



A new corrosion protection approach for aeronautical applications combining a Phenol-paraPhenyleneDiAmine benzoxazine resin applied on sulfo-tartaric anodized aluminum

Alexis Renaud^{a,*}, Marc Poorteman^a, Julien Escobar^a, Ludovic Dumas^b, Yoann Paint^c,
Leïla Bonnaud^c, Philippe Dubois^b, Marie-Georges Olivier^a

^a Department of Materials Science, Materials Engineering Research Center (CRIM), University of Mons, Place du Parc 20, B-7000 Mons, Belgium

^b Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons, Place du Parc 20, B-7000 Mons, Belgium

^c Materia Nova asbl, Avenue Copernic 1, B-7000 Mons, Belgium

ARTICLE INFO

Keywords:

Benzoxazine coating
Aluminum anodizing
Thermal curing
Barrier properties
Electrochemical impedance spectroscopy

ABSTRACT

In this paper, the feasibility to apply a laboratory synthesized Phenol-paraPhenyleneDiAmine (P-ppDA) benzoxazine by spin coating on anodized aluminum substrates followed by thermal curing, has been investigated. Prior to coating, sulfo-tartaric anodizing has been carried out aiming at growing porous oxide layers either on 1050 or 2024-T3 aluminum substrates.

Optimization of the performance of the benzoxazine coatings to protect the aluminum substrates was achieved by working out conditions preventing delamination of the coatings – as observed for non anodized coated substrates – and reducing its curing temperature to a level compatible with the requirements of the aerospace industry.

Compared to bare substrates coated with P-ppDA, it is shown that highly capacitive and durable barrier properties can be obtained for the same kind of coatings when applied on the anodized substrates. Moreover, in order to respect the thermal sensitivity of aeronautical aluminum substrates, such as 2024-T3, the curing temperature can be limited to 140 °C only if the substrates are previously anodized in a sulfo-tartaric acid bath.

1. Introduction

Aluminum alloys are widely used in aircraft applications, especially for series 2xxx (Cu main alloying element) and 7xxx (Zn main alloying element). These alloys offer improved mechanical properties compared to “pure” aluminum (AA1050), but are strongly sensitive to corrosion [1–3] and, therefore, need to be protected. For this purpose, a wide range of organic coatings has been developed and applied onto aluminum substrates providing a passive and/or active corrosion protection. Up to now, epoxy resins are the most commonly used thermoset polymers for such kind of applications [4,5].

Recently, polybenzoxazine resins have been reported to show several remarkable properties such as low water uptake, a high thermal stability, low shrinkage during curing [6] and a low dielectric constant [7]. These characteristics make them very suitable for coating protection applications [8,9]. However, those resins also suffer from some drawbacks, such as a high brittleness, a high curing temperature, and, in the case of bisphenol-based benzoxazine, an irreversible degradation

occurring during curing, accompanied with the release of volatile imino species [8], causing severe defects to appear within the polymer (bubbles, cracks) reducing its reliability. Such defects can be avoided by selecting a more appropriate molecular design. Indeed, benzoxazine monomers are obtained by the simple condensation of formaldehyde, a phenol group and a primary amine, conferring a wide versatility to benzoxazine monomer compositions [10–13]. For instance, phenol-para-phenylenediamine based benzoxazine monomers (P-ppDA), have been recently reported in the literature [9,12,13] showing a higher thermal stability during curing leading to coatings with promising barrier properties. However, after several days of immersion in a NaCl solution, delamination processes at the metal/coating interface have been reported in the literature, leading to a loss of corrosion protection [9]. Another drawback related to this kind of benzoxazine is the high temperature needed for a complete crosslinking of the network. As shown previously [9], this temperature is higher than 220 °C and reduces the mechanical properties of aluminum alloys rich in copper, such as 2024-T3.

* Corresponding author.

E-mail address: alexis.renaud@umons.ac.be (A. Renaud).

Table 1
Elementary chemical composition in weight percent of used aluminum alloys.

Alloy	Cu	Fe	Si	Mn	Mg	Cr	Zn	Ti	Others
1050	0.05	0.4	0.25	0.05	0.05	< 0.05	0.07	0.05	0.03
2024-T3	3.8–4.9	0.5	0.5	0.3–0.9	1.2–1.8	0.1	0.25	0.15	0.15

In order to reduce the risk of delamination, the P-pPDA organic coating was applied on an anodizing layer in this study. Anodizing is a surface treatment also used for improving the corrosion resistance of aluminum alloys. The process consists in an electrochemically driven growth of an oxide layer at the surface of the metal by applying an anodic potential. Performing this treatment in an acid bath allows the dissolution of the grown oxide. In the ideal case of pure aluminum, competition between growth and dissolution of the oxide leads to a particular ordered structure divided into two parts: a barrier layer in direct contact with the metal, and a porous layer of hexagonal columnar cells perpendicular to the substrate [14,15]. However, the presence of alloying elements such as copper may disturb this regular growth and lead to different oxide morphologies [16].

Chromic anodizing (in chromic acid electrolyte) has mainly been used as a very efficient and robust corrosion protection process [17]. However, because of health and environmental issues, such kind of treatment will be prohibited in the near future [18]. Alternative solutions have to be developed reaching aircraft standards related to health and environmental concerns. Other acid electrolyte baths have been investigated to replace chromic acid for these applications, such as sulfuric acid [19], sulfo-tartaric acid [20] or sulfo-boric acid [21]. In addition to the low cost of these substances, the combination of the strong sulfuric acid with the weak tartaric acid, limiting the oxide dissolution, offers a better control of the porosity without altering the conductivity of the electrolyte [22]. Oxide layers obtained from sulfo-tartaric baths have shown a better corrosion resistance compared to those obtained from classical sulfuric acid baths [23,24] and have already been accepted by the aerospace industry as an efficient alternative to a chromic acid bath. Sulfo-tartaric anodizing is usually performed at 37 °C under an applied potential difference of 14 V for about 20 or 30 min. The obtained layers have a thickness ranging from 2 to 7 μm [24,25].

In order to ensure a good corrosion protection, anodic layers can be sealed to obstruct the porosity of the layer. Hot water sealing is the simplest sealing bath [26–28], but several other types of baths containing additives have been studied and developed as reported in the literature [29–32]. When aluminum parts are intended to be painted in the final product, anodizing layers are not sealed but coated with a protective organic primer. As demonstrated at an industrial level, the anodic layer allows increasing the organic coating anchoring due to its high porosity. Nevertheless, there are few scientific papers reporting the improvement of the barrier properties of the global system due to this good matching between the inorganic layer and the organic one. The organic layer is commonly made of an epoxy resin, containing chromium trioxide as corrosion inhibitor [33]. Because of the content of this last toxic chemical in the epoxy layer, such kind of substances should be substituted as well. Several surface technologies are emerging as potential alternatives, such as sol-gel coatings [34–36] and new polymeric organic coatings [37–40].

This work proposes, as an alternative for epoxy coatings, a new corrosion protection system where P-pPDA benzoxazine is coated on

anodized aluminum substrates with the aim of limiting delamination processes occurring after application on not anodized surfaces offering more durable barrier properties. In order to emphasize the role of the anodic layer in the prevention of the loss of the barrier properties, equivalent thickness coatings of P-pPDA have also been applied on bare substrates and characterized to be compared with coatings on anodized aluminum.

The substrate of interest in this paper is AA2024-T3, containing copper as the main alloying element, which enhances the mechanical properties, and, for this reason, is mainly used in the aircraft industry. However, this kind of substrate needs to be covered by a protecting system showing good barrier properties and, at the same time, avoiding curing at too high temperatures. For this reason, part of the study has also been devoted to assess the barrier performance of partially cured P-pPDA benzoxazine, applied on either bare or anodized substrates. However, AA2024-T3 substrates can also be used with a clad deposit of AA1050 on top of its surface in order to improve its corrosion protection. Therefore, both kinds of alloys have been investigated as substrate materials.

2. Experimental

2.1. Preparation process of aluminum substrate

Two aluminum alloys, provided by SONACA S.A. (Gosselies, Belgium) have been selected: AA1050 and AA2024-T3. Details of their chemical compositions are in Table 1.

Aluminum samples (60 mm × 45 mm × 1 mm) were treated prior to anodizing in order to enable the formation of a homogeneous oxide layer. The different steps are: degreasing in acetone, etching in 1 M NaOH at 40 °C for 1 min, desmutting in Turco® Liquid Smut-Go NC Deoxidizer at room temperature for 15 s with rinsing in deionized water between each step.

Anodizing of samples in a sulfo-tartaric bath was carried out using the following concentrations: 40 g/L H₂SO₄ + 80 g/L C₄H₆O₆. The bath temperature was controlled using an outer water flow with set temperature. A fixed anodizing potential difference was applied using a Laboratory Power Supply EA Elektro-Automatik PS-2016-100. Anodizing parameters have been fixed as follows: bath temperature at 40 °C and applied potential difference at 10 V for 25 min. Those settings are close to the ones commonly used in the industry [25].

After pretreatment and subsequent anodizing, samples were rinsed in deionized water, dried with pulsed air and directly coated with an organic solution of benzoxazine precursor in chloroform. This solution was prepared by dissolving 8 g of P-pPDA-benzoxazine precursor (Fig. 1) – synthesized as described in a previous paper [13] – in 40 mL of chloroform, stirring and heating under reflux for 4 h at 70 °C followed by cooling down to room temperature, maintaining stirring for 12 h. This solution was applied on substrates by depositing 1 mL on the samples, spin coated at 2000 rpm for 30 s.

After deposition and drying of the precursor coating, thermal curing

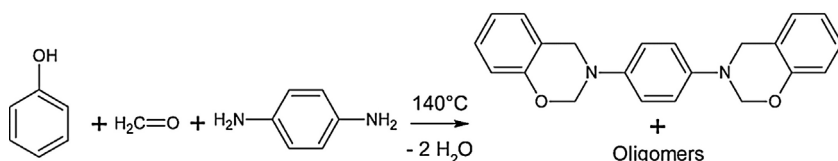


Fig. 1. One pot synthesis of P-pPDA precursor.

Download English Version:

<https://daneshyari.com/en/article/4999151>

Download Persian Version:

<https://daneshyari.com/article/4999151>

[Daneshyari.com](https://daneshyari.com)