Damage mechanisms of directly bonded carbon fibre reinforced thermoplastics and aluminium with nanostructured surface

K M Jespersen¹,2, J C Chung², K Okamoto², H Abe², A Hosoi²*, and H Kawada²³
¹Kanagawa Institute of Industrial Science and Technology (KISTEC), 3-2-1 Sakado, Takatsu-ku, Kawasaki-shi, Kanagawa, 213-0012, Japan
²Department of Applied Mechanics and Aerospace Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan
³Kagami Memorial Research Institute for Materials Science and Technology, 2-8-26 Nishiwaseda, Shinjuku-ku, Tokyo 169-0051, Japan
E-mail: hosoi@waseda.jp*

Abstract. The current study presents a direct bonding method making it possible to obtain a high interface strength of aluminium joined to carbon fibre reinforced thermoplastic (CFRTP) plates by hot pressing. This is achieved by subjecting the aluminium to a combination of anodising, etching, and silane-coupling treatments prior to bonding. Different types of aluminium are subjected to different treatments and bonded to different types of CFRTP laminates. The effect of the surface structure on the static bonding strength and fatigue life measured by single-lap testing is compared and discussed. The bonding strength is found to be highly dependent on the anodisation conditions along with the type of thermoplastic resin.

1. Introduction
In recent years, fibre reinforced plastics are increasingly replacing conventional materials such as steel and aluminium due to their high specific strength and stiffness along with their great fatigue resistance. Particularly in the aerospace and automotive industries, carbon fibre reinforced thermoplastics (CFRTPs) are of interest due to their great formability and productivity, making them suitable for mass production. Furthermore, the possibility of recycling CFRTPs, which is difficult for the thermoset-type counterparts, makes them a suitable material choice for a sustainable future.

Nevertheless, it is rarely feasible to build an entire structure of CFRTPs alone, and thus it is necessary to join CFRTPs to other materials. However, bonding between dissimilar materials contains several challenges. Mechanical joining e.g. by bolts increases the weight of the structure and hole drilling causes stress concentrations. Dissimilar materials can be joined by adhesives, however the adhesive has to be compatible with both materials and generally do not bond well to thermoplastic materials. Furthermore, there are issues such as long curing times and degradation of the bond strength over time. Therefore, alternative bonding methods to join CFRTPs to other materials have been proposed. Some examples are ultrasonic welding [1, 2], friction spot joining [3, 4], laser direct joining [5], induction heating [6], friction lap joining [7].
methods among others. However, these methods require expensive equipment, there is a limitation to the thickness, and they can generally only be applied to small areas.

In response to these challenges, a novel method to directly bond carbon fibre reinforced thermoplastics and aluminium was proposed by the authors [8, 9] (patent: Japanese patent application no. 2016-197812 and 2018-53610). The proposed method is based on carrying out an initial surface treatment by anodising and etching of the aluminium surface in a way that results in either a nano-porous or nano-spike structured surface. The method to establish a nano-spike structure on the surface of Al051 aluminium was proposed by Yu et al [10] for light absorption purposes. This principle was adopted for enhancing the bonding strength with the idea of mimicking easy-to-bond structures found in nature such as pollen, virus molecules, and the feet of a gecko. By performing anodisation of the aluminium surface and subsequently subjecting it to a silane coupling treatment, it was possible to obtain a high bonding strength between the modified aluminium and CFRTPs by hot-pressing [9].

The current study applies the above mentioned method to fabricate nano-porous and nano-spike microstructures on two types of aluminium alloys (A1050 and A5052) and to bond them to CFRTP by hot pressing. The different microstructures are compared to one another and discussed in relation to the bonding strengths measured from single-lap testing. Furthermore, single-lap fatigue testing is carried out for two chosen test cases to compare the effect of the nano-spike structure on the fatigue life.

2. Experimental method

This section will outline the materials and method used to manufacture the nanostructures on the aluminium surface along with the method to join the CFRTP and aluminium.

2.1. Materials

Toray T300B-3K woven fabrics with an average fibre diameter of 7 µm and a [(0/90)₉]₉ layup were used for the CFRTPs. Two types of CFRTPs were made using Polyamide-6 (PA6) and Polyamide-MXD6 (MXD6) as matrix (also known as Nylon-6 and Nylon-MXD6) having a melting point of 225 °C and 243 °C, respectively. The fibre volume fraction of the final composites was $V_f \approx 50\%$. Two types of aluminium (A1050 and A5052) were considered and subjected to different types of surface treatments resulting in a range of different nanostructures on the aluminium surfaces.

2.2. Aluminium surface treatment

Fig. 1 shows a schematic of the process to fabricate a nanostructure on the aluminium surface. Initially the aluminium specimen is degreased by ultrasonic cleaning while submerged in acetone for 10 mins. The aluminium specimen is then anodised in an acidic solution (Fig. 1a) using a carbon cathode and then etched in an acid (Fig. 1b). This process is generally carried out twice. Depending on the anodising and etching parameters along with the chemical solution type, different surface structures can be obtained. Fig. 1c shows an example of a fabricated nano-spike structure on the A5052 aluminium alloy surface.

Considerable experimental work was carried out on finding the optimal anodisation and etching conditions, however the current study will only include the conditions that resulted in the highest interface strengths. The chemical solutions used for the surface treatments are listed in Table 1. The two different aluminium types (A1050 and A5052) were each subjected to two different series of chemical treatments, as listed by a-d below. For each aluminium type, a nano-spike and a nano-porous type of structure was obtained resulting in four different aluminium surface structures as shown in Fig. 2.
Figure 1. Schematic of the (a) anodising and (b) etching surface treatment approach to generate a (c) nano-spike structure on the aluminium. The shown example is on the A5052 aluminium surface.

Table 1. Overview of chemical surface treatments

| ID   | Chemical Solution                  | Current [V] | T [°C] |
|------|------------------------------------|-------------|--------|
| Anod-A | 0.5M Sulfuric Acid                 | 25          | 3      |
| Anod-B | 0.1M Phosphoric Acid               | 160         | 5      |
| Anod-C | 2wt% Citric Acid + 2wt% Ethylene Glycol (2:1) | 400   | 10     |
| Etching-A | 6wt% Phosphoric Acid + 1.5wt% Chromic Acid | -     | 63     |
| Etching-B | 6wt% Phosphoric Acid + 1.8wt% Chromic Acid | -     | 63     |
| Etching-C | 0.5M Phosphoric Acid               | -           | RT     |

(a) **A1050 Nano-spike:**
Anod-C (9h) → Etching-A (48min)

(b) **A1050 Nano-porous:**
Anod-B (60min) → Etching-B (60min) → Anod-B (60min) → Etching-C (30min)

(c) **A5052 Nano-spike:**
Anod-A (60min) → Etching-A (60min) → Anod-A (15min) → Etching-C (50min)

(d) **A5052 Nano-porous:**
Anod-C (9h) → Etching-B (60min) → Anod-C (9h) → Etching-B (20min)

As seen from Fig. 2, varying the anodising treatment conditions and even the type of aluminium has a great influence on the nanostructure developed on the surface of the aluminium. For A1050, a nano-spike structure (Fig. 2a) can be produced by 400V anodising (Table 1) as also reported by Yu et al. [10], however in the case of A5051 the 400V treatment results in a less spiky structure (Fig. 2b) and instead nano-spikes (Fig. 2c) can be produced at 25V anodisation (Table 1). After the anodisation and etching treatments, some of the specimens were subjected to a silane coupling treatment using the coupling agent KBE-9007 by Shi-Etsu Silicones. Other types of silane coupling agents were also tested, but KBE-9007 was found to provide the highest bonding strength.

2.3. Test specimens
The aluminium with different surface structures were bonded to the CFRTPs by hot pressing to form single-lap specimens in accordance to the Japanese standard JIS K6850. The specimen geometry is shown in Fig. 3. Hot pressing was carried out at 290°C for the A1050 cases and at 300°C for the A5052 under a constant load of ~0.13 MPa for 3 minutes. This was followed
Two types of aluminium with 5 different surface structures (nano-porous, nano-spike, silane + as-rolled, silane + nano-porous, silane + nano-spike) were bonded to CFRTPs with PA6 matrices. Furthermore, A5052 aluminium alloys subjected to three different surface treatments (silane + as-rolled, silane + nano-porous, silane + nano-spike) were bonded to CFRTPs with MXD6 matrices, giving a total of 13 different combinations (see also table later).

Figure 2. Images of the fabricated nanostructures used for the single-lap tests.

Figure 3. Single lap test geometry in accordance to the Japanese JIS K6850 standard.

2.4. Single-lap static tensile tests

Single-lap specimens were tested in static tension on a hydraulic testing machine and the average bonding strength was evaluated from the fracture load and the overlap area by \( \tau = \frac{P}{A} \) according to the Japanese standard JIS K6850. Three tests were carried out for each condition and all tests were carried out until failure. For A5052/PA6 and A5052/MDX6 the tests were carried out with an overlap length of 12.5mm. However, for the A1050/PA6 the specimens subjected
to silane treatments broke in the aluminium part instead of at the interface and therefore the overlap was modified to 5mm to be able to obtain interface fracture. This should be taken into account when comparing this data series to the other two.

2.5. Single-lap fatigue tests

Fatigue tests were carried out for two cases both subjected to a silane coupling treatment namely as-rolled A5052/PA6 (Si-AR) and nano-spike A5052/PA6 (Si-NS). The same geometry as for the static tests (Fig. 3) with an overlap length of 12.5mm were used for the fatigue tests. The tests were carried out in load control with a load ratio of \( R = 0.1 \), and at a test frequency of 5Hz. A Total of 12 A5052/PA6 (Si-AR) specimens and 2 A5052/PA6 (Si-NS) were tested. For the Si-AR case, tests were carried out at loads corresponding to 80%, 70%, 60%, 50%, 40%, 30% of the static shear strength (\( \tau_s^{AR} \)). For the Si-NS case tests were carried out at 40% of \( \tau_s^{AR} \).

3. Results and discussion

3.1. Bonding strength comparison

The average shear strengths obtained from single-lap testing are summarised in Table 2. Tests were also carried out for as-rolled aluminium only subjected to degreasing and then joined to CFRTPs, however the interface strength was practically zero and has therefore not been included in Table 2. It is seen that both the nano-porous and nano-spike structures increase the bonding strength, which has previously been discussed to be a result of the anchoring effect of the nanostructure penetrating into the CFRTP surface. All the specimens subsequently subjected to a silane coupling treatment show significantly improved interface strengths as a result of the improved chemical bonding between the surfaces. The A5052/PA6 case generally showed lower bonding strengths than for A1051/PA6, however as previously mentioned it should be noted that the a shorter overlap length was used for A1051/PA6 might affect the results. Nevertheless, the nano-spike structured A1050 type aluminium resulted in higher bonding strength than for nano-porous structure whereas the A5052/PA6 nano-spike case showed a significantly lower bonding strength than the nano-porous structure.

| Bonded materials | Nano-porous | Nano-spikes | Silane + As-rolled | Silane + Nano-porous | Silane + Nano-spikes |
|------------------|-------------|-------------|--------------------|---------------------|---------------------|
| A1050/PA6*       | 5.7 (2.0)   | 11.0 (4.1)  | 24.4 (2.8)         | 23.9 (1.2)          | 24.9 (1.5)          |
| A5052/PA6        | 17.8        | 13.8        | 17.4               | 20.6                | 14.7                |
| A5052/MXD6       | -           | -           | 23.8               | 24.8                | 21.7                |

A detailed discussion on the effect of the nano-spike structure on the A1051 aluminium alloy bonded to PA6 is given in where nano-spike structures of two different heights were also compared. Here it was found that the higher nano-spikes gave higher interface strength. This was discussed to be a result of the increased anchoring effect from the higher spikes. However, for the nano-spikes fabricated on the A5052 aluminium a significantly lower interface strength was obtained despite the spikes being high. Fig. 4 shows high resolution FE-SEM images of the nano-spikes on the A1050 (Fig. 4a) and A5052 (Fig. 4b) aluminium surfaces where it is seen that the overall shape of the spikes is significantly different. Hence, it is likely that the spikes in Fig. 4a simply are stronger than those in Fig. 4b. For the MXD6 matrix case, the overall bonding strengths were higher than for to PA6, which is believed to mainly be due to the higher strength of the MXD6 matrix. Furthermore, the difference between the bonding strength for the nano-porous and nano-spike cases is less visible.
Fig. 4 shows a comparison between high resolution FE-SEM images of the nano-porous structured A1050 and A5052 aluminium cases. Although both up till now have been referred to as nano-porous, it is seen that the structure for A5052 is slightly spiky and might actually be more of a mixture between the A1051 nano-spike (Fig. 4a) and the nano-porous (Fig. 5a) structures. It is possible to be one of the reasons for the difference between the interface strengths of the A1050 and A5052 nano-porous cases.

**Figure 5.** High resolution FE-SEM images of the two types of nano-porous structures

3.2. Experimentally observed damage mechanisms

Fig. 6 shows examples of the fracture surfaces observed by FE-SEM of the A1051/PA6 case on the A1051 side (top images) and the corresponding PA6 side (bottom images) for the silane coupling treated as-rolled and nano-porous cases. Although similar bonding strengths were observed for these cases (Table 2), the fracture surfaces look quite different. It is seen that the nanostructure results in a more ductile fracture with a high amount of matrix remaining on the fracture surface.

**Figure 6.** Examples of the fracture surfaces observed by FE-SEM of the A1051/PA6 case on the A1051 side (top images) and the corresponding PA6 side (bottom images) for the silane coupling treated as-rolled and nano-porous cases.

3.3. Fatigue testing results

Fig. 7 shows the S-N curve obtained from the fatigue tests for the single-lap specimens. Fig. 7a shows the absolute applied maximum load during the fatigue tests as a function of the cycles and Fig. 7b shows the applied average shear load normalised with respect to the static failure shear load of the silane treated as-rolled case \( (\tau_{AF}) \) to include the variation of the bonding
surface area present in the specimens. As is often the case for fatigue testing, a high degree of scatter is observed in the fatigue lifetime. Comparing Fig. 7a and 7b, it seems that including the variation in the bonding area does not affect the scatter of the data. The grey point is an Si-AR specimen, which showed significant bending in the bonding region. Reverse bending of single-lap joints has been found to improve the bond strength up to a certain angle \cite{11} and furthermore non-flat surfaces have been found to lead to longer fatigue lifetimes. This could explain the significantly longer fatigue life of this particular specimen. Furthermore, as even a few degrees of reverse bending in the specimen can significantly affect the strength \cite{11}, it could be one of the causes of the general scatter in the data. However, the degree of bending in the specimens would have to be measured to confirm this.

Nevertheless, it is seen from Fig. 7 that the fatigue lifetime of the A5052/PA6 (Si-NS) case is in the upper part of the scatter band of A5052/PA6 (Si-AR) despite the static strength of A5052/PA6 (Si-NS) actually being lower than A5052/PA6 (Si-AR) (see Table \ref{table:1} previously). This tendency might be related to the ductile fracture as was observed for the A1051/PA6 nano-porous case (Fig. 6). However, further data and additional observations of the fracture surfaces are necessary to confirm this matter.

4. Conclusion
In the current study a direct bonding method to join aluminium and CFRTP by fabricating a nano-porous or nano-spike structure on the aluminium surface was presented. Two types of aluminium subjected to various surface treatment conditions were bonded to two types of CFRTPs and tested by single-lap testing. The presence of the microstructure was found to improve the bonding properties compared to as-rolled aluminium. By applying a silane coupling treatment, the interface strength was improved but the effect of the microstructure became less visible on the measured bond strength. However, it was seen from fracture surface observations that the surface modified aluminium case experienced ductility to a significantly higher extent than the as-rolled case. Fatigue tests were carried out for the A5052/PA6 for silane coupling
Figure 7. S-N Curve for A5051/PA6 single lap test specimens tested in fatigue (a) for the maximum fatigue load and (b) the normalised average shear load including the effect of variation in the surface area.

treated as-rolled and nano-spike structured A5052 aluminium bonded to a CFRTP with a PA6 matrix. Despite large scatter in the data, the results showed a tendency towards longer lifetimes of the nano-spike case. However, additional data is required to confirm this matter.

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