



Degradation of rubber to metals bonds during its cathodic delamination, validation of an artificial ageing test

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ABSTRACT

Rubber-metal assemblies used for submarine applications are often associated to cathodic protection which can lead to cathodic disbonding of the polymer/metal interface.

The degradation mechanisms of polychloroprene/epoxy adhesive/copper–aluminium substrate systems associated to an accelerated ageing test are compared to the degradations resulting from natural ageing conditions in the Mediterranean sea. From destructive tests, a kinetic in four steps is identified for both ageing conditions. This kinetic is confirmed by Electrochemical Impedance Spectroscopy data during ageing. In order to further identify the failure mode, the disbonded surfaces on polymer and steel sides are analyzed using SEM and FTIR. Both ageing conditions present the same type of degradation which validates the fact that the accelerated ageing protocol reproduces the natural conditions. The chemical transformations in delaminated epoxy are very similar to the chemical transformation in epoxy coatings under high energy electron-beam irradiation. However, bidentate metal carboxylates rather than carboxylic acid chain ends are the main oxidation products due to the alkaline environment at the coating-metal interface. It was shown that the metal/polymer interface is not destroyed by an alkaline attack but by a strongly oxidative attack caused by the intermediates of the oxygen reduction.

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1. Introduction

Adhesive systems for rubber-to-metal bonding are widely used in different industrial fields. In military applications, rubber is bonded to metal substrates in acoustic absorbers, sound reflectors and sonar transducers. These systems are associated with cathodic protection in order to prevent the corrosion of metallic structures immersed in seawater. Cathodic protection leads to the generation of a strong alkalinity at the metal/coating interface, which causes the delamination of the coating [1,2]. The mechanisms of cathodic delamination are usually classified into three groups. The first is the dissolution of the substrate oxide phase to which the polymer adheres [1–3]. This mechanism has been identified by ellipsometry used with pH probes under the film which indicates the very high alkalinity reached [4]. Nevertheless, oxide dissolution is widely criticized and depends on the nature of the substrate, the pH of the electrolyte and the potential applied, according to the Pourbaix diagrams. Castle and Watts [5] observe that the oxide is locally

reduced, but the reduction is not a necessary precursor for cathodic delamination process.

The second mechanism is the degradation of the polymer/metal bonds at the interface [6,7]. The build-up of an alkaline environment may not be the only responsible for the loss of adhesion observed between the substrate and the coating. In fact, oxygen reduction produces many reaction intermediates, namely superoxides and hydroxyl radicals that lead to severe oxidation conditions [6,8–10]. The third mechanism proposed is the polymer degradation by alkaline hydrolysis [3,11], sometimes referred to as saponification, or also by polymer oxidation due to intermediate species of oxygen reduction reaction [8,12]. Leng et al. [8] present some results on a polymer/steel system with a defect on the coating, aged in a sodium hydroxide electrolyte without oxygen. In that case, hydroxyl ions are present without oxidative species. They observe that the cathodic delamination rate is reduced.

The mechanisms of cathodic disbonding in the case of rubber to metal assemblies have not been widely studied yet. Stevenson [13] studies ageing of rubber vulcanized on steel and titanium. He reports that these systems are stable in electrochemically inert conditions. Moreover the type of rubber, the application of shear stresses, and the amount of water absorbed do not

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greatly affect the delamination rate. However, rapid failure of the bonds occurs when cathodic potentials are applied to steel. He confirms that hydroxyl ions resulting from oxygen reduction on steel surface are responsible for the rapid delamination but he does not precise the actual failure mechanisms. Boerio and Hong [14] study polychloroprene to steel adhesive bonds using FTIR and X-ray photoelectron spectroscopy. They find that methylene groups linking phenol moieties in the phenolic primer are rapidly attacked by hydroxyl ions, implying bonds failure. They also suggest that inorganic chlorides from polychloroprene are very soluble in water and may contribute to delamination by osmotic effects.

To simulate and accelerate the effects of coating damage in service, some accelerated life tests are proposed. Most of the accelerated life testing protocols that are developed for components under cathodic delamination in a marine environment are based upon the Arrhenius law using an increase in temperature or thermal cycles [15–18]. This approach suffers from two drawbacks. First, temperature may affect the physicochemical properties of the coating in terms of permittivity, strain, chemical bond rupture. Second, an increase of temperature leads to a decrease of oxygen solubility in seawater and, consequently, a decrease in delamination rate. Since cathodic delamination process is electrochemical in nature, the phenomenon can also be accelerated by applying a low cathodic potential on the substrate [19,20], although excess negative potential might merely increase current draw and hydrogen production.

In this paper, the cathodic delamination mechanisms of a rubber to metal system, used for submarine application, is studied. The degradation mechanisms associated to an accelerating life test based on oxygen saturation in seawater are compared to the degradations resulting from natural ageing conditions in Mediterranean Sea.

2. Experimental

2.1. Materials

The substrate is a copper–aluminium alloy used for its very good corrosion resistance in seawater, with 83 wt% of Cu, 9 wt% of Al, 3.7 wt% of Ni, 2.8 wt% of iron and 1.2 wt% of manganese. The rubber is a polychloroprene with silica filler, sulphur vulcanized with 51 wt% of black carbon. Some artificial tests were also performed with a polyurethane elastomer based on 4,4'-Diphenylmethane Diisocyanate, MDI, and hydroxyl terminated polybutadiene. The thickness of the elastomer is 2 mm. The adhesive used is a com-

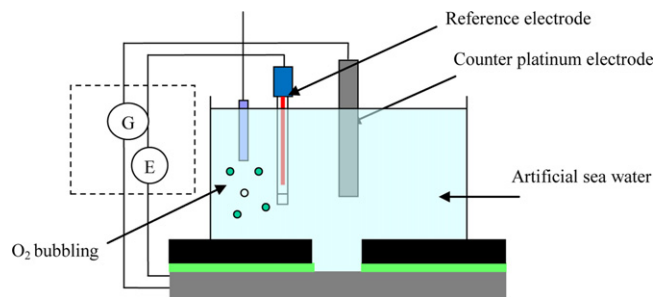


Fig. 1. Artificial ageing test protocol.

mercial epoxy based on the diglycidyl ether of bisphenol A (DGEBA), cured with trioxatridecane diamine, with 5 wt% of silica.

2.2. Samples preparation

For the test at high pH, epoxy adhesive films, with a thickness of 1 mm have been applied on a steel substrate covered with a release agent and heated up to 50 °C for 4 h. The coating film is easily removed from the substrate after cure.

For assemblies, the substrate is cleaned in a hexafluoroethylene bath and sandblasted with corundum 120. The rubber, preliminarily abraded on one face, is stuck on the sandblasted substrate with the epoxy adhesive under a pressure of 2 bar. Then, the complete system is cured for 4 h at 50 °C. The epoxy adhesive thickness is about 20 μm. The samples are linearly scribed down to the substrate with an area of about 20 mm² (20 mm × 1 mm).

2.3. Ageing protocols

For the test at high pH, epoxy adhesive films and assemblies are immersed in a 1 M NaOH solution (pH 14) during 2 months. An electrolyte free of oxygen is provided by argon bubbling.

The experimental protocol used for artificial ageing is represented in Fig. 1. A plastic cell is stuck on the sample and filled with an artificial simplified seawater at ambient temperature (18–22 °C), based on NSA 91-411 with a pH of 8.2. This electrolyte is carbonates free in order to avoid scale deposit (CaCO₃ and Mg(OH)₂). A three electrode system is used to apply a cathodic protection potential of $-0.8 V_{SCE}$ which is in the oxygen reduction domain. Some destructive tests were also performed at $-1 V_{SCE}$ to compare the influence of the cathodic potential on polymer degradation kinetics. A saturation of the electrolyte in oxygen is provided by oxygen bubbling with a concentration regulated between 18 and 20 mg/L

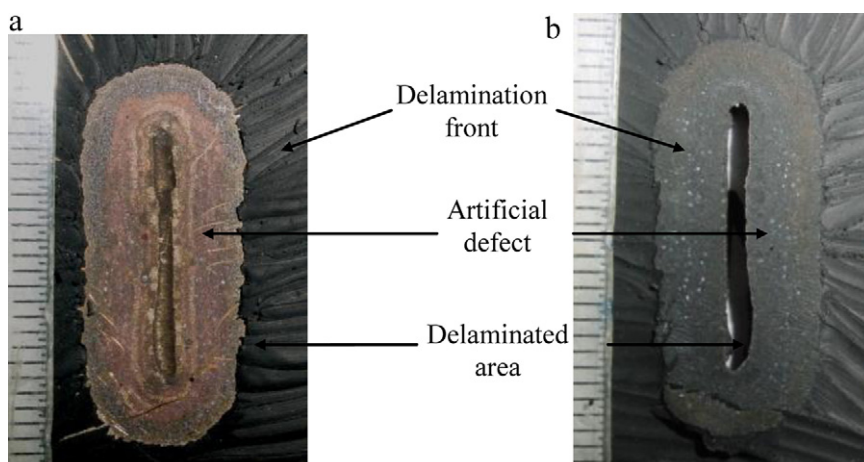


Fig. 2. Typical photographs of sample after manual removal: (a) substrate side, (b) rubber side.

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