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SURFACE PRETREATMENTS ON CFRP AND TITANIUM FOR MANUFACTURING ADHESIVELY BONDED BI-MATERIAL JOINTS

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Abstract

Adhesive bonding is a highly desirable joining technique to join composites to metals. The surfaces of both composite and metal substrates have to be carefully treated before bonding them together, in order to avoid interface failure between the adherend's surface and adhesive. This paper describes the surface pretreatments on carbon fiber reinforced plastic (CFRP) and Titanium for the manufacturing of adhesively bonded CFRP-Titanium joints. Different treatments were applied in order to roughen and activate both substrate surfaces. The quality of the surface pretreatment using different treatment methods was initially checked by contact angle measurements. Destructive tests on the bonded specimens after various surface pretreatments, including those which provided the lowest contact angle, were performed to validate the mechanical performance of the surface treatment on the bond quality. The test procedure and results on adhesively bonded CFRP-CFRP specimens and Titanium-Titanium specimens will be presented and discussed. 100% cohesive failure in both CFRP-CFRP and Titanium-Titanium joint types guarantees the high quality of the adhesively bonded joints, and proves that the respective surface pretreatments on CFRP and Titanium excludes adhesive failures in bonded CFRP-Titanium joints.

1. Introduction

The desire to minimize the environmental impact has stimulated innovations to reduce the fuel consumption and thus carbon dioxide emissions in the aerospace industry. The key to achieve this goal is to reduce the weight of aircraft structures without compromising the structural integrity. Within this scope, a promising lightweight structural solution to achieve Hybrid Laminar Flow Control (HLFC), a technology to reduce drag and improve fuel efficiency [1], is to adhesively bond a perforated Titanium skin to inner structures made of carbon fiber reinforced plastic (CFRP) using a certified adhesive for aerospace applications. Adhesive bonding is preferable to mechanically fastening

methods in joining composites to metals due to the fact that it diminishes the weight penalty caused by mechanical fastening.

The key to the success of the adhesive bonding of Titanium to CFRP relies on suitable surface pretreatments on the surfaces of both substrates prior to bonding them together. The purpose of the surface pretreatment is to promote strong adhesion between the substrate and adhesive to produce reproducible high and durable bond strengths. With the properly selected surface pretreatment, the adhesive failure at the adhesive/substrate interface should be excluded in the bonded joint.

Adhesively bonding composites to metals creates a bi-material interface. It is imperative that both the surface of the Titanium and surface of the CFRP should be carefully prepared. It is worth noting that the best surface pretreatment procedure for the Titanium is not necessarily the best for the CFRP. As a result, two optimum sets of surface pretreatment procedures for both the Titanium and the CFRP have to be determined separately.

The surface pretreatment of CFRP and surface pretreatment of Titanium have been extensively studied, which is summarized in a review paper [2]. Various Titanium alloys, including the most used Ti-6Al-4V in aerospace industry, have been used to study the effects of various surface treatments. However, the effects of surface treatments on commercially pure grade 2 (CP 40) Titanium is missing. Moreover, the application of UV/Ozone as a surface pretreatment of CFRP and Titanium for structural bonding is insufficiently studied.

UV/Ozone treatment is a very effective cleaning method to thoroughly remove organic contaminations from the surface without changing its macroscopic roughness [3]. Research has indicated that UV/Ozone treatment can improve the adhesion between metal and epoxy [3,4]. For this reason, the effects of UV/Ozone treatment on CFRP and Titanium are studied in this paper.

In this research, the surface pretreatments of CFRP and Titanium including cleaning with a solvent, grit blasting and UV/Ozone treatment are investigated. The effects of these surface pretreatments are evaluated with contact angle measurements, SEM and destructive tests. This paper describes the investigated surface preparation methods and discusses the evaluation results of different treatment methods.

2. Surface pretreatments

2.1. Materials

The manufacturing of hybrid composite-to-Titanium bonded joints involves the Titanium substrate, the CFRP substrate and adhesive. The Titanium substrate investigated is commercially pure grade 2 Titanium (CP 40) with a thickness of 0.8 mm. The used adhesive is FM 94 epoxy adhesive film.

The CFRP substrates were manufactured by vacuum infusion of a HexFlow[®] RTM 6 epoxy system into a stake of HexForce[®] G0926 fabrics. Only one side of the CFRP plate is equipped with a peel-ply (DIATEX 1500EV6) that does not contain release agent or silicon.

2.1. Surface pretreatments of Ti

In Fig. 1, a process flow for the surface pretreatment of Titanium is provided. Firstly, it is important to clean the surface to make it free from contaminations such as marking ink, grease etc. Secondly, the adhesion properties of Titanium can be significantly improved when applying mechanical surface pretreatment such as grit blasting or abrasion to the surface [5, 6]. Grit blasting or abrasion can remove the old and inactive oxide layer and roughen up the surface at a macroscopic level, a new active oxide layer on the surface will form later on. Thirdly, UV/Ozone treatment process removes traces of organic contaminants gently and oxidizes the inorganic substrates, it also activates the surface and

enhances the adhesion between metal and epoxy. At last, the application of AC-130 (3M) sol gel can create a layer on the activated surface to enhance the initial adhesion and durability [7]. Water based primer such as BR 6747 (Cytec) [8] or EW 5005 (3 M) [9] can be applied afterwards to optimize the connection between sol gel and epoxy adhesive.



Figure 1. Process flow for the surface pretreatment of Titanium

The surface treatment methods for Titanium is summarized in Table 1. The purpose of using this matrix is to find the surface preparation approach that provides the lowest contact angle. The effects of sol gel and primer were investigated using DCB tests, which will be described in the next section.

Table 1. Surface pretreatment matrix for Titanium

Methods	Abbreviations
As is	As is
PFQD cleaning	P
PFQD cleaning + 3 Bar Corundum Grit Blast + PFQD cleaning	P3GP
PFQD cleaning + 3 Bar Corundum Grit Blast + PFQD cleaning + optimum UV/Ozone (4 exp. times: 2, 3, 4, 5 minutes)	PGPUV (time)
PFQD cleaning + 5 Bar Corundum blast + PFQD cleaning + optimum UV/Ozone (4 exp. times: 2, 3, 4, 5 minutes)	

The solvent cleaning was implemented by cleaning the surface with a piece of cloth soaked with PF-QD a quick drying wide spectrum cleaning solvent. The abrasive blasting treatment was carried out in a sand-blasting cabinet, corundum grits were used under a continuous high pressure of 3 bar or 5 bar pressure. The distance between the specimen and the blast gun was around 10 cm to 15 cm. For the UV/Ozone treatment, the distance between the specimen and UV lamps was roughly 35 mm. Different durations of UV/Ozone treatment as listed in Table 1 were tested to find the optimal treatment duration.

2.2. Surface pretreatments of CFRP

In Fig. 2, a general surface preparation flow for the CFRP is provided. It comprises three basic steps. The surface has to be cleaned thoroughly so that it is free from any contamination. Next to it, the surface of CFRP has to be adapted to the required roughness, this can be done with many means, such as light sanding, abrasion or grit blasting. At last, the surface free energy of the surface must be increased sufficiently by either atmospheric plasma or UV/Ozone, creating a surface with excellent wetting characteristics [10].

A matrix of surface preparation methods for the CFRP substrate is summarized in Table 2. It is worth noting that all the surface pretreatment was implemented after the removal of the peel-ply. The pretreatment methods for the CFRP are similar to those for the Titanium. One abrasion treatment was added for the CFRP, which was carried out manually with a Scotch-Brite TM CF-SR handpad of size 150 mm * 115mm with a very fine grit size. The surface of the CFRP was rubbed in arbitrary directions with the abrasion pads until the surface was uniformly abraded.

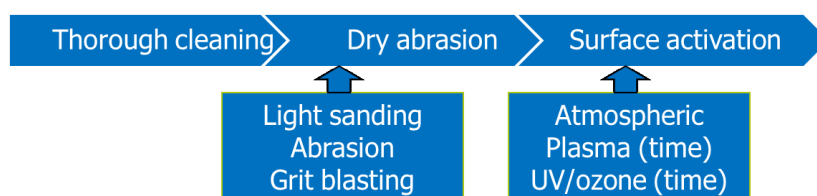


Figure 2. Surface preparation flow for CFRP.

Table 2. Surface pretreatment matrix for the CFRP

Methods	Abbreviations
As is	As is
PFQD cleaning	P
PFQD cleaning + 2 Bar Corundum Grit Blasting + PFQD cleaning	P2GP
PFQD cleaning + 3 Bar Corundum Grit Blasting + PFQD cleaning	P3GP
PFQD cleaning + 2 Bar Corundum Grit Blasting + PFQD + UV/Ozone (3 min, 4 min...)	P2GPUV (time)
PFQD cleaning + UV/Ozone (7 min)	PUV
PFQD cleaning + Scotch-Brite abrasion + PFQD cleaning + UV/Ozone (7 min)	PSPUV

3. Evaluation methods of the surface pretreatments

Three methods were employed to examine the effects of the surface pretreatment. Contact angle measurement (CAM) is an effective method of evaluating the wetting properties of the surface pretreatments listed in Table 1 and 2. Scanning Electron Microscope (SEM) is used to check the surface morphology of the treated CFRP specimens. The DCB test is a destructive testing method which is commonly used to validate the mechanical performance of the surface treatment on the bond quality.

For the contact angle measurement evaluation, each pretreatment was applied to 3 specimens, and 5 contact angle measurement were made for each specimen on a 45 mm*45 mm sized surface. The contact angle between the water droplet of 5 μ l volume and the surface of a treated sample was taken by curve fitting the droplet profile and measuring the angles formed between the tangents of the fitted curve and the horizontal axis.

For the SEM evaluation, the CFRP surface of interest was dissected from the treated sample to fit into the sample chamber. The CFRP samples had to be sputter-coated with gold to make the surface conductive. The morphology of the treated surfaces after roughening was checked.

The DCB test is a widely used destructive method to examine the quality of the adhesively bonded joints. In this research, the energy release rate of bonded joints is not of interest. The purpose of the DCB test was to investigate the fracture surface. As proper surface pretreatment is expected to generate cohesive failure in the bonded joints. Instead of testing bi-material CFRP-Titanium joints, 5 adhesively bonded CFRP-CFRP and Titanium-Titanium joints were tested respectively. 100% cohesive failure in both joint types guarantees the high quality of the adhesively bonded joints, and proves that the respective surface pretreatments on CFRP and Titanium excludes adhesive failures in bonded CFRP-Titanium joints.

4. Evaluation results

4.1. Contact angle measurement results

In Fig. 3. the contact angle measurement results of Titanium are given. As can be seen from Fig. 3(a), grit blasting together with solvent cleaning already lowers the contact angle significantly. In addition to grit blasting and solvent cleaning, UV/Ozone treatment dramatically reduces the contact angle. The contact angle decreases with UV/Ozone duration in general, as can be seen in Fig. 3(b). It appears that grit blasting under 3 bar pressure and 3 min UV/Ozone exposure treatment can offer very low contact angles. Only a slight improvement in the contact angle with longer UV/Ozone treatment can be obtained at the cost of efficiency.

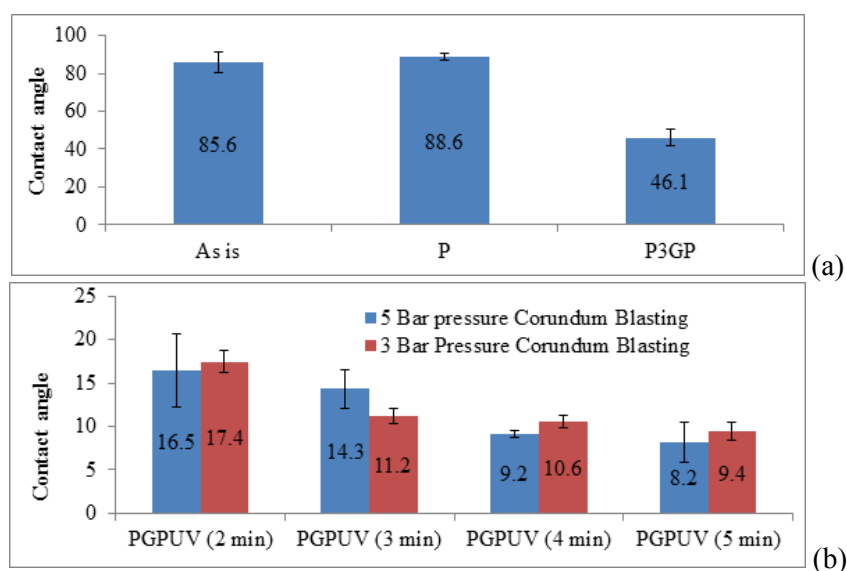


Figure 3. Contact angle measurement results of Titanium. (a) effects of cleaning and grit blasting. (b) effects of UV/Ozone duration.

It was observed that 5 bar grit blasting generated more severe plastic deformation in the treated Titanium specimen than 3 bar grit blasting. As a result, the PGPUV (3 min) with the grit blasting pressure of 3 bar is selected as the optimal surface pretreatment for the Titanium specimens. The effects of the application of sol-gel and/or primer system on the surface treated with this approach were also investigated with DCB tests, which will be described in the next subsection.

In Fig. 4, the contact angle measurement results for the CFRP substrates are given. As can be seen, difference in the contact angles of the two surfaces with the same treatment can be observed.

From Fig. 4(a), it can be observed that the contact angle is very high when applying solvent cleaning and grit blasting. The effects of the duration of the UV/Ozone treatment is examined on the surface initially without peel-ply. This set of tests was done to find the optimum duration of UV/Ozone treatment. As shown in Fig. 4(b), 7 minute UV/Ozone exposure results in the lowest contact angle with only little scatter.

The method by which the surface is abraded is related to the different contact angle measurements, see Fig. 4(c). After cleaning with PFQD, 7 minute UV/Ozone treatment already provides very low contact angles. The application of grit blasting further lowers the contact angle. For the surface initially equipped with peel-ply, the contact angle was so low that it was not possible to measure the angle

when grit blasting was applied in combination with UV/Ozone. It is indicated with the value of 5 degrees without scatter in Fig. 4(c). Higher contact angle is obtained when Scotch-Brite abrasion was applied.

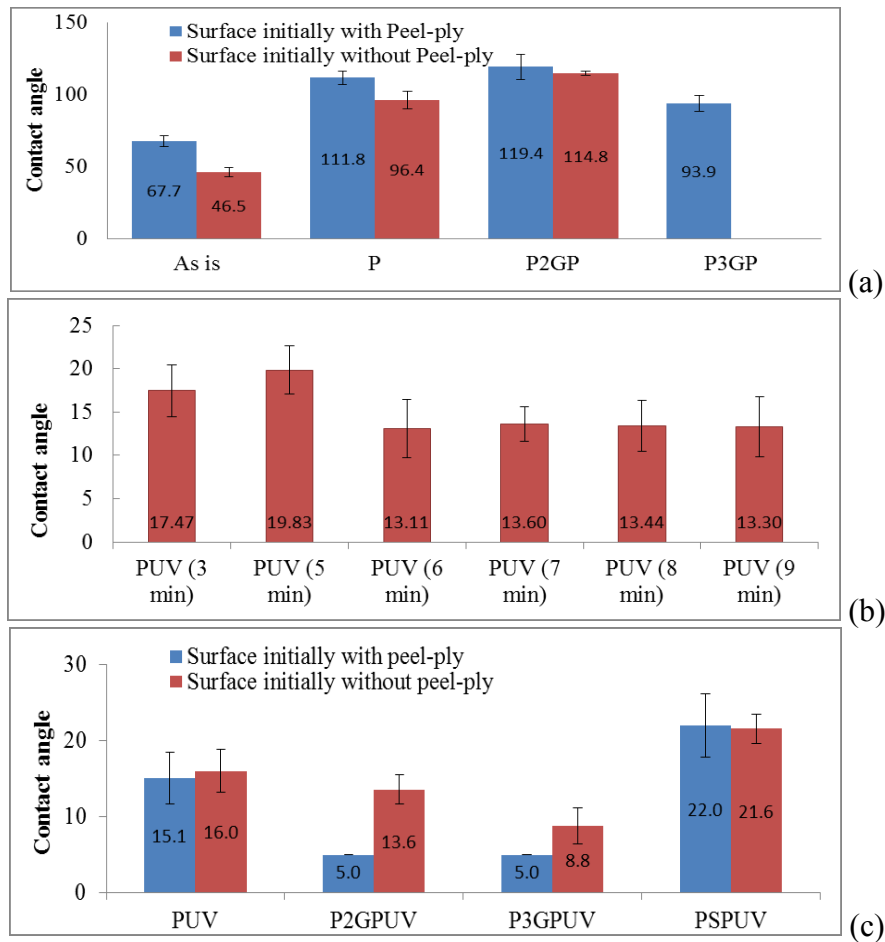


Figure 4. Contact angle measurement results of CFRP. (a) effects of cleaning and grit blasting. (b) UV/Ozone duration effects on the surface initially without peel-ply. (c) Abrasion effects, 7 min UV/Ozone was applied to all.

4.2. SEM results

In Fig. 5, the morphologies of the CFRP surface after the application of different abrasion methods are summarized. For the surface initially with peel-ply, it can be observed that the grit blasting under 3 bar pressure results in a more coarse surface than created by 2 bar grit blasting. No fiber cutting can be observed on this surface treated with any abrasion methods. On the contrary, fiber cutting can be observed on the surface initially without peel-ply after grit blasting. It can be observed that 3 bar grit blasting creates severer fiber cutting than 2 bar grit blasting. A lot of debris can be observed on the surface treated by Scotch-Brite abrasion. It explains why PSPUV pretreatment on the CFRP results in a bit higher contact angle shown in Fig. 4.

4.3. DCB test results

The surface pretreatments investigated using DCB tests are summarized in Table 3. The typical load-displacement curves of two joint types are depicted in Fig. 6.

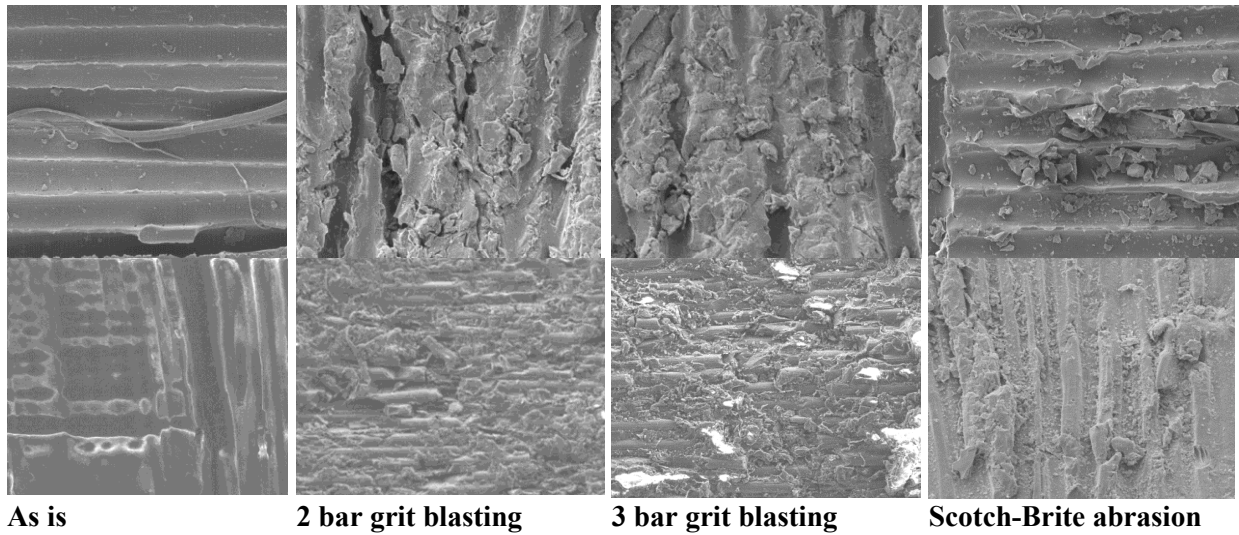


Figure 5. Abrasion effects on the surface morphology of the CFRP. The morphologies of the surface initially with peel-ply are in the 1st row and the morphologies of another surface are in the 2nd row.

Table 3. Surface pretreatments investigated by DCB tests

Titanium-Titanium		CFRP-CFRP	
W	PGPUV (3 min)	CGPP	P2GPUV + initially with peel-ply
Sol gel	PGPUV + AC 130 sol gel	CWPP	PUV + initially with peel-ply
EW5005	PGPUV + sol gel + EW 5005 primer	CWPP	PUV + initially without peel-ply
BR6747	PGPUV + sol gel + BR 6747 primer	CGWP	P2GPUV + initially without peel-ply

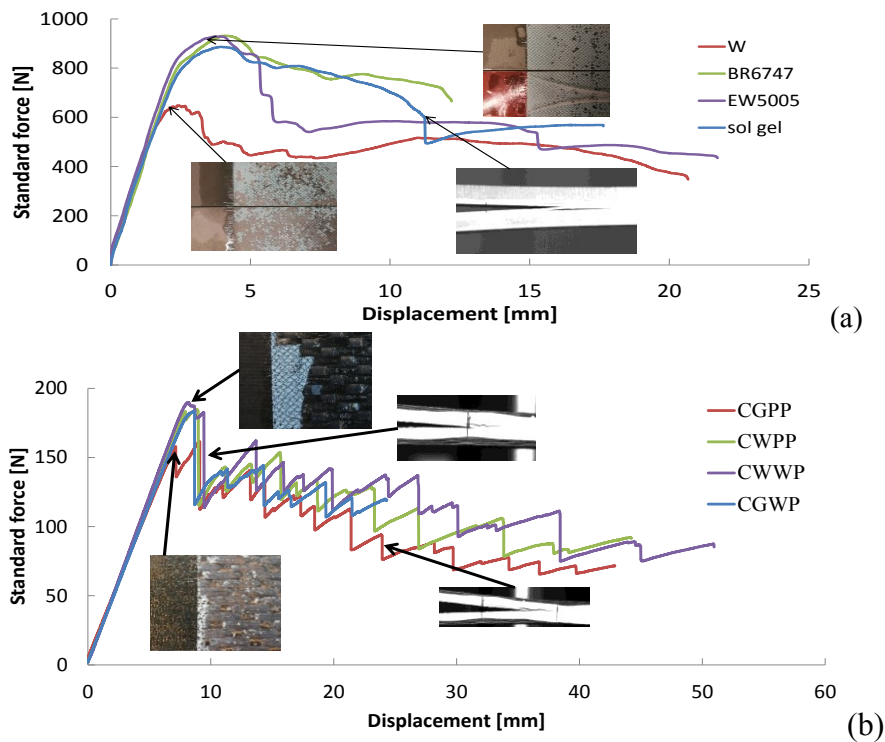


Figure 6. Load-displacement curves (a) for Titanium-Titanium joints. (b) for CFRP-CFRP joints.

From Fig. 6 (a), it can be seen that PGPUV (3 min) pretreatment of Titanium generates adhesive failure in the bonded joints and results in a lower maximum applied load. The application of sol gel and/or primer results in 100% cohesive failure and leads to higher maximum applied load in the curves. The drops in the curves after the maximum applied load are related to the disbonding between the Titanium specimen and backing beams which were bonded to the Titanium-Titanium specimen in order to avoid yielding in the DCB specimen. It is worth noting that the initial crack is at the interface between two treated Titanium surfaces that are bonded with FM 94 epoxy adhesive film.

In Fig. 6 (b), a higher maximum applied load is associated with the initial cohesive failure in the joints. After the initial cohesive failure, the interlaminar failure in the CFRP adherend leads to the plunge in the load. The fiber-matrix debonding is the dominant failure afterwards. The stick-slip crack propagation is related to the brittle nature of the CFRP specimen.

5. Conclusion

The surface pretreatments listed in Table 1 and Table 2 were tested to find the optimal surface preparation methods for the Titanium and CFRP respectively. It has been proven that UV/Ozone pretreatment is very effective for both the Titanium and CFRP examined. For the Titanium, although PGPUV (3 min) treatment provides the lowest contact angle, the application of sol gel and primer is necessary. For the CFRP, the selected surface preparation methods creates very good adhesion between the CFRP and FM 94 adhesive. Fibre-matrix debonding is the dominant failure in this case.

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References

- [1] K.S.G. Krishnan, O. Bertram and O. Seibel. Review of hybrid laminar flow control systems. *Progress in Aerospace Sciences*, 93:24–52, 2017.
- [2] P. Molitor, V. Barron, T. Young. Surface treatment of Titanium for adhesive bonding to polymer composites: a review. *International Journal of Adhesion and Adhesives*, 21(2):129-36, 2001.
- [3] S. Bok, G-H Lim, B. Lim. UV/ozone treatment for adhesion improvement of copper/epoxy interface. *Journal of Industrial and Engineering Chemistry*, 46:199-202, 2017.
- [4] J. Seo, W.S. Chang, T-S. Kim. Adhesion improvement of graphene/copper interface using UV/ozone treatments. *Thin Solid Films*, 584:170-5, 2015.
- [5] M. Akram, K.M.B. Jansen, L.J. Ernst and S. Bhowmik. Atmospheric pressure plasma surface modification of Titanium for high temperature adhesive bonding. *International Journal of Adhesion and Adhesives*, 31(7):598-604, 2011.
- [6] N. Brack, A.N. Rider. The influence of mechanical and chemical treatments on the environmental resistance of epoxy adhesive bonds to Titanium. *International Journal of Adhesion and Adhesives*, 48:20-7, 2014.
- [7] 3M Surface Pre-Treatment AC-130. *Technical Data Sheet*, 2012.
- [8] Cytec BR 6747-1 Bonding primer. *Technical Data Sheet*, 2010.
- [9] 3M™ Scotch-Weld™ Structural Adhesive Primer EW-5005. *Technical Data Sheet*, 2018.
- [10] J. Bishop. A Review of Current Trends in Surface Pretreatment prior to Structural Adhesive Bonding. *MMS 7, MMS 8 and MMS 11 IAG Meeting*. 2003.