



Thermal curing of *para*-phenylenediamine benzoxazine for barrier coating applications on 1050 aluminum alloys

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ABSTRACT

Polybenzoxazine coatings have been applied by spin coating of a solution, prepared from a laboratory synthesized phenol, *para*-phenylenediamine benzoxazine (P-pPDA), on 1050 aluminum alloy. A heat treatment was performed on the coating to polymerize the benzoxazine monomer by a ring opening mechanism attested for by Fourier Transform Infrared spectroscopy (FT-IR) and followed by Differential Scanning Calorimetry (DSC). Dielectric Analysis (DEA) showed curing to proceed at a temperature range up to 230 °C, without thermal decomposition taking place, as has already been reported in the literature for commercial bisphenol-a benzoxazines (Ba-A). The barrier protection has been evaluated by Electrochemical Impedance Spectroscopy (EIS) for 30 days in a sodium chloride solution (0.1 M). The results were fitted with equivalent electrical circuits in order to understand the electrochemical behavior of such a system. The initial barrier properties of both precursor and polymerized coatings appear to be excellent for coatings having a thickness of only 5 μm. Though delamination occurs in the polymerized coating during saline tests after several days of immersion, such kind of coatings have remarkable properties with respect to epoxy coatings as they show a high geometrical stability during curing and a very low water uptake during saline tests.

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1. Introduction

Aluminum alloys, such as the 2xxx (Cu) and 7xxx (Ti) series, are widely used in the aircraft industry as they offer improved mechanical properties compared to pure aluminum (1050). However, these alloys are strongly sensitive to localized corrosion [1–3] and, therefore, need to be protected. In order to improve their corrosion resistance, several types of coatings have been developed and are commonly used at an industrial level such as anodizing layer [4], conversion coating [5] and organic coatings [6]. These coatings are often chromate-containing layers [4–6], showing excellent anti-corrosive performance, but due to the high bio-toxicity of chromate, the use of such kind of compounds will be banished in the aircraft sector by 2017. As a consequence, several new technologies and alternatives, avoiding the use of chromate, have been investigated: sol-gel coatings [7–11], new anodizing layers [12–15] and the elaboration of organic-, inorganic- or hybrid coatings [16–19]. Epoxy

resin coatings are currently used as organic coatings to prevent corrosion of aeronautic structures. However, they suffer from some drawbacks such as water uptake, which can be at the origin of corrosion, blistering and delamination processes [20,21] when water diffuses to the metal-coating interface. Moreover, most applied epoxy coatings show a limited thermal stability and therefore cannot be applied on engine parts.

Recently, polybenzoxazines have gained an increasing interest due to their potential of combining the excellent properties of traditional epoxy- and phenolic resins. This class of polymers offers highly attractive properties such as high glass transition temperatures, low absorption of water, near zero shrinkage [22] and good dielectric properties [23].

Benzoxazine monomers can be easily synthesized by the reaction of three basic compounds: a phenol, an amine and formaldehyde. By changing the different groups of the components, several types of benzoxazines can be elaborated with a large panel of different properties [24,25]. Amongst the few studies in the literature about the use of this new polymer family as an alternative for epoxy coatings and their potential performances as barrier protective coatings, the authors have recently published a paper

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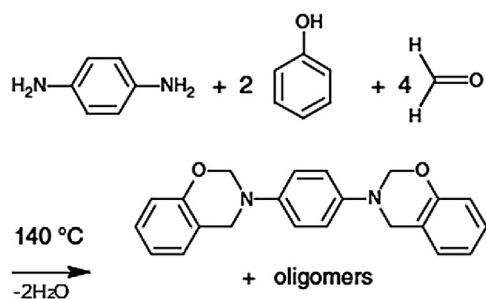


Fig. 1. One pot synthesis of P-PPDA precursor.

showing the barrier properties of a commercial bisphenol A, aniline benzoxazine (Ba-A) coating applied on aluminum 1050 [26]. Although a performant barrier coating could be fabricated by applying an in acetone dissolved Ba-A monomer solution by dip coating onto the aluminum substrate and subsequent step curing successively at 180 and 200 °C, the thermal polymerization of this kind of monomer appeared to be accompanied by an irreversible degradation with the release of volatile imino species [27]. Consequent out-gassing can then be responsible for the formation of voids in the cured materials and decrease the performance and reliability of the synthesized coatings. Alternatively, a thermally stable benzoxazine precursor based on phenol and *p*-phenylene diamine benzoxazine (P-PPDA), according to a reaction represented in Fig. 1, can be synthesized by an easy and scalable one pot process [28].

The increased thermal stability of P-PPDA compared to Ba-A can be explained by the fact that the aminophenyl moiety is trapped between two benzoxazine rings limiting its cleavage during the network formation (Fig. 2), hence resolving the outgassing drawback. Moreover, bulk cured P-PPDA materials show excellent fire resistant properties with LOI values of 38% [28] making it a very attractive alternative as nonflammable material to replace halogenated materials for instance for coatings inside an airplane.

In this work, a diamine based benzoxazine was synthesized according to a procedure presented elsewhere [28], leading to an obtained precursor consisting of a mixture of P-PPDA monomers and some oligomers. In this paper, this precursor mixture has been used without carrying out any further purification to prepare a neat, thick coating (from 4 to 7 μm) on an aluminum substrate. A 1050 aluminum alloy was chosen because of its intrinsic corrosion resistance performance, which is an advantage if the barrier properties and the organic water uptake are to be highlighted. This alloy is often used as clad layer of a 2024 aluminum alloy in order to obtain a good compromise between corrosion resistance and mechanical properties for aeronautic applications. The initial benzoxazine was dissolved in a solvent and deposited by spin coating. After room temperature drying, a final heat treatment was applied to polymerize the coating. The structural transformation after thermal curing was followed by Fourier Transform Infrared spectroscopy (FT-IR) and Dielectric Analysis (DEA). The polymerization degree was estimated from data obtained by Differential Scanning Calorimetry (DSC). Finally, the barrier properties and the water uptake of the polybenzoxazine coatings applied on aluminum substrate were assessed by Electrochemical Impedance Spectroscopy (EIS) versus immersion time in a 0.1 M NaCl neutral solution. The coating performances were determined before and after curing treatment.

2. Experimental

2.1. Preparation process

The selected substrate material was a 1050 aluminum alloy (AA). Its chemical composition in weight percent is: <0.40%Fe,

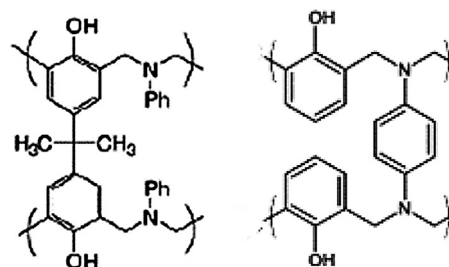


Fig. 2. Polymerized structure of Ba-A (left) and P-PPDA (right).

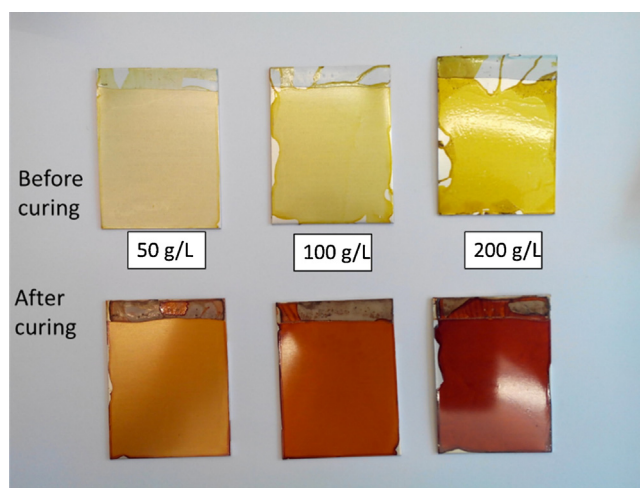


Fig. 3. Coatings obtained by spin coating for different concentrations of P-PPDA solutions, before and after curing.

<0.25%Si, <0.07%Zn, <0.05%Cu, <0.05%Mg, <0.05%Ti, <0.05%Mn and Al accounts for the remainder.

Each sample surface (60 mm × 45 mm × 1 mm) was first cleaned and degreased in acetone. A consecutive etching is needed before benzoxazine deposition in order to improve the surface wettability and coating adhesion. This was performed as follows: first, an immersion in a 1 M NaOH bath maintained at 50 °C for 60 s, followed by rinsing with deionized water and, finally, a neutralization in HNO₃ (50 vol%) carried out for 60 s at ambient temperature. The monomer solution was prepared by dissolving laboratory synthesized P-PPDA precursor in chloroform (from 50 to 200 g/L), obtaining a yellow-orange solution after reflux for 4 h at 60 °C. After cooling and stirring during 12 h the solution is deposited onto the substrate by a spin-coating process at 3000 rpm for 30 s.

The drying process of the coated aluminum consisted in leaving the sheets at room temperature for 24 h.

After deposition and drying, a thermal treatment was carried out to obtain the cross-linked polymer by successive step curing at 140 °C during 60 min, 180 °C and 200 °C, with each time a dwell of 2 h, 220 °C during 30 min and, finally, at 230 °C during 30 min. Thereafter, samples were allowed to slowly cool down to room temperature.

2.2. Characterization

The surface roughness of the substrate (*R_a* and *R_z*), before and after pretreatment, was measured by surface profilometry (NanoJura High Precision Surface Metrology System—NJHP 505).

FT-IR measurements were carried out in the 370–2000 cm⁻¹ range in order to follow the structural curing of the polymer by using a Perkin Elmer Spectrum 2000 apparatus and the results were

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