

# Bonding Properties Between Nitrile–Butadiene Rubber and Aluminum Alloy Treated by Anodizing Methods

Xiao-Feng Zhang,<sup>1</sup> Li Fan,<sup>2</sup> Xu-Hui Zhao,<sup>1</sup> Li-Qun Zhang,<sup>1,2</sup> Li Liu,<sup>1,2</sup> Yu Zuo<sup>1</sup>

<sup>1</sup>*School of Material Science and Technology, Beijing University of Chemical Technology, Beijing 100029, China*

<sup>2</sup>*Center of Advanced Elastomer Materials, Beijing University of Chemical Technology, Beijing 100029, China*

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**ABSTRACT:** In this work, the bonding properties between the LD7 aluminum alloy anodized by sulfuric acid or phosphoric acid and nitrile–butadiene rubber (NBR) were investigated. The bonding properties between the anodized aluminum alloys and NBR were compared with those between aluminum alloys treated by burnishing or sandblasting and NBR. The results revealed that, in comparison with sulfuric acid anodized samples, samples anodized in phosphoric acid solutions showed higher 90° peel strength. Under the same conditions, an increase in the anodic film thickness in the studied range may improve the adhesion property between rubber and an aluminum alloy. In comparison with aluminum alloys treated by burnishing or sandblasting, the surface of the

anodized aluminum alloy showed homogeneously dispersed pores, which resulted in better and homogeneous bonding properties. A vacuum-drying process on the anodized aluminum alloys after they were coated with adhesives facilitated penetration of the adhesive molecules into the pores on the oxide layer, which considerably improved the bonding properties. In addition, rubber macromolecules could also penetrate the pores in the aluminum oxide layer, leading to a strong physical anchor–hold interaction after a long time of soaking and diffusion. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 283–289, 2009

**Key words:** alloys; rubber; adhesion

## INTRODUCTION

Because of their light weight and high strength, composites of aluminum alloys and rubber have become more and more popular among the many metal–rubber composite materials. Compared with steel, aluminum alloys show some merits, such as lighter weight, higher heat conductivity, better elasticity, and better performance at a high speed. However, aluminum alloys also have some shortcomings, and easy oxidation is one of them. When exposed to air for a very short period of time, the surface of an aluminum alloy reacts with oxygen to form a nanoscale oxidized layer, which has a loose and non-uniform structure and leads to poor bonding performance between the aluminum alloy and rubber.<sup>1</sup> Thus, surface treatments of aluminum alloys are usually carried out to improve the bonding properties. Recently, dry sandblasting has been frequently adopted to effectively remove rust on metal surfaces;<sup>2</sup> this, however, results in a surface too smooth to achieve good bonding strength with rubber. Therefore, effectively improving the roughness

on the metal surface to increase the contact area between the adhesives and aluminum alloy is one of the keys to enhancing the bonding strength.

Anodizing provides the answer to that problem. An aluminum alloy treated by the anodizing process shows high hardness, good abrasion resistance, anti-septic properties, and strong bonding with substrates,<sup>3,4</sup> and it has been widely used in modern industry. Anodizing is an electrochemical reaction on the alloy surface when the aluminum alloy is placed as the anode in the proper electrolyte.<sup>5,6</sup> When electricity is added, a reaction will take place, forming an oxide layer on the alloy surface. The oxide layer produced by the anodizing process has a double-layer structure. The inner layer is thin and compact, whereas the outer layer is thick, and in it, many nanoscale holes vertical to the surface are distributed uniformly.

Adhesive molecules can easily penetrate those holes and form a strong anchor–hold structure. Therefore, it is very proper to use the oxide layer as a transition layer between an aluminum alloy and other composite materials. For example, most parts made with an aluminum alloy in airplanes, including the cover skin, are designed to use the anodized oxide layer to bond the aluminum alloy and dope. The anodized oxide layer is also the place of adhesion for adhesives to bond the aluminum alloy and

Correspondence to: L. Liu (liul2001cn@yahoo.com.cn or 2005000365@grad.buct.edu.cn).

**TABLE I**  
**Specified Conditions of the Anodizing Processes**

Process	Electrolyte	Characteristic	Voltage (V)	Current density (A/dm <sup>2</sup> )	Anodizing time (h)
1	180 g/L sulfuric acid	Constant-current oxidation		1	0.5
2	acid			1	1.0
3	100 g/L phosphoric acid	Constant-voltage oxidation	20		0.5
4	acid		20		1.0
5			30		0.5

other metals. However, few articles have been published on improving the bonding strength of aluminum alloy–rubber composite materials with the anodizing technique.

In this study, we chose nitrile–butadiene rubber (NBR) to study the adhesion technique and performance with aluminum alloys and especially the relationship between anodizing and bonding properties. NBR contains strongly polar cyanide groups and possesses high oil resistance, which makes it widely used in oil-sealing materials.

## EXPERIMENTAL

### Materials

NBR (nitrite content = 41%; trademark 220S) was supplied by JSR Co. (Yokkaichi, Japan). The substrate to which rubber was bonded was the LD7 aluminum alloy. The adhesive (Chemlok 250) was purchased from Lord Co. (Shanghai, China). Other additives, including silica and curing ingredients, were bought from a chemical store.

The recipe for the rubber composite was as follows: NBR, 100 phr; ZnO, 5 phr; setearic acid (SA), 1.5 phr; sulfur (S), 2 phr; N-cyclohexyl-2-benzothiazole sulphenamide (accelerator CZ), 1 phr; tetramethyl thiuram disulfide (accelerator TT), 1 phr; N-cyclohexyl-N'-phenyl-p-phenylene diamine (antioxidant 4010A), 1 phr; polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (resin) (antioxidant RD), 1 phr; and white carbon black, 50 phr. The chemical composition of the aluminum alloy LD7 included the following: Cu, 1.9–1.5; Mg, 1.4–1.8; Fe, 1.0–1.5; Ni, 1.0–1.5; Ti, 0.02–0.1; Si, <0.35; and Al, the balance.

### Anodizing processes

Two kinds of anodizing methods were applied in this experiment: anodizing with 180 g/L sulfuric acid (98 wt %) and anodizing with 100 g/L phosphoric acid. The sample size was 60 mm × 25 mm × 3 mm. A small hole with a diameter of 1.5 mm was dug at the edge of the samples to link a wire, and lead board was used as the cathode. A pulse/direct-current power supply (TH-10A, Tsinghua Unisplendour Co., Ltd., China) was used in the entire

anodizing process. The typical anodizing process was as follows. Samples were washed with water before being degreased and deoiled by acetone, and then they were further deoiled with alkaline solutions. Before and after anodizing, samples were washed with deionized water again. Then, the samples were dried for tests and measurements. The specified conditions for the anodizing processes are listed in Table I.

### Burnishing and sandblasting processes

Typically in the burnishing process, the samples were burnished with sandpaper to remove rust and then cleaned with acetone and dried.

In the sandblasting process, the samples were first degreased and deoiled with acetone and then sandblasted with quartz sand. Then samples were cleaned with compressed air and acetone and dried.

### Preparation of the samples

After the anodizing process, the surface of the aluminum alloy sample was washed with deionized water. Then, there were two methods for drying and adhesive coating. First, samples were dried under the vacuum condition under 150°C for 2 h, then uniformly covered with Chemlok 250 on the surface, and dried again under the vacuum condition for another 0.5 h. Second, samples were dried in a normal atmosphere under 150°C for 2 h, then coated with Chemlok 250, and dried again in the normal atmosphere for another 0.5 h.

After being coated with the adhesive, the aluminum alloy samples were bonded with NBR compounds and then placed into a mold to vulcanize the rubber at the temperature and pressure of 150°C and 150 kg/cm<sup>2</sup>, respectively.

### Measurements

A TT230 digital vortex thickness tester (Beijing Shidai Keji, Ltd., Beijing, China) was used to measure the thickness of the aluminum oxide layer by two modes: continuous measurement and individual measurement. The 90° peel experiment was carried out to evaluate the bonding strength between the

metal and rubber according to Chinese National Standard GB7760-87. Images of the sample morphology were taken with a Hitachi S-4700 scanning electron microscope (Hitachi Ltd., Tokyo, Japan). For scanning electron microscopy (SEM) testing, samples were cut to the size of 0.5 cm × 0.5 cm × 3.0 mm and coated with gold. The energy-dispersive spectra of the samples were measured with a PV7746/40 ME device (EDAX, USA) on an effective area of 10 mm<sup>2</sup>.

## RESULTS AND DISCUSSION

### Effects of the anodizing processes

The thickness of the oxide layer on the aluminum alloy surface after treatment with different processes was measured, the 90° peel strength between the aluminum alloy and the rubber for the composites dried under the vacuum condition was also measured, and the results are listed in Table II. From Table II, it is clear that, in comparison with the sulfuric acid method (processes 1 and 2), samples treated in phosphoric acid solutions (processes 3–5) showed higher 90° peel strength. This mainly resulted from the obvious differences between the surface microstructures, topographies, and compositions of the anodic films that underwent sulfuric acid anodizing and phosphoric acid anodizing.<sup>7,8</sup> Meanwhile, under the same electrolyte conditions (processes 1 and 2 or processes 3 and 4), an increase in the anodizing time produced a thicker oxide layer and improved the adhesion property between the rubber and aluminum alloy. Because holes were formed by stress concentration when the oxide layer grew vertically to the surface, the increase in the layer thickness led to an increase in the vertical depth of the holes, which effectively enlarged the adhesive surface area. In comparison with processes 3 and 4, samples made with process 5 showed higher 90° peel strength. On the one hand, this is related to the increase in the thickness of the oxide layer. On the other hand, this is related to the microstructure of the pores of the oxide layer caused by different anodizing voltages. Generally, the pore diameter of the oxide layer on aluminum increases with an increase in the anodizing voltage,<sup>9–11</sup> and

**TABLE II**  
Peel Strength Between the NBR and Aluminum Alloy Treated by Different Anodizing Methods

Property	Anodizing process number				
	1	2	3	4	5
Thickness of film (μm)	7.0	11.0	8.0	13.0	15.0
Peel strength (kN/m)	10.5	14.4	14.6	19.1	21.5

**TABLE III**  
Influence of the Drying Conditions on the Peel Strength Between the NBR and Anodized Aluminum Alloy

Drying condition	90° peel strength (kN/m)
<i>In vacuo</i>	21.5
Under atmospheric pressure	18.5

this is helpful for the adhesive penetrating the pores and improves the bonding strength.

At the beginning of anodizing, a thin but compact alumina barrier layer is formed on the surface of the aluminum alloy (ca. several tens of nanometers). Because the volume of the alumina is smaller than that of the consumed aluminum alloy, when the barrier layer is formed, the inner stress of the barrier layer is centralized and produces pulling stress at the outer surface of the barrier layer, which leads to a crack at the outer surface of the barrier layer. However, a high current density and a partial temperature increase around the crack would seal the crack. Under such conditions, it would finally produce holes and form a hole-rich layer above the barrier layer. Obviously, the number and diameter of the holes are highly affected by the electrolyte and the electrolysis voltage.

### Effects of the drying conditions

Table III compares the peel strength of the anodized aluminum alloy and NBR material prepared under different drying conditions (e.g., *in vacuo* and under atmospheric pressure). The peel strength of the composites dried *in vacuo* was obviously higher than that of the composites dried under atmospheric pressure. Adequate soakage and adhesion of the adhesives to the bonding surface are prerequisites to basically ensure high bonding strength. To allow adhesive molecules to penetrate the holes produced by anodizing, the air in the holes has to be removed first. Apparently, it is more effective to dry *in vacuo*, and this can also get adhesive molecules into holes more easily. In that case, the contact area of the adhesives and the small openings of the anodized layer are effectively increased, and the bonding strength between the adhesive layer and aluminum alloy will be improved. The anchor-hold interaction offered by the small openings of the structure is sufficiently developed.

### Comparison of the anodizing process and other treatment methods

Table IV compares the bonding strength of the NBR and aluminum alloy with different treatment methods. The results show that the drying condition has little influence on the bonding properties in both burnishing and sandblasting treatments. The reason

**TABLE IV**  
**Comparison of the Peel Strengths Between the NBR and Aluminum Alloy Treated by Different Methods**

Treatment method	Anodizing		Burnishing		Sandblasting	
Drying conditions	<i>In vacuo</i>	AP	<i>In vacuo</i>	AP	<i>In vacuo</i>	AP
90° peel strength (kN/m)	21.5	18.5	5.2	5.3	16.2	15.5

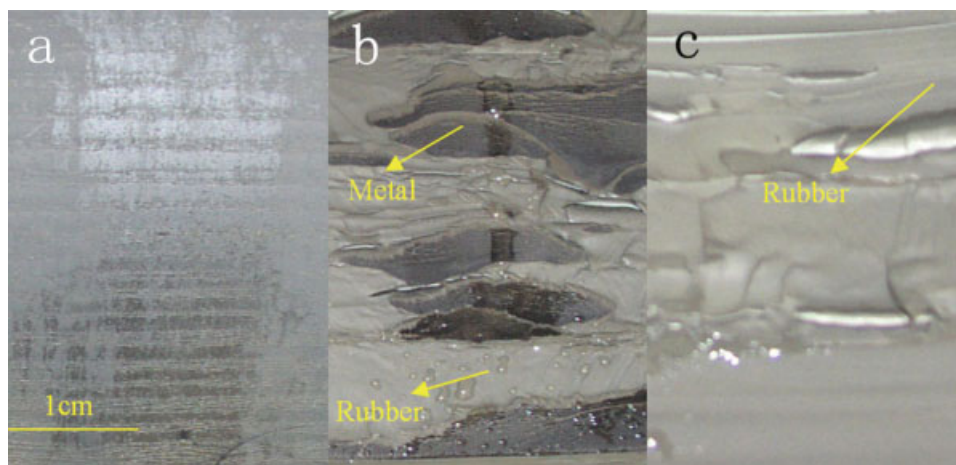
AP = under atmospheric pressure.

is that the surfaces from these two kinds of treatments are so smooth that drying under either condition will not have much influence on the movement or penetration of the adhesive molecules. With the anodizing treatment, especially under vacuum-drying conditions, the highest bonding strength is achieved. Moreover, the burnishing treatment results in the worst bonding performance. This demonstrates that the treatment of the metal surface plays a key role in improving the bonding properties.

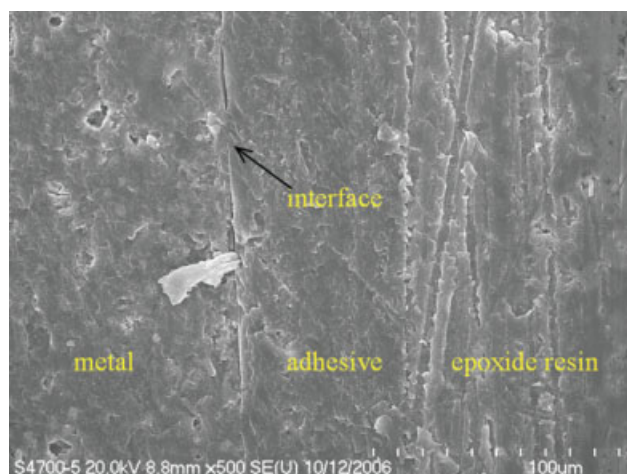
Figure 1 shows the surface topography of the aluminum alloy with three different treatments after the peel experiment. According to Figure 1(a), the surface of the aluminum alloy was very smooth, and failure took place between the adhesive and the alloy. The alloy surface was exposed, so the peel strength was extremely low. Figure 1(b) shows that under the sandblasting treatment, part of the peeling was rubber failure, which made a good contribution to the peel strength, whereas part was a failure between the rubber and adhesive, which also made a small contribution. The peel strength under the sandblasting treatment was not uniformly distributed because of the nonuniformly distributed roughness caused by the sandblasting treatment. Sandblasting treatment can improve the peel strength between a metal and rubber to a certain level, but the peel strength can drop very quickly

because of failure between an adhesive and rubber. In comparison with these two processes, anodizing is the process that results in the best bonding properties. Figure 1(c) shows that the alloy surface is not exposed after peeling off, and the failure happens right in the rubber itself; this suggests that the adhesive molecules are firmly anchored to the small openings of the oxide layer.

To observe the bonding surface of the adhesive and anodized oxide layer, an epoxide resin technique was used to prepare the sample for SEM testing. First, the adhesive was spread homogeneously on the metal surface. When the adhesive solidified, the metal with the adhesive was inserted into a plastic pipe, the diameter of which fitted the metal's size. The epoxide resin was put into the pipe to fill the space between the metal and pipe. After the resin solidified, the pipe was cut, and the sample was obtained. A section of the sample was polished before SEM observation, and the result is shown in Figure 2. Figure 2 shows a clear interfacial layer between the adhesive and alloy surface. Some regions are vague; this suggests good bonding. Some regions are clear, and this suggests poor bonding. The adhesive molecules that penetrated the oxide layer cannot be clearly seen in the picture because the thickness of the layer is very small (at a micrometer level), whereas the small openings are at a



**Figure 1** Surface topography of the aluminum alloy treated with three different methods after peeling: (a) burnishing, (b) sandblasting, and (c) anodizing. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



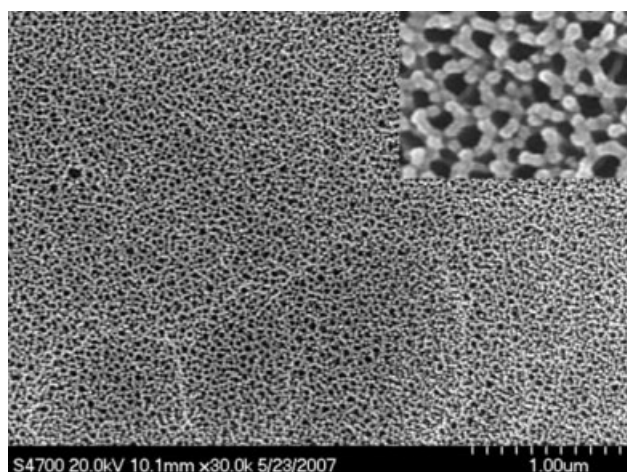
**Figure 2** Bonding surface of the adhesive and oxide layer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

nanolevel, and the oxide layer could be damaged during polishing.

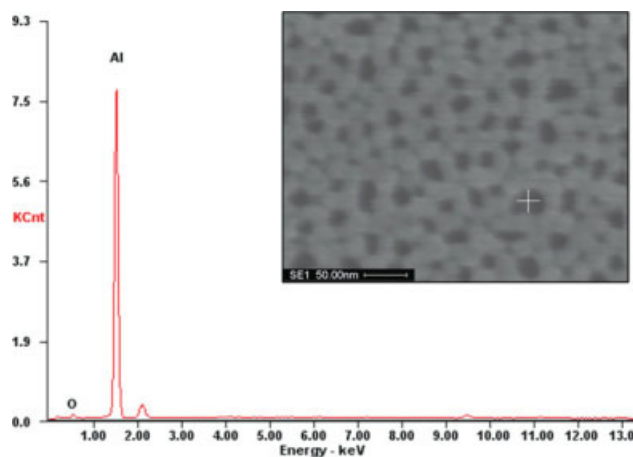
#### Permeation effect of NBR into the oxide layer

There are two types of interactions between an adhesive and metal: one is physical, and the other is chemical. For the oxide layer formed by anodizing, the physical interaction is very important. In this article, because some ingredients in the Chemlok adhesive contain functional groups, such as phenolic resin, which can have both types of interactions, the system has been simplified by the deduction of the adhesive to investigate the permeation of rubber macromolecules.

Figure 3 suggests that there are lots of small openings on the alloy surface with the anodizing treatment, and they are all well distributed and are



**Figure 3** SEM photograph of the alloy surface treated with the anodizing method.



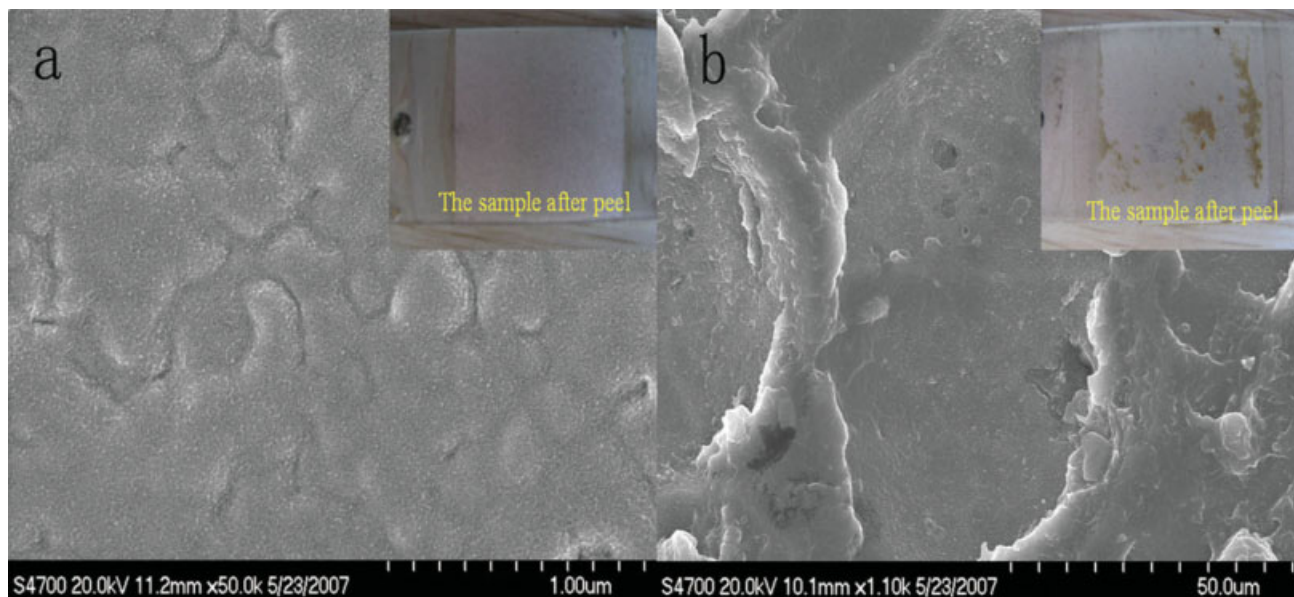
**Figure 4** Energy spectrum analysis of the alloy surface treated with the anodic oxidation method. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

several tens of nanometers in size. Because of the different growing rates, the heights of the small openings are different.

Figure 4 shows that abundant oxygen and aluminum exist on the treated surface, and other elements such as copper and magnesium that exist in the alloy are not found on the surface.

After being pressing with a pressure of 15 MPa, the composites of the anodized aluminum alloy and rubber compound (including sulfur, nano-SiO<sub>2</sub>, and other fillers and additives) were set for 1 day or 10 days before testing to investigate the penetration of rubber by SEM and to measure the element distribution on the peeled surface. The results are displayed in Figures 5 and 6.

Figure 5 shows the topography of the peeled alloy surface of the composites 1 day and 10 days after the anodized aluminum alloy was bonded with rubber. Unlike Figure 3, the small openings on the nanoscale could no longer be found. The draped morphology in Figure 5(a) was formed after rubber was peeled off from the surface of the metal. The rubber layer left on the substrate was very thin, and the surface of the metal was almost exposed. The inset of Figure 5(a) is a picture of the sample after the peel experiment, and the rubber layer can hardly be observed. In contrast, in the inset of Figure 5(b), the rubber-rich phase can be clearly observed; the peel experiment was carried out 10 days after the adhesion. At a larger magnification, as shown in Figure 5(b), it can be clearly seen that part of the rubber remained on the alloy surface after peeling. Besides, the rubber layer was very thick, and the aluminum alloy substrate was totally covered; this indicated that the combination of the metal and rubber was very strong.



**Figure 5** Surface topography of the peeled surface placed at (a) 1 day and (b) 10 days. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

As is well known, uncured rubber can flow, and the behavior follows Newton's Law of Flow:

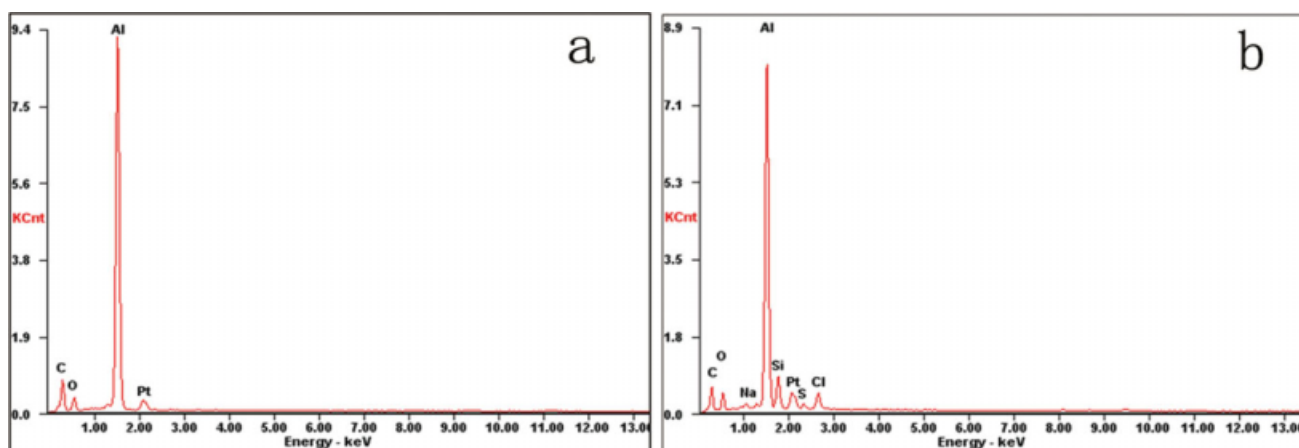
$$\varepsilon = \sigma_0(t/\eta) \quad (1)$$

where  $\varepsilon$  is the strain of the rubber,  $\sigma_0$  is the stress of the rubber,  $\eta$  is the viscosity of the rubber and  $t$  is the flow time.

Equation (1) shows that the flow deformation of NBR gross rubber is directly proportional to the time under a certain viscosity and tension. NBR molecules can fully soak the surface of an anodized oxide layer after a long flow process. In particular, some of the NBR molecules with lower molecular weights will be helpful in increasing the rate and

depth of soakage and then forming stronger adhesion interaction.

The energy spectrum in Figure 6 confirms these analyses. In Figure 6(a), a significant amount of carbon element appears in addition to aluminum and oxygen, indicating that a small quantity of NBR macromolecules soaked into the holes in the oxide layer. To acquire a specimen from the sample that was set for 10 days, the sample was first placed in acetone. The rubber on the peeled surface swelled, but those that penetrated the holes could not swell much because of the confined space. After 24 h, the interaction between the outside rubber layer and aluminum surface became very weak. The rubber-rich layer



**Figure 6** Elemental distribution of the peeled surface placed at (a) 1 day and (b) 10 days. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

could be easily detached, whereas the rubber in the holes was not pulled out. With this specimen, the status of rubber penetration could be evaluated more accurately. Therefore, the area in which the outside rubber-rich layer was uncovered was studied with SEM and energy dispersive X-ray spectroscopy, and the result is shown in Figure 6(b). Silicon (from nano-SiO<sub>2</sub>) and sulfur elements emerged with a higher content of carbon and oxygen in comparison with Figure 6(a), and this indicated that with the prolongation of the setting time, the rubber molecules had enough time to soak and diffuse on the surface of the alloy and penetrate the openings, and this led to strong physical bonding interactions.

### CONCLUSIONS

1. The effects of anodizing on the bonding strength of the LD7 aluminum alloy to rubber were studied. Compared with samples anodized with sulfuric acid, samples anodized in phosphoric acid solutions showed higher 90° peel strength. Under the same electrolyte conditions, an increase in the anodic film thickness in the studied range was beneficial to the adhesion property between the NBR rubber and aluminum alloy.
2. Drying anodized aluminum alloys *in vacuo* facilitated the penetration of the adhesive molecules into the anodized oxide layer.
3. In comparison with aluminum alloys treated by burnishing or sandblasting, the surface

of the anodized aluminum alloy had homogeneously dispersed holes, which resulted in better and homogeneous bonding properties.

4. SEM and energy dispersive X-ray spectroscopy experiments showed that the rubber could continuously penetrate the aluminum oxide layer with time and that the penetration efficiency and depth also increased. This produced firm anchor-hold physical interactions.

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