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## An interfacial adhesive analysis of repairing composite patches by electrochemical impedance spectroscopy

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#### ARTICLE INFO

### ABSTRACT

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Keywords: composite patch adhesive surface preparation corrosion electrochemical impedance spectroscopy Composite patches, commonly adhesively bonded, are being used to restore general metallic structures, and not only in the aerospace industry. This solution is gaining weight in the naval industry. The adhesive layer, used to attach these patches to the metal surface, concentrates most of the failures detected in those repairing layers. The durability, understood as the bonding strength, is usually treated in terms of the mechanical performance, the parameter commonly studied in most of the published reports. Not many studies are currently found that include the presence of an aqueous aggressive environment, a major concern when referring to the marine structures. Thus, this work deals with the analysis of the corrosion aspects in the composite patches technology. The recording of the impedance spectra was the main method used in this study. The metal surface finishing plays a key role in the adhesion ability and then the present study reflects the analysis of several metal finishing as well. In particular, the grinding and slasting have been compared. The sand blasted surface has been additionally coated with a thin protective zinc rich primer (ZRP) that promotes an improved adhesion. The presence of ZRP at the bottom of the adhesive seems to benefit the corrosion performance without damaging the bonding strength.

## 1. Introduction

The composite patches repairing technology has been used in the aerospace industry since the late 70 s [1]. Aerospace metallic structures show important susceptibility to degradation by cracking caused mainly by fatigue or stress corrosion [1,2]. The main advantages of patch repair methodology are high directional stiffness, which allows reinforcing in the desired direction; suitable durability, low density and good formability, properties that help to significantly expand the service life of current airframe structures [3]. Composite patches applied on top of the defective areas provide inhibition of the crack growth by reducing the stress level at those sites. Adhesively bonded composite patches, based on a fibre reinforced epoxy resin, have been recognized as a successful design to repair the cracked components and/or to reinforce the damaged parts [3]. Debonding is the most common type of failure in these patches so that the improvement of the interfacial area between the top composite and the metal substrate concentrates most of the current efforts in research.

Concerning the particular case of the marine structures, the loading-unloading cycles along with the highly corrosive

http://dx.doi.org/10.1016/j.electacta.2017.03.181 0013-4686/© 2017 Elsevier Ltd. All rights reserved. environment are responsible of the crack nucleation and further growth leading to the failure of the structure. Therefore, a prompt intervention and reparation becomes necessary to avoid the undesired fracture. The use of the bonded composite patches has been quite recently revealed as a promising technology that has found use in a range of various applications covering the reparation of damaged parts of large vessels, oil floating platforms, warships and other offshore structures [4–11], or even the rehabilitation of civil engineering structures [12]. Composite patches have been proved able to restore many complex shapes and they are applicable in almost any environment as well, including underwater conditions, both vital requirements in the case of the marine structures. Moreover, in advantage to the traditional ways as part replacement or welding, they are less costly, less harmful and less time-consuming [7,13–15].

Once the composite patch has been properly designed and firmly fixed to the substrate damaged area, the assessment of the service life performance and durability is essential to ensure the quality of the repairing method [4,8,16,17]. Numerous recent publications concern this issue and a variety of testing techniques are currently being used. Some of them draw upon analytical methods [18–22] while others employ non-destructive techniques such as infrared imaging or thermography [7,16,23,24] to check the patch quality. Most of the already referred works focus their





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analyses on the identification and progression of the defects and cracks under the composite patch as well as on the bonding strength under loading. Commonly characteristics such as the defects depths and sizes, crack growth rate or critical stresses to failure are studied.

The interfacial adhesive plays a crucial role when analysing the entire composite performance, not only concerning the bonding strength but also it offers a physical barrier to avoid any possible galvanic influence [8]. The importance of this bonding line has been intensely emphasized in the studies concerning this topic. Thus the patches fail at those locations where the adhesive bonding layer is defective [6,8], and no failures have been referred to the composite layer itself.

The substrate preparation prior the adhesive application is an important step in order to improve the quality of the adhesion composite/metal. A rough and pollutant free surface will be essential properties to enhance the adhesion ability [25]. In this line, one of the purposes of the present study is the analysis of the influence of several surface finishing procedures in the adhesive resin efficiency. In particular, the grinding and the sand blasting procedures have been assessed, while the adhesive characteristics remain invariable.

On the other hand, although the presence of a marine environment has been pointed as a detrimental factor for the adhesive bonding joint [6], just a minor number of authors have included in their research the patch durability assessment under the effect of a corrosive medium [26]. A possible reason may lie in the novelty of this technology for the particular case of the ship industry. No studies referring to the patch performance on steel substrates combining the influence of an aggressive environment have been published so far, to the author's knowledge. Thus, the main motivation of this paper focuses on the adhesive behaviour at the composite/metal interface depending on the metallic finishing (grounded or sand blasted). From the corrosion point of view, this aspect is directly linked to the patches durability when applied on a hull marine steel. The electrochemical impedance spectroscopy technique will be the main tool employed in the study.

### 2. Experimental

### 2.1. Tested specimens description

The metal substrate employed in this study was a marine hull steel plate 5 mm thick (grade A). Two different composite patches were prepared, named as system A and system B, Table 1 summarized the main details. The difference between them concerns essentially the metal surface preparation. Since the sand blasting process used in the preparation of system B significantly worsens the corrosion performance [27], a former protection layer is required before the complete composite patch assembly and then a Zn-rich primer (ZRP) was firstly applied. The composite consists in a laminated carbon fibre reinforced epoxy resin (CFRP) prepared at ambient conditions and consisted of four plies of unidirectional carbon fibre, each ply having 200 g/m<sup>2</sup> weight/area ratio. The composite was bonded to the marine hull steel with an epoxy based adhesive resin (Resoltech 3350/3356<sup>®</sup>) about 1.2 mm thick and cured at 70 °C for 5 hours, following the supplier' instructions.

Since the main purpose of this study is focused on the assessment of the adhesive/substrate interface, two additional specimens were specifically prepared in order to get information located on this interface. These samples are referred as system A1 and system B1.

A thermal study by Differential Scanning Calorimetry (DSC) was performed to analyse the adhesive characteristics, the specific experimental details are described in the following section. Fig. 1 depicts the comparison of the first and the second heating scan from 20 °C up to 250 °C. The solid line, corresponding to the first heating scan, clarifies that the followed curing conditions were not



Fig. 1. DSC curves of the adhesive used to join the top composite patch to the marine hull steel, the 1st (solid line) and 2nd (dashed line) heating runs are shown.

#### Table 1

Description of the specimens considered for this work.

|             |                          |  |   | - 1  |
|-------------|--------------------------|--|---|--|
| Sample code | Substrate<br>preparation | Primer   | Adhesive  | Top layer  |
| System A    | Grinding                 | по   | Epoxy resin (Resoltech 3350/3356 $^{\ensuremath{\mathbb{R}}}$ ) 1.2 mm thick      | Laminated carbon fiber epoxy resin<br>(CFRP)<br>2 mm thick |
| System A1   | Grinding                 | no   | Epoxy resin (Resoltech 3350/3356 $^{\ensuremath{\mathbb{R}}}$ ) 300 $\mu$ m thick | no   |
| System B    | Sand blasting            | ZRP, based on epoxy-polyamide<br>resin.<br>Solid content: 60% vol.                               | Epoxy resin (Resoltech 3350/3356 $^{\ensuremath{\mathbbmm}}$ ) 1.2 mm thick       | Laminated carbon fiber epoxy resin<br>(CFRP)<br>2 mm thick |
| System B1   | Sand blasting            | SU µm thick<br>ZRP, based on epoxy-polyamide<br>resin.<br>Solid content: 60% vol.<br>50 µm thick | Epoxy resin (Resoltech 3350/3356 $^{\rm I\!E}$ ) 300 $\mu m$ thick                | no   |
| System C    | Sand blasting            | ZRP, based<br>resin.<br>Solid content: 60% vol.<br>50 μm thick                                   | no  | no   |

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