

# Dependence of amino-functionalization on interfacial adhesion strength in epoxy/Al laminated composites

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## Abstract

In epoxy/Al laminated composites, the interface between polymers and metals plays the role of load transfer from epoxy to Al. However, the interfacial bonding between epoxy and aluminum tends to be weak. In this paper, in order to improve the interfacial strength the dendrimer layer---poly (amido amine) (PAMAM) was used to realize the amino functionalization of the interface of epoxy/Al laminated composites. The amino functionalization was tuned by controlling the hydroxyl group concentration through different Al surface treatments. The results show the interfacial adhesion strength between aluminum and epoxy was highly dependent of amino group content. The adhesion strength of epoxy/Al interface is increased by 50 % after PAMAM layer was introduced into the NaOH-treated interface between epoxy and Al surface.

## 1. Introduction

With the rapid development of space technology, the pressurized systems on spacecraft are required to satisfy more rigorous requirements for operating fluid management and propulsion systems. Composite overwrapped pressure vessels (COPVs) have been widely utilized in the aerospace and automotive industries due to the unique combination of properties, providing an inherently safe, lightweight and cost effective storage source for pressurized fluids<sup>[1]</sup>.

However, the weak strength of epoxy/aluminum interface in COPVs limits their application seriously. It was reported that because of Inconsistent deformation between composite layer and liner, after recycling usage (charging and discharging), there buckled and delaminated at the interface<sup>[2,3]</sup> which seriously limits the service time of this composite. In order to improve the security and life of these composites, it is crucial to tune the interface between composite layer and liner. Fowkes and Owens et al<sup>[4,5,6]</sup> summarized two basic adhesion mechanisms: mechanical interlocking and adsorption theory. The mechanical interlocking theory of the adhesion

states that adhesive could penetrate into the pores, holes and crevices and other irregularities of the adhered surface of a substrate to increase the adhesion area, and locks mechanically to the substrate. In our research, different aluminum surface treatments (chemical etching) were undertaken to increase microrough adherend surface which increase adhesion strength due to mechanical interlocking<sup>[7,8]</sup>. Adsorption mechanism states that two phases are connected by chemical bonds, or an organic adhesion promoter layer is normally introduced to the interface. The organic adhesion promoter layer with two reactive groups can act with two phases to improve adhesion strength<sup>[9,10,11]</sup>. As reported, the silane coupling agent was introduced to improve the durability of aluminum bonded to the epoxy resin<sup>[12,13,14,15]</sup>. However, the improvement of interfacial adhesion is very limited, because silane coupling agent molecule can only supply a small quantity of reactive groups to participate in chemical reactions<sup>[16]</sup>, and cannot merge well into the polymer composite system without spoiling the epoxy resin properties.

Here we introduce poly(amido amine) (PAMAM) dendrimer with many Amino groups at the periphery and good solubility into the interface. Moreover, PAMAM can be manipulated on a molecular level for in situ functionalization to anchor different terminal groups<sup>[17]</sup>, which could be used as curing and toughening agent. These superiorities implies that PAMAM is possibly used as a good adhesion promoter. Our previous study indicated the introduction of PAMAM layer onto alumina surface<sup>[18]</sup> results in the obvious enhancement of adhesion strength. Moreover, the hydroxyl group concentration directly affects the interfacial bonding configuration. In this work, the aluminum surface was differently treated with different media, which results in different concentrations of hydroxyl group. The effect of different Al surface treatments on interfacial adhesion strength in epoxy/PAMAM/Al laminated composites was systematically investigated.

## 2. Experimental

### 2.1 Substrate treatment

Samples of  $\text{Ø}15$  mm $\times$ 2mm and 25mm $\times$ 100mm $\times$ 2mm were machined from commercially available aluminum 5A03 alloy sheet with a thickness of 2 mm. Samples were punched into disks of 15 mm diameter (XPS) and 25mm $\times$ 100mm. For the investigation, four different surface states of aluminum sheets were prepared in this section by the following treatment procedures: the 'reference state' of the substrate is set by consecutive ultrasonic cleaning in acetone for 15 min at room temperature. After initial metal preparation and degreasing, the aluminum sheets were etched in a hydrofluoric/nitric acid solution, chromic/sulfuric acid solution or sodium hydroxide solution to get the other three surfaces. All solutions used in this experiment were freshly prepared for each series of treatments. Relatively large volumes (~2 liters) of etchant were prepared for series of tests, to minimize effects of bath depletion on the results. The four chemical etching were used the surface treatments on aluminum. Table.1 shows the chemical etching details .

### 2.2 PAMAM layer preparation

The dendrimer used is poly-(amidoamine) (PAMAM) dendrimer (G0) with ethylenediamine (EDA) core and amino surface groups (Aldrich Incomp.). The schematic chemical structure is shown in Fig.1. The dendrimer was dissolved into methanol to form 20 wt% solutions. Methanol (AR, Harbin Chemical Regent Plant 98%) was distilled once under reduced pressure prior to use and stored at 4 °C until use.

The amine-terminated PAMAM dendrimer layer was prepared by immersing the pre-treated substrates in a PAMAM/methanol solution at  $22 \pm 2$  °C for 1 hour. The solution concentration is  $10^{-3}$  M/L. After taking out from solutions, the substrates are rinsed by ethanol and water, and then dried by nitrogen.

### 2.3 Characterization

The surface topography of aluminum specimens with different chemical etching was characterized by scanning electron microscope (SEM). Fourier Transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy analysis (XPS) were used to verify each step of PAMAM layer preparation. OCA20+DCT21 contact angle measuring system was adopted to test surface contact angle of aluminum surface with and without PAMAM layer.

Interfacial shearing strength between Al and epoxy was tested by instron 5699. Two samples coated

with PAMAMA layer were spliced by epoxy. The sample size is shown in Fig.2.

Each laminated composite sample underwent 15 times testing of interfacial adhear strength. The average value for each laminated composite sample was substituted into the following formula :

$$\tau = \frac{P}{B \cdot L} \quad (1)$$

Where  $\tau$  tensile shear strength, P the maximum Shear failure load of the sample, B the width of shear plane, L the length of shear plane.

## 3. Results and Discussion

The surface morphology of aluminum specimens with different chemical etching is shown in Fig.3. There doesn't appear any change on the aluminum surface cleaned by acetone ultrasonic (Sample A, Fig. 3 a)), because there isn't any chemical reactions in this treatment process. When the aluminum surface was etched by HF/HNO<sub>3</sub> (Sample B), there appears a quite number of holes on the Al surface (Fig.1B). When the aluminum surface was etched by CrO<sub>3</sub>/ H<sub>2</sub>SO<sub>4</sub>(Sample C), there also appears some holes on the Al surface. But it is obvious that the holes density here is lower than Sample B. This is because the HF/HNO<sub>3</sub> has stronger oxidizability than CrO<sub>3</sub>/ H<sub>2</sub>SO<sub>4</sub>. When the aluminum surface was etched by NaOH(Sample D), as there is a serious chemical reaction between aluminum and NaOH solution, a part of aluminum was really etched away. As shown in Fig.3 d), the aluminum surface becomes much rougher but there is no visible hole.

Although the native oxide formed onto aluminum is amorphous at microscopic scale, it is generally agreed that the native oxide on aluminum consists of a mixture of pseudo-boehmite and bayerite<sup>[19]</sup> and it looks then reasonable to assume that the local atomic arrangement (at nanoscopic scale) will reflect the structure of these two oxides<sup>[20]</sup>. The structure of the native oxide on aluminum provides possibility for introducing PAMAM layer.

To confirm the adsorption of PAMAM layer on aluminum surface, the XPS was conducted on Sample A where there contain some groups reacting with PAMAM. Fig.4 shows typical XPS profiles of Sample A surface coated with PAMAM layer. As shown Fig. 4(a), the C 1s peak is decomposed into four components located at 285eV , 286eV, 288.4eV and 290.1eV, which are ascribed to C-C (C-H), C-N, N-C=O and CO<sub>3</sub> bonds respectively. The appearance of C-C (C-H), C-N, N-C=O

confirms the adsorption of PAMAM layer onto aluminum surface.

The O1s peak (Fig. 4(b)) has been decomposed in three characteristic peaks corresponding to the oxide component of the oxidized layer (Al–O) at 531.6eV, the hydroxyl component (Al–OH) at 533eV and a component (noted  $C_xO_yH_z$ ) at 532.3eV corresponding to oxygen-functionalized carbonaceous contamination.<sup>[20]</sup>

The Al2p peak (Fig. 4(c)) is usually decomposed into three components. Two main components appear in the Al 2p peak (Fig. 4(c)) at 72.3eV and 74.8eV, which correspond to the metal (labeled as Al0 in Fig. 4(c)) and the oxide (labeled as AlIII in Fig. 4(c)) respectively. The small peak denoted AlIII int at 74.2eV is assigned to aluminum ions located at the metal/oxide interface<sup>[21]</sup>.

As PAMAM structure contains N element, the N1s (Fig. 4(d)) will also signal the reaction between alumina and chemical groups in PAMAM. In addition, parameters (peak line shape, FWHM) of the N1s peaks corresponding to the different interactions have been obtained. Based on the previous results reported by D. Mercier<sup>[20]</sup>, we use the same parameters in the present study to fit our experimental results. However, as it seems very unlikely that metallic aluminum can be present at the surface of our samples, the peak corresponding to interaction with pure aluminum is ignored and only three peaks are introduced in our fitting process (80% Gaussian -20% Lorentzian; FWHM = 1.5eV). The fitting spectrum is shown in Fig.4 (d). The peak at 400.5eV can be ascribed to donor-acceptor interactions between the amine terminations of the molecule and aluminum cations (Lewis-like mechanism leading to O–Al...N bonds). The feature at 401.4eV corresponds to the interaction between PAMAM and hydroxyl groups, which leads to the formation of Al–OH...N hydrogen bonds (Bronsted-like mechanism). The third component at 402.8eV is ascribed to interaction with carbonaceous contamination ( $C_xO_yH_z$ ...N bonds).

The above results conclude that besides van der Waals attraction, there is chemical bonding on the interface of PAMAM and aluminum oxide. And the adsorption behavior of PAMAM to alumina correlates to the substrate state very much.

The adsorption of PAMAM to aluminum surface was further verified by FTIR-ERS, as shown in Fig.5. Judging from the amide peak intensities, the G0 PAMAM yields a significant coverage on all the different substrates. The amide I and amide II bands at 1648 and 1556 cm<sup>-1</sup> (G0 PAMAM bulk ) have

the similar shifting trend towards higher frequency (Fig.5b). Because the amide I and amide II bands are assigned to ( $\nu C=O$ ) and intricate ( $\delta NH + \nu CN$ ), the different chemical shifts are attributed to the inductive effect of hydroxyl group or Al<sup>3+</sup> and their group electronegativity. This observation gives us further proof for the chemical interaction of the PAMAM with the Aluminum surface.

The quantitative analysis of XPS and FTIR are shown in Table 2. We note that the N content is basically proportional to hydroxyl concentration. Namely, NaOH treatment results in most adsorption of PAMAM while acetone treatment results in least adsorption of PAMAM. The quantitative analysis of FTIR also proves this point, meaning that Amide I + II peak area is largest in the case of NaOH treatment. Fig.6 summarizes the interfacial shear strength between aluminum and epoxy. There are two key aspects worth highlighting. On the one hand, without PAMAM layer, the interfacial shear strength has some relationship with the surface treatment method. We can see that CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> treated aluminum surface has strongest adhesion (up to 6.2 MPa) with epoxy, while acetone treated surface has weakest adhesion (4.6MPa) with epoxy, a little weaker than NaOH treated surface. As well known, one of the two basic adhesion mechanisms---mechanical interlocking indicates that the interface configuration is highly related to adhesion strength. As shown in surface morphology of aluminum treated by different solutions in Fig.7, the HNO<sub>3</sub>/HF and CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> solutions causes the higher density holes, thus the mechanical interlocking effect should be stronger. As confirmed by adhesion property, the HNO<sub>3</sub>/HF and CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> solution treatments give rise to higher interfacial shear strength. This is in good agreement with the previous observation. On the contrary, NaOH and acetone treatments do not give rise to too many holes, so the mechanical interlocking effect is weak. It is reasonable that their corresponding interfacial shear strengths are smaller than the first two cases. This result can be explained by mechanical interlocking mechanism. As seen from SEM images, the HNO<sub>3</sub>/HF and CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> cause quite a number of holes on the aluminum surface, which will be embedded by epoxy thus forms the “mechanical lock”. So the adhesion strength must be higher.

On the other hand, after adsorption of PAMAM to treated aluminum surface, the interfacial shear strength has further enhancement compared to that without PAMAM. In the case of NaOH treatment, the interfacial shear strength reaches up to 7.1MPa

after introduction of PAMAM layer, which has an increase by 50% in comparison with that in the case of acetone treatment (4.6MPa). The adhesion strengths of HNO<sub>3</sub>/HF and CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> treated interface subside to NaOH treatment. The further enhancement can be schematically explained by Fig. 7. As discussed previously, both XPS and FTIR results support the viewpoint that PAMAM layer has been chemically adsorbed to the treated aluminum surface. Moreover, the additional NH<sub>2</sub> groups promote the post curing process of epoxy. These two aspects mainly contribute this further enhancement of adhesion strength by PAMAM layer.

#### 4. Conclusion

The interfacial shear strength depends on treatment method and adsorption of PAMAM layer. CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> treatment results in the strongest adhesion strength, up to 6.2MPa due to strong mechanical interlocking effect. The interfacial shear strength is further enhanced after PAMAM adsorption on aluminum surface. However, the strongest adhesion strength (7.1MPa) happens to the NaOH treated interface, which has an increase by 50% in comparison with that in the case of acetone treatment (4.6MPa). This means that the adsorption effect dominates the adhesion mechanism.

#### 5. Acknowledgements

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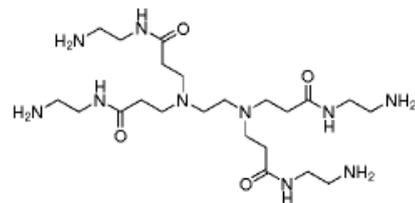
**Table.1** The chemical etching details

Sample	Aluminum surface treatment	Solution composition	Immersion time	T(°C)
A	Acetone ultrasonic cleaned	as much as suffices	10 min	20
B	HF/HNO <sub>3</sub> Etched	HF 13% HNO <sub>3</sub> 35% deionized water 52% (volume fraction)	1.5 min	20°C
C	CrO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub>	CrO <sub>3</sub> 50g/L H <sub>2</sub> SO <sub>4</sub> 250g/L	14 min	60°C

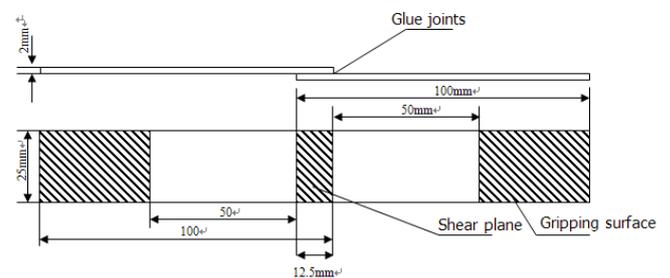
	Etched	(deionized water)		
D	NaOH Etched	50g/L (deionized water)	5 min	65°C

**Tab.2** The quantitative analysis of XPS and FTIR for four samples

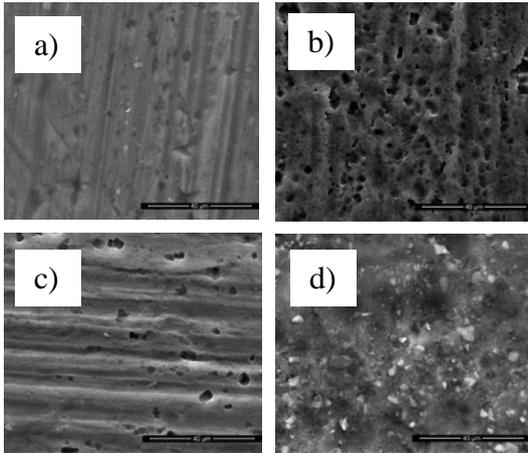
Aluminum surface treatment	XPS		FTIR
	N1s Elemental percentage analysis	Substrate Hydroxylation percentage	amide I + II peak area (A.cm <sup>-1</sup> )
Acetone ultrasonic cleaned	3.5%	28%	1.8
HF/HNO <sub>3</sub> etched	4.7%	33%	2.5
CrO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> etched	17.2%	41%	2.6
NaOH etched	17.5%	58%	7.6



**Fig.1** The schematic chemical structure of PAMAM

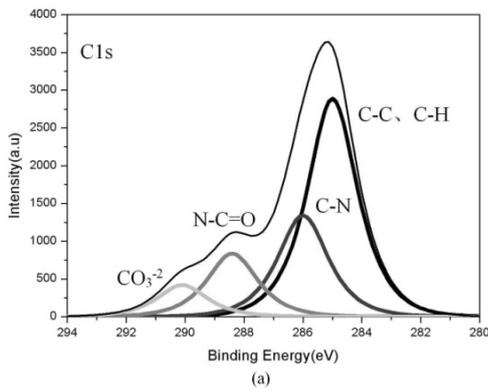


**Fig.2** Sample size of Interfacial shearing strength test

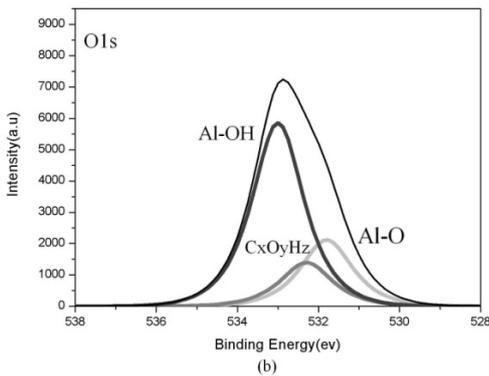


**Fig.3** Surface morphology of aluminum after different surface treatments

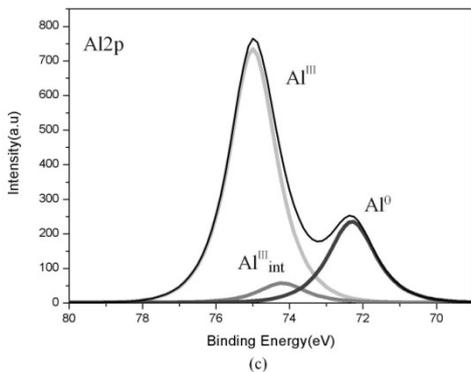
a). Acetone ultrasonic cleaned; b). HF/HNO<sub>3</sub> etched; c). CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> etched; Dd) NaOH etched



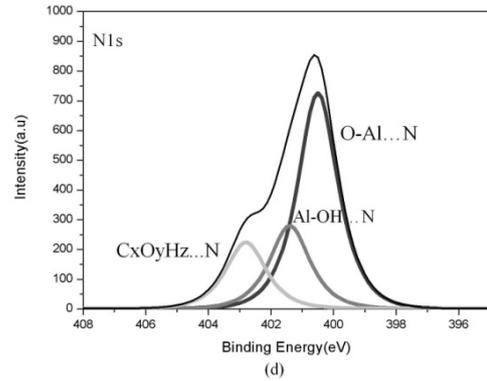
(a)



(b)

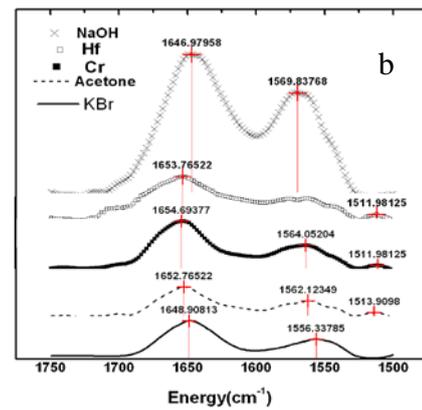
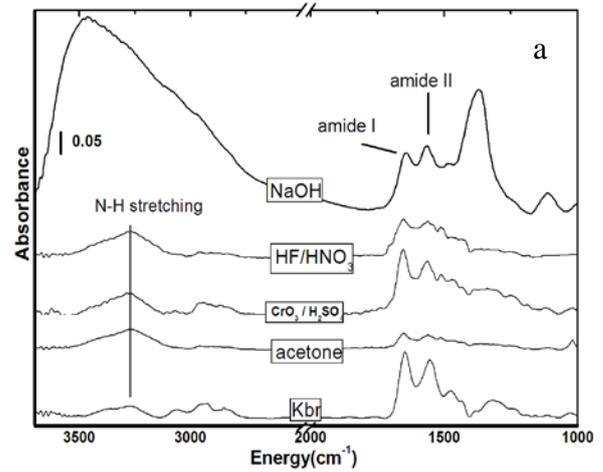


(c)

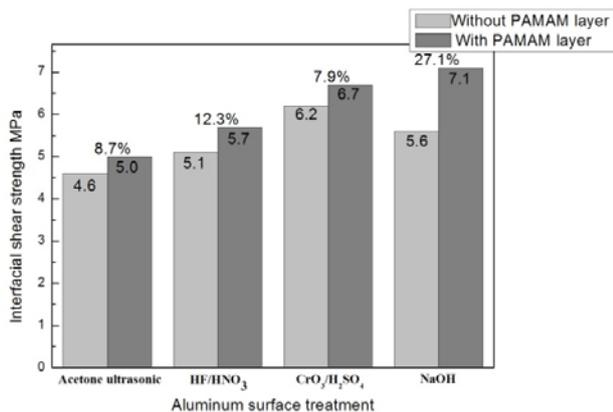


(d)

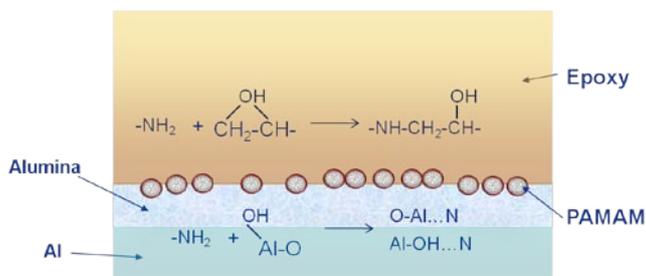
**Fig.4** Decomposition of the (a) C 1s; (b) O 1s and (c) Al 2p (d)N1s peaks for aluminum samples coated with PAMAM layer.



**Fig.5** a. FTIR-ERS of amine-terminated PAMAM bulk and PAMAM-treated surfaces; b. The details of the amide region



**Fig.6** Interfacial shear strength of samples with and without PAMAM



**Fig.7** Schematic of PAMAM as adhesion promoter between Al and epoxy

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