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Design and durability of titanium adhesive joints for marine applications

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ABSTRACT

Comparative measurements of strength and Griffith's critical strain energy release rate G_{Ic} were carried out on adhesively bonded joints with different surface treatments of titanium, before and along 13 weeks of accelerated aging in salted or deionized water at 50 °C. Thermo-mechanical measurements were carried out on the bulk epoxy adhesive, with the same aging conditions. A combined surface treatment of sanding, degreasing and chemical etching showed the best durability, whereas a treatment using an additional sulphuric anodic oxidation showed the best adhesion before aging. Aging decreased the strength and the critical strain energy release rate of bonded joints by 30–70%. Joint design with a finite element calculation using a cohesive failure law at the interface, accounting for surface treatment, aging effects and safety factors, can thus be performed, from a limited set of experimental values.

1. Introduction

Marine structures of all types increasingly use composite materials, in particular sailboats. Composite materials properties are well recognized in the marine industry, in particular specific density, mechanical performance, ease of implementation, adaptability to complex geometries, absence of corrosion, reduced maintenance costs, fire resistance and insulation to heat and electricity. These advantages are even more important for racing boats with the use of carbon fibre reinforced composites and hybrid composite-titanium assemblies to benefit from the low density, high strength and excellent corrosion resistance of titanium where required. Traditional assembly techniques like screws, rivets or bolts are inadequate for such composite parts as they generate stress concentrations and add weight. Shipbuilders therefore seek to replace these methods by adhesive bonding that offers the desired lightweight and stress spreading properties while reducing galvanic corrosion problems and manufacturing costs. Bonding still suffers from an arduous process control and a low reproducibility. Sources of variability are multiple: choice of adhesive, storage and processing conditions, bond thickness, geometry, presence of defects that are difficult to detect, and finally the lifetime behaviour in marine environment (temperature, salt water, UV rays). One must also consider the important difference that exists between laboratory and shipyard production conditions, in particular for bonding large composite structures that are subject to heterogeneous surface conditions and anisotropic strains. Titanium-composite bonding thus still remains an issue nowadays [1–3] with the necessity to better understand specificities of titanium surface preparation to determine the best strategy for bonding. Moreover, current design criteria do not often include the aging of composites in the presence of seawater. These doubts about durability and variability of bonded joints and the lack of safety factors for design explain a certain lack of trust from shipbuilders. Solutions to improve properties and durability of bonded joints require efficient titanium surface treatments to increase the adhesion of epoxy and its durability. Bonding as an assembly technique should be considered from the design level and adapted to the mechanical and environmental lifetime of the structure while achieving an optimal weight reduction.

Metallic surfaces are usually covered with various impurities like dust, greases, adsorbed water and fragile oxide layers but regardless of the substrate material, a good adhesion requires a clean and stable surface [1–3]. Wetting by the adhesive requires a high surface energy, bonding requires physicochemical interactions, and mechanical anchoring of the adhesive requires a given surface roughness. All this could be achieved by surface treatments which mostly consist of chemical and mechanical techniques: cleaning with solvents or detergents, abrasion, chemical acidic etching or anodizing in an electrochemical cell to generate thick and strong oxide layers [1–3]. The natural surface oxides of titanium alloys are thinner than those of aluminium but much more stable, also providing micro-roughness. Recommended titanium etching solutions are based on a concentrated nitric acid combined with hydrofluoric acid. Recommended titanium electrochemical anodizing solutions are usually chromic or sulphuric [1–4].

In epoxy-metal bonding, the metallic surface ions interact with the amines during the process, creating an interphase with properties different from those of bulk epoxy [5–8] in particular

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for strength and durability [9]. The thickness of the interphase was found to be about 600 μm for chemically etched titanium with a diglycidyl ether of 1,4-butanediol (DGEB)/Isophoronediamine (IPDA) epoxy [6,7]. Studies showed a significant influence of the loading speed, the temperature and the joint thickness on the ultimate strength, the thinner the bond, the higher the joint shear strength, with an optimum of less than 1 mm for epoxies [10–14].

The aging mechanisms of epoxy in marine environments are dominated by water absorption, which is mostly reversible. Other involved mechanisms are the irreversible loss of additives in the surrounding environment by diffusion, the polymer chains damage by UV radiation and oxidation, and the mechanical damage of cyclic recrystallization of salt ions within the material. The seawater aging of a glass fibre reinforced epoxy for 18 months at 50 °C was reported to result in no modulus loss but in an ultimate strength loss of 40% with a partial recovery after drying [15]; seawater was shown to be slightly less detrimental than deionized water. Adhesively bonded steel/epoxy joints showed a significant drop in strength after immersion in seawater [16]. Metallic–epoxy interphase layers were also found to be sensitive to water absorption [9]. The metal-oxide/adhesive interface of bonded joints is, however, recognized to be the most critical location during wet aging. Absorbed water molecules condense into the interfacial porosity and dissolve the substrate's oxide layers, creating an osmotic pressure that will grow blisters. Interfacial water also disrupts the Van der Waals chemical bonds. But in certain conditions, water might foster oxides layer growth into the interfacial porosity and improve adhesion [17]. Aging mechanisms are accelerated by thermal activation according to the Arrhenius law, which is generally used to limit the duration of aging tests by presenting an excellent symmetry with real world aging curves [15].

Design tools for adhesively bonded composite joints for marine applications have been investigated previously [10,18] but pointed out the difficulty of failure modelling and the need for more reliable input data. In recent years, Cohesive-Zone Modelling (CZM) has been successfully applied to model fracture in adhesive joints and composite repairs in various modes [19–25]. Numerical simulations using a CZM appeared to be appropriate for a design purpose by providing quantitative predictions for both the strengths and failure mechanisms of adhesively bonded composite joints presenting mixed-mode fracture [26].

The objectives of this study were therefore to reach performance and durability for marine composite-titanium bonded joints by testing different surface treatments, and to propose a finite element method suited to the joint design. This was achieved by comparative measurements of fracture toughness G_{Ic} and ultimate strength on bonded joints with different surface treatments of titanium, before and after aging in salt water and deionized water. The focus of study was the epoxy–titanium bond, which is less controlled than the thoroughly studied epoxy-composite bond. The surface treatments were chosen based on the literature review [1,6,7] and on the actual practice of shipbuilders. The adhesive's bulk properties during aging were characterized as well. A finite element model based on CZM and using the experimental data was then proposed to predict the failure of complex structures. This model was developed for design purposes with the aim of requiring few experimental data as input and providing a conservative solution as output.

2. Experimental

2.1. Materials

The metallic substrates used were Ti–6Al–4V titanium grade 5 alloy (Bibus Metals AG, Switzerland). This alloy has a density of 4.43 g/cm^3, a Young's modulus of 114 GPa and a yield strength of 828 MPa (according to the manufacturer). The polymer adhesive was the Araldite 420 A/B from Huntsman Advanced Materials GmbH, Switzerland. The weight ratio of the epoxy monomer A with the amine hardener B was A=100/B=40. Once reticulated, this adhesive has a density of 1.15 g/cm^3, a Young's modulus of 1850 MPa and a tensile strength of 37 MPa (according to the manufacturer and from Ref. [23]). The Araldite 420 components A and B were mixed and vacuumed during 10 min to get the bubbles out. The curing cycle was a 12 h isotherm at room temperature followed by a 10 h isotherm at 80 °C, according to shipbuilding practice.

Table 1
Labels and steps of the different surface treatments.

«D»	«S+D»	«D+E»	«S+D+E»	«S+D+Ind. E»	«B+D+Ind. A»
Degreased	Sandblasted	Degreased	Sandblasted	Sandblasted	Bead blasted
	Degreased	Etched	Degreased	Degreased hot	Degreased
			Etched	Etched (Industrial)	Etched
					Anodized (Industrial)
					Cleaned/ MEK

2.2. Surface treatments

Before any polymer application, the titanium substrates surfaces were treated as presented in Table 1. The treatment "D" was degreasing, "S+D" and "D+E" are single surface treatments as they consist of one operation (sanding or etching) while "S+D+E", "S+D +Ind. E" and "B+D+Ind. A" were combined treatments as they consist of two or more operations, including degreasing and etching or anodizing.

The degreasing step was achieved in an ultrasonic cleaning bath with acetone during 5 min. Abrasion was carried out by sandblasting or bead blasting. The chemical etching treatment consisted in immersing the substrate in a 7.5 wt% NH_4HF_2 solution during 5 min followed by a rinse in an ultrasonic cleaner with distilled water during 5 min. All these steps were performed at room temperature, except for "S+D+Ind. E" which used a proprietary cleaning and etching surface preparation by Steiger SA (Switzerland). The anodizing performed for "B+D+Ind. A" was an anodic sulphuric oxidation carried out by PMA Bonnans SA (France) 2 weeks before the bonding operation, this surface was therefore wiped clean with methylethylcetone (MEK) just before bonding. In all other cases, the epoxy was applied directly after the treatment.

2.3. Methods

2.3.1. Bulk adhesive properties measurement

The polymer samples for bulk property and water intake measurements were $60 \times 10 \times 2$ mm^3 samples cast between two glass plates with release agent (Frekote 770-NC, Henkel, Germany) and cut to shape with a diamond saw. The thermo-mechanical and viscoelastic properties of the bulk adhesive polymer during aging were monitored by dynamic mechanical analysis (DMA Q800, TA Instruments, USA) using a dual cantilever setup with a distance of 35 mm between contacts. A sinusoidal strain of 0.1% was applied at 1 Hz to the material and the resultant stress was measured with a temperature ramp of 5 °C/min between ambient and 110 °C, to reduce potential drying effects of the sample during test. The glass transition temperature T_g was determined at peak *tanδ* and peak *E"*. DMA and swelling measurements were repeated on a minimum of 3 samples. Water intake measurements were repeated on