic tests were performed at 0.5 m/s on a Zwick HTM5020 high-speed servo-hydraulic machine, using a 50 kN piezo-electric load washer (Kistler9051a) to record load at a sampling frequency of 0.95 MHz, for 60 ms, with no in-built filter employed.

Table 3: Test matrix for SLJ tests

| Test Label | Loading Velocity | Grit-blasting time (s) |
|------------|------------------|------------------------|
| QS_T10     | Quasi-static     | 10                     |
| QS_T20     | (1 mm/min)       | 20                     |
| QS_T40     | Dynamic          | 40                     |
| DY_T10     | Dynamic          | 10                     |
| DY_T20     | (0.5 m/s)        | 20                     |
| DY_T40     |                  | 40                     |

As shown in Figure 1(b), one side of the joint was speckled for full-field strain measurement using two-dimensional digital image correlation (2D-DIC) with LAVision Strain Master software. Joint deformation was obtained from the relative displacement of identifiable black dots placed at known points on either side of the overlap (see Figure 1(b)). For dynamic tests, a Photron SA1.1 high-speed camera recorded the test at 100,000 frames per second (fps), with a resolution of 512 × 92 pixels. For quasi-static tests, a LAVision camera at 14 fps was employed. At least five repeats of each test were performed.

3. RESULTS AND DISCUSSION

3.1 Contact angle, surface energy and surface roughness

Figure 3(a) presents contact angle measurements using DIW and EG for non-grit-blasted (T0) and grit-blasted (T10, T20 and T40) composite adherends, with error bars representing one standard deviation. The DIW contact angle increases from 98° for T0 specimens, to 145° for T20 specimens, corresponding to near-superhydrophobicity. T40 specimens show a minor reduction in DIW contact angle. The EG contact angle shows a slight increase from T0 to T10 and then decreases with further increase in grit-blasting time (T10 to T40). Figure 3(a) also presents the polar component of surface energy as a percentage of total surface energy, calculated from the average DIW and EG contact angles using the OWRK method [38]. Contaminants from the silicon-based mould release used during composite manufacturing resulted in a misleading ratio for non-grit-blasted adherends, so the T0 value is not shown. The ratio increases from T10 to T20 and remains at a similar value for T40. The reason for not presenting the total surface energy is discussed in the following paragraphs.

Figure 3(b) presents the roughness, $R_a$. The measurements taken perpendicular and parallel to the length of the composite adherend were not significantly different owing to the large diameter of the grit-blasting gun.
nozzle. As expected, the roughness increases with increasing grit-blasting time. The standard deviation also increases from T10 to T40, which is to be expected since the gun was hand-held during the grit-blasting process. Higher roughness can assist adhesion by increasing the total contact area between the adhesive and the adherend, provided the adhesive penetrates the surface irregularities.

Figure 3. (a) Contact angle and polar component of surface energy as a percentage of total surface energy, (b) surface roughness, R_s, of composite samples with different surface treatments

The influence of surface roughness should be considered when interpreting contact angle and surface energy measurements [40–42]. The Wenzel [41] and Cassie-Baxter [42] models propose methods to correct measured contact angles for roughness, resulting in “apparent” contact angles. There is no clear boundary between when these models should be applied, but the apparent DIW contact angle is expected to follow Wenzel behaviour on surfaces with mild roughness, and Cassie-Baxter behaviour on highly rough surfaces [43]. Moreover, the chemical composition also affects the contact angle measurement [44]. The hydrophobicity of the T0 specimens (95.8°) is believed to be due to the chemical composition of the surface, which contains the residue from the release agent. But, the sharp increase in DIW contact angle for T10 specimens (129°) and further increase for T20 and T40 specimens (145.5° and 141.6°) is due to the increase in surface roughness. The large size of the increase suggests that the surfaces are displaying behaviour consistent with the Cassie-Baxter model. However, liquids in the Cassie-Baxter state generally exhibit low slide angles, i.e. the water droplet is expected to roll off the surface if it is slightly tilted, an effect known as the lotus effect [45]. Here though, the water droplet remained stuck to the surface-treated composite, even when the surface was tilted, indicating extremely high water-droplet-adhesion. Such a combination of super-hydrophobicity and high water-droplet-adhesion is due to the so-called “rose petal effect” [46] which results from a hierarchical surface structure for which the liquid penetrates larger-scale features, but not smaller-scale features. Saleema et.al [47] also reported such behaviour for Zinc oxide nanotowers and referred to it as a “sticky Cassie state”. This type of penetration is expected to enhance adhesion through micro-mechanical interlocking.

Surface energy is calculated from the DIW and EG apparent contact angles, i.e. angles corrected for roughness. The Cassie-Baxter model needs the fraction of solid and air contacting the liquid to calculate the apparent contact angles, parameters which are not readily available from profilometry measurements and are difficult to determine experimentally. Kubiak et. al. [48] recommends a simplified methodology which employs parameters available from profilometry, but this only applies to behaviours described by Wenzel and Cassie-
Baxter models and is not suitable for the special “sticky Cassie state” [41] observed herein. Thus instead of presenting the total surface energy and its components in Figure 3(a), the polar component as a percentage of total surface energy is presented, since this is indicative of the relative improvement in the adhesion properties of the surface. Taken together, the contact angle, surface energy and roughness measurements suggest that the T20 and T40 specimens should exhibit better adhesion than the T10 specimens.

Table 4 summarises the contact angle and $R_a$ measurements for the aluminium adherends that were acetone-degreased only and those that were degreased and etched in NaOH. Etching results in an increase in DIW contact angle, a decrease in EG contact angle and an increase in $R_a$. Reference [36] which employed a similar surface treatment on AA6061 alloy, also reported an increase in DIW contact angle and similar magnitude of $R_a$, and found the resulting surface to be favourable for adhesion.

### Table 4: Contact angle and surface roughness for aluminium adherends

| Surface Treatment | DIW contact angle (°) | EG contact angle (°) | Roughness $R_a$ (µm) |
|------------------|-----------------------|---------------------|---------------------|
| Degreased only   | 66.36 ± 4.87          | 76.13 ± 6.34        | 0.25                |
| NaOH etched      | 86.36 ± 7.70          | 72.51 ± 3.22        | 1.04                |

3.2 Scanning electron microscopy and Energy-dispersive X-ray spectroscopy

Figure 4 shows SEM micrographs and EDX measurements of non-grit-blasted (T0) and grit-blasted (T10, T20, and T40) composite surfaces. The images corroborate the above finding that surface roughness increases with increasing grit-blast time. The T0 specimen in Figure 4(a) exhibits a smooth matrix surface with negligible visibility of carbon fibres. Grit-blasting of thermoplastic polymers leads to plastic deformation, micro-ploughing, micro-cutting, and ductile tearing [49]. In Figure 4(b), which shows a T10 specimen, the green arrow shows slightly exposed carbon fibres, while the macro-scale image shown in the inset is comparable to the surface of a pristine composite apart from some glaze from the release agent. Figure 4(c), which shows a T20 specimen, indicates a plasticised matrix surface with numerous grooves and craters. A longer grit-blast time leads to a higher surface temperature, which softens the matrix and assists its ductile flow [49]. This results in the mean $R_a$ being twice that of the T10 surface (see Figure 3(b)). However, no fibre damage is evident for T20 specimens, and the inset shows a translucent surface.

Finally, Figure 4(d), which shows a T40 specimen, indicates that micro-ploughing and micro-cutting have resulted in a reduction in surface matrix area (blue arrow), high carbon fibre exposure (green arrow), significant quantities of damaged fibres (red arrow), and areas where broken fibres and matrix have been eroded away (yellow boundary). The inset shows that the translucent matrix surface has been removed, exposing the carbon fibres. From these images, the adhesion strength for the T10 specimens is expected to be highly dependent on the surface chemistry, while for the T20 and T40 specimens, the adhesion strength will be dependent on both surface chemistry and topography.
Figure 4. SEM micrographs and EDX measurements of composite surface: (a) T0, (b) T10, (c) T20, (d) T40, and (e) EDX measurements. Insets (white boundary on the top right) show a representative macro topography.

In the EDX results, Figure 4(e), negligible aluminium was found, indicating no alumina deposits from the grit-blasting. With increased grit-blasting time, an increase in carbon content and a decrease in nitrogen content is seen, which correlates with the SEM findings of increased carbon fibre exposure on the surface. The oxygen content increases for grit-blasting times up to 20 seconds, but then decreases. This suggests that the T20 specimens have the highest polar group content, which correlates with the contact angle measurements. Reasons for the decrease in oxygen content will be discussed later when the XPS results are examined.

3.3 X-ray photoelectron spectroscopy

Figure 5(a) presents the average atomic concentration (at.%) of elements for the composite adherends, obtained from XPS measurements at three points on each specimen, with the error bars representing one standard deviation. The concentration of C1s increases continuously from T0 to T40, which is due to increasing carbon fibre exposure with longer grit-blast time. Due to the release agent residues, a relatively high silicon (6.2 at.%) and oxygen content (16.3 at.%) was found on T0 specimens, but with only 10 seconds of grit-blasting, the silicon content drops to just 2.0 at.%. High silicon and oxygen content due to release agent residues and reduced silicon content after surface treatment has been previously reported in [10,21,50]. In addition, the O1s spectrum for the T0 specimen has a peak at 532 eV, close to the Si-O binding energy (532.5 eV), confirming the presence of Si-O. Following grit-blasting, the peak shifts to 531.2 eV, indicating a reduction in Si-O content. This supports the hypothesis given earlier that the hydrophobicity seen for T0 specimens is due to release agent residues. The O1s content decreases with increasing grit-blasting time, a trend which is opposite to that seen for the polar content of surface energy in Figure 3. However, the reduction in O1s does not necessarily relate to a lower adhesive bond strength [32], as it could also be due to an increase in various oxidised carbon species. The survey spectra for composite specimens with different surface treatments (T0, T10, T20, and T40) are provided in the supplementary data, Figure 5(c).
Figure 5. XPS measurement for composite samples with different surface treatments: (a) atomic percentage of elements from survey-spectra, (b) concentration percentage of carbon-based functional groups from high-resolution spectra of the C1s peak.

To examine this, high-resolution spectral analysis was performed at one point for each non-grit-blasted and grit-blasted adherend. Figure 5(b) shows the concentration percentage (conc.%) of various functional groups (FGs) from the high-resolution spectra of C1s, as well as the total conc.% of polar groups. The conc.% of a FG was computed by expressing the at.% fraction of that FG, estimated from deconvolution of the survey spectrum, as a percentage of the at.% of the C1s. Following the procedures in the handbook of XPS [51], peaks at 248.8 eV, 285.9 eV, 287.7 eV, and 288.7 eV were identified as carbon (C-C, C=C) bonds, alkoxy (C-O) and amine (C-N) bonds, amide (N-C=O) and carbonyl (C=O) bonds, and carboxyl (O-C=O) bonds, respectively. It can be seen from Figure 5(b) that grit-blasting results in a decrease in conc.% of carbon-carbon bonds and an increase in conc.% of polar FGs. Relative to the non-grit-blasted (T0) specimen, the T20 specimen shows the largest increases in conc.% of polar FGs (33%), compared to 11% for T10 and T40. Polar groups increase surface polarity, resulting in increased secondary hydrogen bonding between adhesives and substrates [15,50,52]. This is expected to improve adhesion via the physical adsorption mechanism. The high-resolution spectra of C1s peak for composite specimens with different surface treatments (T0, T10, T20, and T40) are provided in the supplementary data, as Figures 5(d) – 5(g).

More specifically, from Figure 5(b), the T20 specimen shows a 28% increase in amide and carboxylic groups relative to the T0 specimen, while the T10 and T40 specimens show a 12% and 3% increase respectively. Moreover, the T20 specimen shows a 36% increase in amine groups over the T0 specimen, while the T10 and T40 specimens show a 10% and 15% increase respectively. When the treated adherend is bonded using an epoxy adhesive, the amide and the carboxylic groups can react with the unreacted epoxide groups in the adhesive to form hydrogen and covalent bonds [13,15,50,53]. In addition, amine groups catalyse these reactions, leading to higher crosslink density and improved matrix/adhesive interaction [13,53]. Covalent and hydrogen bonding, together with polymer-crosslinking, collectively result in improved bond strength by the chemical bonding mechanism. All these findings thus suggest that the T20 treatment should lead to the most favourable conditions for adhesive bonding with an epoxy adhesive.

The observed chemical changes on the composite surface after a physical grit-blasting process could be attributed to a localised high temperature, resulting from repeated impingement of the surface with the abrasive media. Arjula et al. [54] studied solid particle erosion of thermoplastic polymers and found that matrix softening
occurred for PPS, which had the lowest glass transition temperature ($T_g$) of the polymers studied (90°C). Guo et al. [55] observed changes in the surface elemental composition of PA12 when polished using a magnetic-field assisted finishing method, and attributed the changes to mechanical/thermal reaction during the polishing process. Therefore, it is highly likely that the PA12 matrix, having a $T_g$ of only 46°C [56], could be significantly affected by local high temperatures in a mechanical/thermal grit-blasting process.

3.4 Lap shear strength (LSS) and Work-to-failure (WF)

The non-grit blasted composite adherends (T0) were not bonded and tested as very poor joint bonding occurred due to the presence of release agent residues from the composite manufacturing process. Figure 6(a) shows representative force-deflection curves for quasi-static and dynamic tests on specimens grit-blasted for the three different times. As can be seen, the maximum force, $F_{\text{max}}$, is relatively unaffected by either the loading rate or the grit-blasting time. The reason for this is that the aluminium adherend is ductile, with a yield stress of just 111 MPa [57]. Consequently, it yields at a joint load of about 5.5 kN (Figure 6(a)) and undergoes extensive plastic deformation and strain localisation prior to joint failure at ~9 kN. Before the metal yields, the deformation of the aluminium and composite adherends is almost the same, since their stiffnesses are well-matched (70 GPa for the aluminium [57], 63 GPa for the composite [34]), but after that the plastic deformation of the metal adherend dominates the joint response, and the final deformation of the composite adherend is negligible (< 0.1 mm) compared to the overall joint deformation (1 to 2.25 mm).

In previous studies [6,8–10,13–15,20,30,31] on the effect of surface treatment on the adhesive bonding of composite materials, the lap-shear strength (LSS) has been used as an indicator of surface treatment effectiveness. The LSS is given by, ASTM D 5868 [35]:

$$LSS = \frac{F_{\text{max}}}{A_{\text{nom}}}$$  \hspace{1cm} (1)

where $F_{\text{max}}$ is the peak force and $A_{\text{nom}}$ is the nominal overlap area. In joints involving materials with high yield strength, like steel or composite, the complete overlap area participates in load transfer (“adhesive global yielding”), and LSS is a good indicator of the effectiveness of the surface preparation. However, since $F_{\text{max}}$ varies little here, LSS is not an effective differentiator between results for the different loading rates and surface treatments. This is because, as will be shown with the DIC results in the next section, the failure here is due to localised large adhesive strains at the overlap edges due to the yielding of the aluminium. On the other hand, it can be seen from Figure 6(a) that the deformation of the joints varies considerably with joint parameters, with much larger deformation in evidence for dynamic loading (dashed lines) than for quasi-static loading (solid lines), and with the T20 surface treatment (blue lines) giving the largest joint deformation, among the three treatment times, for both loading rates. As a result, in addition to LSS, the work-to-failure (WF), which is the area under the force-deflection curve will also be reported here. The WF or energy absorbed by the joint is:

$$WF = \int_{s_1}^{s_2} F(s) \, ds$$  \hspace{1cm} (2)

where $F(s)$ is the force and $s$ is the deformation of the gauge length.

Figure 6(b) shows the average LSS and WF for all tests. The error bars indicate one standard deviation computed from at least five repeats for each configuration. As anticipated from the force-deflection curves, the difference between all the LSS values is small, although the dynamic rate values are slightly higher than the quasi-static values, and the LSS for the T20 treatment is also slightly above those for the T10 and T40
treatments. Even though the adhesive is significantly strain-rate dependent [58], the LSS of the joint is not, because the plastic deformation of the aluminium dominates the response, and the yield strength and hardening rate of this aluminium are not significantly strain-rate dependent [59].

Figure 6. SLJ tests at QS and DY velocities for different surface treatments: (a) representative force-deformation curves, (b) mean LSS and WF. Error bars for LSS not shown for clarity – standard deviation for each LSS value is between 0.3 and 0.8 MPa.

In contrast, the WF clearly differentiates the different joints. At the QS loading rate, the T20 and T40 specimens show 90% and 21% increases in WF relative to the T10 specimens. Corresponding figures for the DY tests are 31% and -23% (i.e. the T40 WF is lower than the T10 WF). Increasing the loading rate leads to 104%, 41%, and 28% increases in WF for T10, T20, and T40 treatments respectively. The lower strain-rate effect for the T20 and T40 specimens, compared to the T10 specimens, and also the reasons for a lower WF for T40, than for T20, despite the highest roughness, will be discussed later when failure mechanisms are examined.

In the previous sections, it was shown that the T20 surface treatment led to the best combination of roughness with minimal fibre damage (SEM pictures), the highest oxygen content (EDX measurements), reduced silicon contaminants from the release agent, the highest conc. % of polar groups (contact angle and XPS measurements), and also the highest conc. % of polar groups favourable for interacting with an epoxy adhesive (XPS measurements). It can be seen from Figure 6(b) that all these factors result in the T20 treatment giving the highest LSS, and the highest WF.

3.5 Failure surface analysis

At the overlap ends of bonded joints, the adhesive experiences high shear stress due to differential shear in the adherends [60], and high peel stress due to the eccentric load path [61]. Figure 7 presents DIC results for the QS_T20 specimen, showing the development of transverse normal strain (peel strain) and shear strain at different load levels until just before final joint failure. As noted above, since the aluminium alloy used here has a low yield stress, the metal adherend yields and deforms plastically, while the composite adherend remains elastic all the way to joint failure. The plastic deformation leads to transverse (width) contraction and adherend thinning due to the Poisson’s ratio effect, as seen in Figure 7(a), increasing the peel strain in the adhesive at the composite free-end. In addition, the plastically deformed aluminium adherend leads to increased differential shearing in the adhesive at the composite free-end, as seen in Figure 7(b). Since the peel and shear strains in the adhesive are higher at the composite free-end than at the metal free-end, primary crack initiation occurs at the composite free-end.
Figure 7. Digital image correlation results for QS_T20 specimen: (a) transverse normal (peel) strain, (b) shear strain. Bottom images in (a) and (b): development of peel and shear strains with increase in load till peak force and further decreasing force until just before final failure.

Figure 8 presents images of failure surfaces, as well as joint deformation just prior to final failure. Figure 8(a), which is for a QS_T20 specimen, defines the colours used to identify different regions. In accordance with ASTM D5573-99 [62], four failure modes are identified:

(i) thin-layer cohesive (blue boundary),
(ii) dissipative adhesive with light fibre-tearing (red boundary),
(iii) dense fibre-tearing (yellow boundary), and
(iv) interfacial (pink boundary, shown in Figure 8(b)).

Different stages of the colour change due to stress-whitening, labelled ‘0’ to ‘4’ in Figure 8(a), are used to estimate the degree of plastic deformation in the adhesive. For failure modes (i) and (ii) (blue and red boundaries), the adhesive colour lightens considerably, indicating substantial plastic flow and energy absorption by the adhesive. Modes (ii) and (iii) are characterised by the appearance of carbon fibres on a thick layer of adhesive left on the aluminium adherend. In mode (iii), there are regions such as those labelled A, B, C and D in Figure 8(a) which are densely populated with strands of carbon fibre that have been removed from the composite surface. Because the fibres in this material are stretch-broken, this requires relatively little energy, and there is also little evidence of adhesive plastic deformation in these regions, so mode (iii) is believed to be a lower energy mode than modes (i) and (ii). The fourth mode (pink boundary) involves the least energy absorption as the failure abruptly occurs at the adhesive – composite adherend interface.

Examining the quasi-static results first, for the QS_T10 and QS_T20 specimens, Figure 8(b) and (d) respectively, stable propagation (identified by stress-whitening) of the primary crack proceeded to roughly halfway along the overlap, before a secondary crack initiated at the metal free-end leading to abrupt joint fracture. The T10 specimen, Figure 8(b), predominantly exhibits high-energy mode (i) failure at the composite free-end and low-energy mode (iv) failure at the metal free-end. The T20 specimen, Figure 8(d), shows high-
energy mode (i) failure near the composite free-end, high-energy mode (ii) failure in the central overlap region, and low-energy mode (iii) at the metal free-end. For the QS_T40 specimen, Figure 8(f), the occurrence of the primary crack was closely followed by the initiation of the secondary crack. Both cracks propagated a small distance into the overlap region before abrupt joint failure. The specimen exhibits high-energy failure modes in small regions at the overlap ends (mode (i)) at the composite free-end, mode (ii) at the metal free-end), with low-energy mode (iii) evident in the large central overlap region. Large regions of low-energy mode (iii) failure can be attributed to the damaged, and eroded fibre-matrix region due to longer grit-blasting times, as observed in the SEM micrograph in Figure 4(c). These findings are consistent with Figure 6(b) which indicated that the T20 treatment results in the highest WF.

Figure 8. Failure surfaces of SLJ specimens: (a) Illustration of meaning of different colours and labels (QS_T20 specimen), (b) QS_T10, (c) DY_T10, (d) QS_T20, (e) DY_T20, (f) QS_T40, and (g) DY_T40. Top image in (b)-(g): failure surfaces, bottom image: deformation just prior to final failure.

Turning to the dynamic test results in Figure 8, the DY_T10 specimen, Figure 8(c), looks qualitatively similar to the QS_T10 specimen, Figure 8(b), with mode (i) (thin-layer cohesive) failure near the composite free-end, and mode (iv) (interfacial) failure towards the metal free-end. How then, can the large difference in WF between the QS_T10 and DY_T10 cases, seen in Figure 6(b), be explained? Well, the loading rates used here, 1 mm/min and 0.5 m/s, translate respectively to strain rates of 0.067/s and 2000/s at the adhesive layer. May et.al. [58] showed that the adhesive used here exhibits highly strain-rate dependent properties, with 40-170% increases in tensile yield stress, tensile strength, shear yield stress and mode II fracture toughness relative to quasi-static values, for 2000/s. Thus, the T10 joints, for which mode (i) cohesive failure is the primary energy-absorbing mechanism, exhibit a WF which is highly sensitive to loading rate.
The DY_T20 specimen, Figure 8(e), shows a combination of modes (i), (ii) and (iii), similarly to the QS_T20 specimen, Figure 8(d), but the area displaying mode (ii) failure (dissipative with light fibre-tearing) is larger under dynamic loading, while the areas displaying mode (i) and (iii) failure are smaller. Mode (ii) is the dominant energy-absorbing mode for the T20 specimens, and fibre-matrix interface failure is typically not very strain-rate-dependent, so the WF is less sensitive to loading rate than the for the T10 specimens. Comparing the side views in Figure 8(d) and Figure 8(e), it can be seen that the primary crack extends further before the secondary crack appears under dynamic loading.

The DY_T40 specimen, Figure 8(g), shows longer primary crack propagation before the secondary crack appears, compared to the QS_T40 specimen, Figure 8(f). It also exhibits less mode (i) (cohesive) failure than the QS_T40 specimen which would tend to reduce the WF, but there is also a shift from mode (iii) (dense fibre tearing, very dark regions) towards mode (ii) (dissipative adhesive failure with light fibre tearing), which tends to increase the WF. Overall, the WF is larger for dynamic loading, Figure 6b), but the T40 specimens show the least strain-rate dependency.

Since both the DY_T20 and DY_T40 specimens show fibre-tearing as a dominant failure mode, the failure surface images of the aluminium adherend from all tested specimens were processed to quantify the fibre-tearing area. The mean fibre-tear failure area for DY_T20 was 162.8 mm$^2$ (SD: 13.6 mm$^2$) and for DY_T40 specimens was 225.8 mm$^2$ (SD: 39.3 mm$^2$), i.e. DY_T20 specimens had 39% less fibre-tearing area than DY_T40. This indicates that excessive fibre exposure and damage at the longer grit-blasting time leads to easier removal of the fibres from the composite surface.

Figure 9 shows SEM micrographs of failure surfaces, with the loading direction indicated by the green arrows. Figure 9(a) presents a region of the metal adherend in the QS_T10 joint where mode (i) thin-layer cohesive failure occurred. Extensive ductile adhesive deformation is seen, with some regions of exposed metal. The metal surface is seen to be cratered due to the pickling effect of the NaOH etching. Figure 9(b) shows a region on the thick adhesive layer sticking to composite adherend, in the QS_T10 joint. The cusps along the loading direction indicate the shear deformation of the adhesive. The SEM observations of the QS_T10 joint where mode (iv) interfacial failure occurred (figures not shown), displayed a significantly smoother failure surface. The DY_T10 joint displayed similar failure surfaces as for the QS_T10 joint. The smooth grit-blasted composite surface of the T10 specimens (Figure 4(b)) resulted in a negligible mechanical interlocking between the adhesive and the substrate, leading to smooth failure surfaces. Therefore the T10 joint strength is significantly dependent on the adhesion mechanisms like chemical bonding and physical adsorption.

The SEM image at the bottom, left of Figure 9(c) presents a region of the metal adherend in the QS_T20 joints where mode (ii) dissipative failure in the adhesive with light fibre tearing occurred. Sparsely populated carbon-fibres on the ductile-deformed thick adhesive layer can be seen. The SEM observations of DY_T20 joints (figures not shown) revealed a slightly greater extent of fibre-tearing and a slightly reduced extent of dissipative failure than the QS_T20 joints. The SEM image on the bottom, right of Figure 9(c) focuses on an area of dissipative adhesive failure in the same QS_T20 metal adherend. This mode is widely observed in the T20 joints. The image shows extensive ductile deformation in the adhesive, seen as homogenous hairy structures. This could be attributed to the fact that the adhesive satisfactorily penetrated the grooves and craters of the grit-blasted composite surface, establishing micro-mechanical interlocking and consequently resulting in
the hairy adhesive failure surface. Moreover, light fibre tearing in spite of the absence of fibre exposure on the grit-blasted T20 surface (Figure 4(c)) suggests the existence of strong adhesive-adherend interaction. Slower and longer primary crack propagation in T20 joints (Figure 9) could be attributed to the failure path alternating between the adhesive-PA12 matrix interface and CF-PA12 interface, and collective energy absorption of the dissipative and fibre-tearing modes. As a result of this, the highest joint deformation and consequently work-to-failure is observed for T20 joints.

Figure 9. SEM failure surfaces: (a) thin-layer cohesive failure of QS_T10, (b) thin-layer cohesive failure of QS_T10, (c) adhesive dissipative and light fibre tearing failures of QS_T20, (d) dense fibre tearing failure of QS_T40, and (e) dense fibre tearing failure of DY_T40.

Figure 9(d) presents a region of the metal adherend in the QS_T40 joint where mode (iii) dense fibre tearing failure occurred. Strands of carbon fibre yarns which were torn away from the surface of the composite adherend are observed on the thick adhesive layer. Figure 9(e) presents a region of the metal adherend in the DY_T40 joint where mode (iii) dense fibre tearing occurred. In contrast to the QS_T40 joint, strands of carbon
fibre yarns are absent. However, the DY_T40 joints display significantly higher fibre tearing relative to the DY_T20 joints. Damaged surface fibres of the composite adherend due to the long grit-blasting time resulted in a weak interfacial layer between the surface carbon fibres and the matrix, as explained by the model of weak boundary layer [40], causing a dense fibre tearing failure mode and ultimately limiting the WF of T40 joints.

4. CONCLUSIONS

In this work, an evaluation has been made of grit-blasting as a pre-treatment for carbon-fibre thermoplastic composite to aluminium bonded joints tested at static and dynamic loading rates. The treated composite surfaces have been studied using various surface chemistry and topography characterisation techniques.

Important results from this study are summarised below:

1. DIW contact angle measurements showed simultaneous super-hydrophobicity and high water-droplet adhesion. The ratio of polar surface energy to total energy was the highest for T20 and T40 specimens (12.7%, 25.2% and 24.8% for the T10, T20, and T40 specimens respectively).

2. The surface roughness increased with increase in grit-blasting time, with $R_a$ values of 0.54 µm, 1.1µm, 2.2 µm and 2.9 µm for the T0, T10, T20, and T40 specimens respectively. However, the T40 specimens displayed fibre damage and fibre-matrix erosion, resulting in a weak fibre-matrix interface.

3. The T20 specimens displayed the highest atomic percentage (34.6 at.%) of polar groups followed by the T40 (28.7 at.%) and T10 (28.8 at.%) specimens. Silicon contamination from the release agent residues, reduced from 6.2 at.% for T0 specimens to 2.3 at.% for T20 specimens.

4. The T20 specimens recorded the highest work-to-failure for both quasi-static and dynamic loading rates. Relative to the T10 specimens, T20 specimens showed 90% and 31% higher work-to-failure at 1 mm/min and 0.5 m/s loading rates, respectively.

A strong relationship between surface chemistry and topography, with adhesion strength, has been observed. A composite surface with plasticised matrix and minimal fibre exposure or damage has been found to yield the best lap shear strength and work-to-failure, at both quasi-static and dynamic loading rates. The desired composite surface was achieved with a grit-blast duration of 20 seconds, with the nozzle held perpendicular to, and 300 mm from, the adherend surface. Therefore, this study demonstrates the suitability of alumina grit blasting with optimal parameter settings, as a surface treatment for CF/PA12 composite. This simple but effective surface preparation process is highly compatible with fast robotic manufacturing, making it an attractive option for low-cost, repeatable, high-throughput bonding of hybrid joints in automotive structures. The optimised grit-blasting procedure developed here will be employed to bond through-thickness reinforced hybrid joints in a future study.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: