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EFFECT OF ANODIZING ELECTROLYTE FOR STRUCTURAL ADHESIVES BONDING STUDY OF ALUMINIUM-CARBON LAMINATES COMPOSITES

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ABSTRACT

Fibre metal laminates (FMLs) are multi-component materials that utilize metals, fibres and matrix resins. These composite laminates are in demand in the market for their stiffness and rigidity for structural applications. Their strength is highly dependent on the mechanical interlocking mechanism between the metal surface and the composite laminates. Therefore, the metal surface must be well-treated to ensure a good interfacial interaction between the metal surface and the composite laminates. In this research, FMLs were fabricated using aluminium 6061 and carbon fibre/epoxy laminates. The aluminium surface was treated using anodizing techniques and the effects of three different anodizing electrolytes were systematically investigated to obtain the optimum interfacial strength. The surface morphology was characterized using atomic force microscopy and scanning electron microscopy (SEM). The mechanical strength of these laminate systems was characterized using a universal testing machine via tensile and lab shear techniques. It is predicted that different anodizing electrolytes will result in different anodized surface morphologies that will contribute to the interfacial interaction and the strength of FML systems.

***Keywords*:** Anodizing; fibre-metal laminate; surface morphology; mechanical properties.

INTRODUCTION

Fibre metal laminates (FMLs) have the potential to offer significant improvements to weight savings and durability in airframe structures [1]. FMLs are an advanced hybrid material system consisting of metal layers bonded with fibre-reinforced polymer layers [2-4]. FMLs were originally developed at Delft University of Technology, Netherlands [5]. FMLs are a combination of the best properties of the metal and the composite, which make them especially suitable for the aerospace industry, because of their good fatigue characteristics as well as their lower density. FMLs provide a number of advantages compared to conventional aluminium alloy or even fibre-reinforced plastics. FMLs also have higher specific strength and stiffness, which results in crack growth resistance and fatigue performance. Furthermore, FMLs offer simple production and maintenance methods, easy inspection during service, higher impact resistance and less environment degradation compared to composites [6-11]. However, there are some issues that emerge with hybrid composites, especially in aluminium-carbon composite. Since the strength of these hybrid systems is only based on the mechanical interlocking mechanism between the metal surface and the composite laminates themselves, this bonding is not effective on smooth surfaces. This will result in the problem of adhesive

failure under the stress applied to the system [12]. The fibres in FMLs are insensitive to the fatigue loading, while the metal layers exhibit crack initiation and propagation. The fibres transfer load over fatigue cracks in the metal layers and restrain the crack opening. These FML systems are also easily corrosive when exposed to a humid environment. The existence of a small percentage of voids will act as a point of weakness that will initiate a crack during a loading event and make the product fail faster than the required service period [13]. On the other hand, the presence of water in a humid environment in long-term service offers a risk of electrogalvanic corrosion due to the electrode potential between the carbon and aluminium surface. The aluminium surface in contact with exposed carbon fibre from the composite will tend to corrode [14]. It was proven that the interfacial bonding mechanism will malfunction and accelerate the failure of the composites system due to exposure to air [15]. Therefore, the surface of the aluminium must be treated to prevent corrosion events occurring. Anodic oxide produced by anodizing is one of the best conversion coatings that can protect aluminium in corrosive and abrasive media. It also gives a better appearance to the aluminium surface. Anodizing has greatly extended the applications of aluminium and its alloys [16]. The synthesis and anodization of aluminium to produce nanoporous alumina have been investigated over the years and most of the reported work used phosphoric acid electrolyte with the aid of a temperature-controlled water bath to anodize the aluminium template at low temperatures and in some cases extremely low temperatures [1]. In this work, an aluminium surface was treated by anodizing techniques and the effects of three different anodizing electrolytes were systematically investigated to obtain the optimum interfacial strength.

MATERIALS AND METHOD

Materials

H_3PO_4 (phosphoric content 85%, R&M Chemicals), H_2SO_4 (sulphuric content: 96%, Fisher Scientific),and HNO_3 (nitric content: 65%, Fisher Scientific) were used. Other chemical reagents were all reagent grades and used without further purification.

Anodizing

Aluminium 6061 was used as the template in the phosphoric acid electrolyte. The aluminium template was cut into three pieces and was etched by HNO_3 and water with a ratio of 1:3 to clean away possible grease on its surface. The samples were later rinsed with distilled water and were anodized in three different electrolytes as follows: 11% phosphoric acid (H_3PO_4), 11% sulphuric acid (H_2SO_4) and 11% nitric acid (HNO_3). The voltage was set up to be constant at 30V at ambient temperature. Samples were anodized for 30 mins and 60 mins at a constant current density of 1.5A/ft^2. A stainless steel electrode served as the cathode electrode and an aluminium sample was set to be the anode electrode. A schematic diagram of the electrochemical cell set-up for the anodization process is shown in Figure 1.

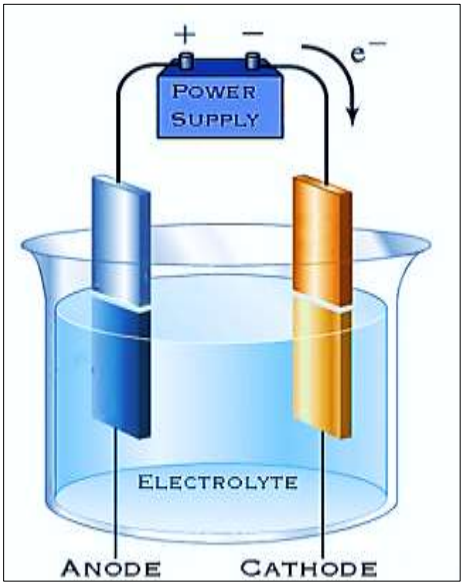

Figure 1. The electrochemical cell set-up for the anodization process.

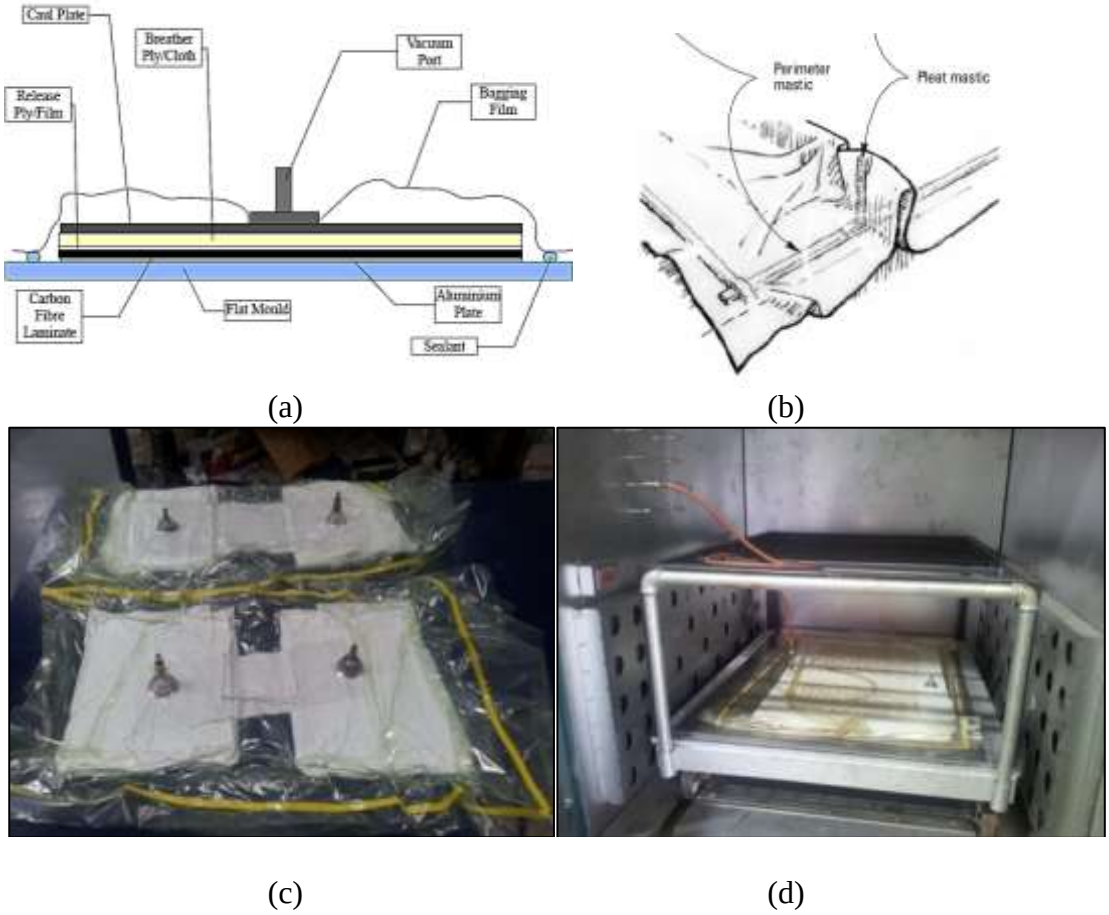

Figure 2. (a) Schematic diagram of vacuum bagging techniques; (b) Pleat or rabbit-ear in thevacuum bagging process; (c) Final look of evacuated carbon-fibre laminates after undergoingthe vacuum bagging process; (d) Oven curing process.

Vacuum Bagging Technique

These aluminium plates were laminated with commercial pre-preg carbon fibre via the vacuum bagging process as shown in Figure 2. The vacuum bagging technique consists of a vacuum port, bagging film, aluminium plate, sealant tape, flat mould, carbon fibre laminates, release film, caul plate and breather cloth. After being evacuated, samples were inserted into an oven for the curing and post-curing process to completely cure with polymeric resin. Afterwards, the samples were ready to be cut according to the specimen for mechanical testing which involved tensile and lap shear tests.

RESULTS AND DISCUSSION

Characterization of the Anodized Surface

Scanning Electron Microscopy

The surface microstructure of the anodized samples was observed by scanning electron microscopy (SEM). Samples were cut into 2 cm × 2 cm size and were run at 2kX magnification using an SE2 signal, as shown in Figure 3. The pores are clearly visible in Figure 3(a) and (b) compared to (c), (d), (e) and (f), where the pores are not clearly present on the surfaces. For the phosphoric acid anodic film in (a), the pore and cell wall dimensions of the film were estimated in the range of 0.29–1.18 µm and 0.12–0.24 µm, respectively. For the phosphoric acid anodic film in (b), the pore and cell wall dimensions of the film were estimated in the range of 0.6–1.8 µm and 0.3–0.9 µm, respectively. The film thickness of (a), (b), (c), (d), (e) and (f) was about 2µm, 2.5 µm, 3.8 µm, 4.6 µm, 14.2 µm, and 28.9 µm, respectively. From these values, phosphoric acid anodic film gives the lowest thickness, followed by sulphuric and nitric acid anodic film. With double the time, the thickness will also be higher, where (a), (c) and (e) all have lower thickness values compared to (b), (d) and (f). This is because the longer time causes more chemical reactions to occur during the anodizing process. It was found that the non-uniform surface distribution of phosphoric acid anodic film leads to the increase in surface roughness and the solvency of phosphoric acid for oxide film is stronger, resulting in a thinner and more porous film [17]. Roughly, the three phosphoric, sulphuric and nitric acid anodic films show uneven pore distributions on their surfaces, have irregular pore mouth shapes and contain various pore sizes. The phosphoric acid anodic film yields a more porous and higher micro-rough surface compared to the sulphuric acid anodic film, while the nitric acid anodic film is porous with cracks. The cracks are clearly seen in (f) when the time was doubled. This case shows that nitric acid was not a good electrolyte for the anodizing process. These cracks will make the surface worse, initiate failure and make it unsuitable as a platform for adhesives. During lamination, holes may cut through load-carrying fibres, reducing the strength of even the most wisely designed composites, resulting in delamination [18].

The porosity of the anodized layer decreased in the order: phosphoric acid anodic film > sulphuric acid anodic film >nitric acid anodic film, while the thickness of the anodized layer decreased in the order: nitric acid anodic film > sulphuric acid anodic film > phosphoric acid anodic film.

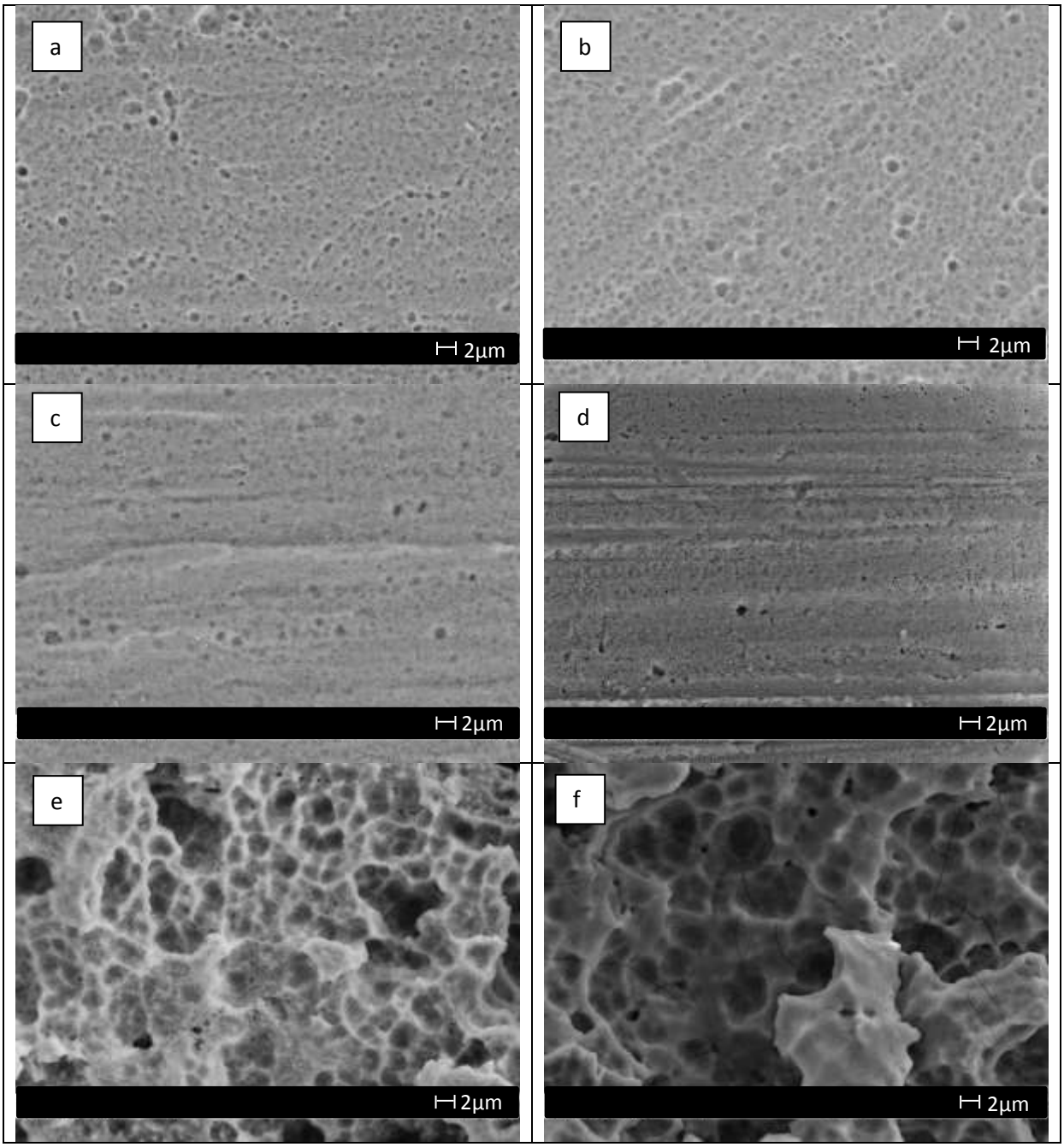

Figure 3. SEM images of anodized samples:(a) phosphoric acid, 30 mins; (b) phosphoric acid, 60 mins; (c) sulphuric acid, 30 mins; (d) sulphuric acid, 60 mins; (e) nitric acid, 30 mins; (f) nitric acid, 60 mins.

Atomic Force Microscopy

The topography of anodized aluminium was observed by atomic force microscopy [1]. The purpose of this characterization method is to image a surface by attractive and repulsive interaction forces between atoms attached at the tip of a cantilever and samples. AFM images with a scanning size of 5 µm were recorded as shown in

Figure 4, while Figure 5 shows the RMS value of the three different electrolytes at 30 and 60 minutes reaction time.

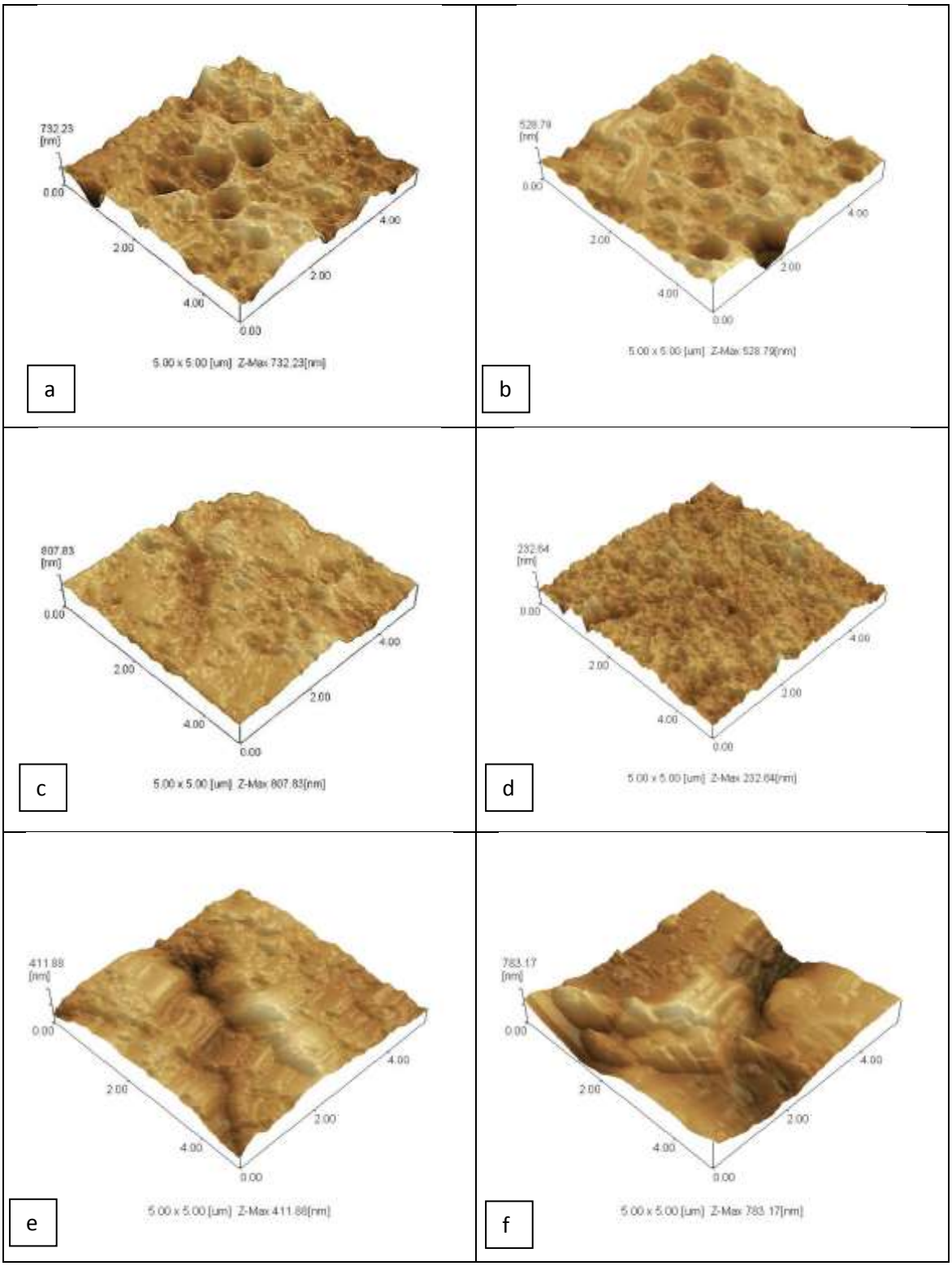

Figure 4. Three-dimensional (3-D) AFM topographical image of anodized samples: (a) phosphoric acid, 30 mins; (b) phosphoric acid, 60 mins; (c) sulphuric acid, 30 mins; (d) sulphuric acid, 60 mins; (e) nitric acid, 30 mins; (f) nitric acid, 60 mins.

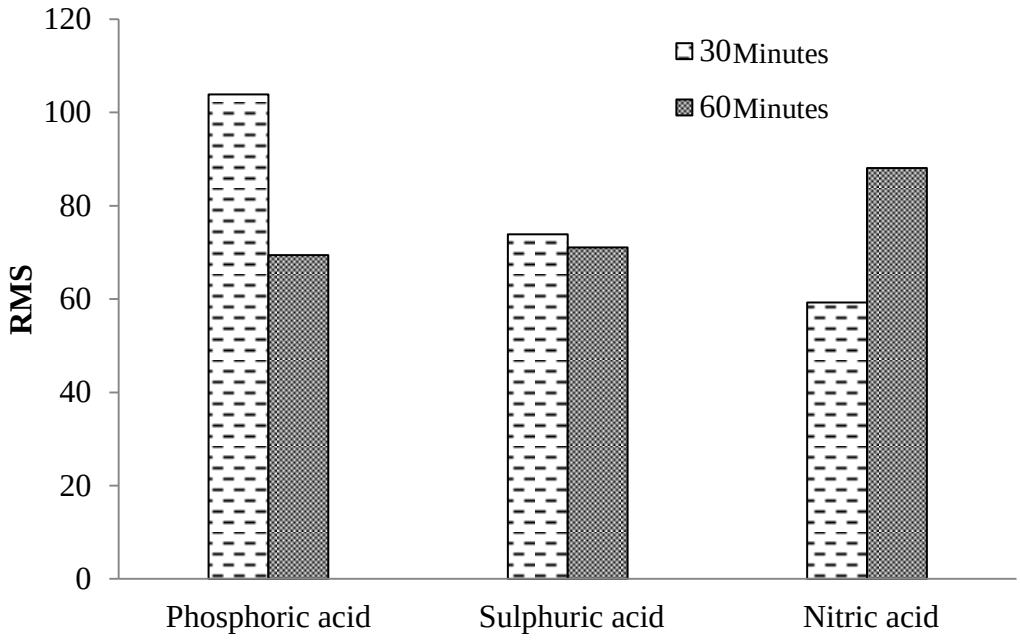

Figure 5.RMS value for the three different electrolytes at 30 minutes and 60 minutes.

From the comparison of the electrolytes, in the first 30 minutes, phosphoric acid anodic film shows the highest RMS followed by the sulphuric and nitric acid anodic films. In contrast, after a 1 hour anodizing period, the RMS value was inversely proportional. As mentioned earlier, the solvency of phosphoric acid for oxide film is stronger. For the first 30 minutes (phosphoric acid), it produces higher roughness until the dissolution of oxide reaches the optimum level and starts to slow down over time. Reducing the dissolution rate causes the roughness to decrease as well. On the other hand, nitric acid shows a different behaviour from phosphoric acid, and the RMS value was still higher after 60 minutes because the dissolution rate of nitric acid is slower. Irregularities in the surface texture indicate the surface roughness. Irregularities can be defined as the peaks and valleys of the aluminium surface. Using phosphoric acid gives the roughest surface on the aluminium plate. Thus, the surface has greater height differences between the peaks and valleys, resulting in the non-uniform contours shown in Figure 4.

From time comparisons, doubling the anodizing period makes the surface become either rougher or less dependent on the electrolyte properties. Increase of the anodizing time was coherent since it contributed to the rougher surface, but it may affect the surface microstructure when the electrolyte reaches the optimum condition. In this study, both phosphoric and sulphuric acid result in an acceptable surface microstructure and morphology,unlike nitric acid which caused cracks on the film as shown in Figure 3(d) and (f). It was stated that increasing the surface roughness of the layer enables the epoxy matrix to penetrate into the irregularities on the surfaces and the pores of anodized surfaces, which generate an effective interlocking mechanism in the interfacial region between the carbon fibre/epoxy and aluminium surfaces [19]. In addition, an extremely smooth surface was unable to create a distinct effect on the surface of the adherent [20]. The surface roughness of the anodized layer decreased in the order: phosphoric acid anodic film > sulphuric acid anodic film >nitric acid anodic film.

Mechanical Testing

Mechanical testing was conducted to determine the mechanical properties of the interface between the aluminium plates and the carbon fibre laminates. The cross-head motion rate was set to be 3mm/min, using the 5582 Instron Universal Testing Machine. The tensile strength of the laminated samples is clearly shown in Figure 6.

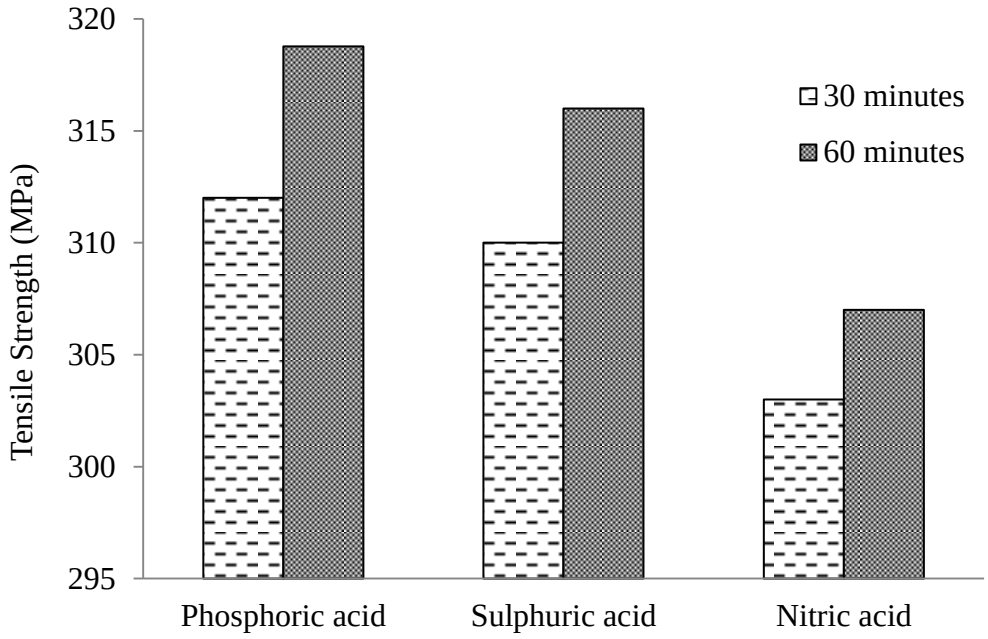

Figure 6. Effect of different anodizing electrolytes on the tensile strength of laminated samples.

Laminated samples with phosphoric acid surface treatment demonstrated the highest strength of 312MPa, followed by the sulphuric acid and nitric acid surface treatment. At double the time, a downward pattern was evident, where the highest strength was the phosphoric acid anodic film, followed by the sulphuric and nitric acid anodic films. This downward value of tensile strength showed that phosphoric acid anodic film provided a rougher surface that exhibited better adhesive properties for the lamination process. Roughness plays a role in the subsequent propagation at the interface, as the rougher surface effectively slows down the growth of multiple interfacial cracks [21]. In this case, phosphoric acid and sulphuric acid show very little difference in strength, which is roughly 0.64%, compared to nitric acid where the difference is twice as much. This shows that nitric acid was unsuitable as an electrolyte for the anodizing process for adhesion purposes. It was reported that when aluminium and carbon fibre are bonding to each other physically, it is hard to bend or to break them apart [22]. Therefore, the maximum tensile strength of laminated samples by different anodizing electrolytes decreased in the order: phosphoric acid anodizing > sulphuric acid anodizing > nitric acid anodizing.

The lap-shear strength of the samples using different anodizing electrolytes prior to bonding is shown in Figure 7. The result shows that the maximum lap-shear strength of the bonding joints was influenced by the different anodizing electrolytes.

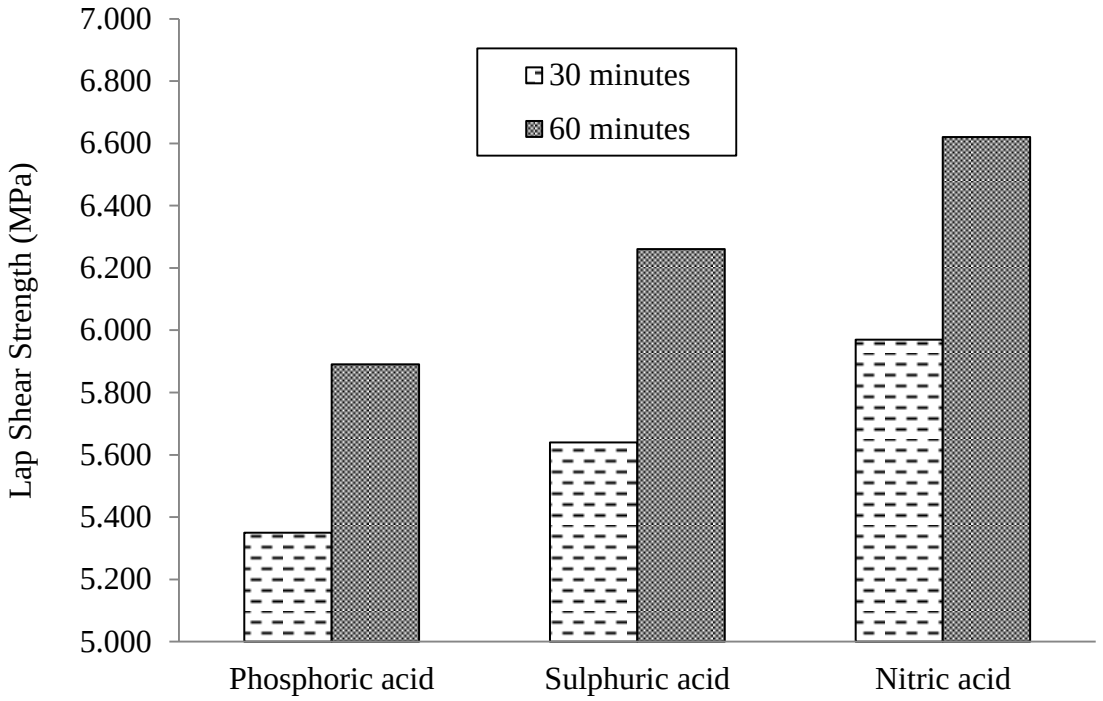

Figure 7. Effect of different anodizing electrolytes on the lap-shear strength of adhesion joints.

A more porous anodic film provides more channels for resin to fill in, resulting in better adhesion and a stronger mechanical lock between laminates, as shown previously by the tensile results. Because of the adhesive glue used during the sample preparation, the laminate samples were not really stuck and the true shear strength was not readily obtained from this study. Hence, the most porous film displayed the lowest shear value and vice versa for both 30 minutes and 60 minutes. However, this result has an insignificant effect on the mechanical properties for this testing, due to the small difference of shear strength for each sample, which was only 5%. It is recommended that further mechanical testing such as flatwise and flexural testing should be done to obtain better results. Also, for the lap-shear sample preparation, samples should be prepared using the same epoxy/resin from pre-preg carbon fibre instead of using adhesive glue to have better adhesive contact between FMLs.

CONCLUSIONS

In this research, different anodizing electrolytes formed different surface morphology, roughness and different tensile and shear strength. Phosphoric acid anodic film contributed to higher porosity compared to sulphuric acid and nitric acid anodic film. Higher porosity is beneficial to improve the lap-shear strength and also beneficial to form a composite intermediate layer that provides a much increased area for physicochemical interactions and enhances the mechanical interlocking effect.

ACKNOWLEGDEMENTS

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