

Evaluation of Green Corrosion Inhibitors for Applying in Food Packaging

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Abstract. In this study, the inhibitor effect of *Solidago chilensis* extract as green corrosion inhibitor for anodized aluminum alloy samples was evaluated in NaCl 3%wt solution. This study was carried out for application on cans for pack of foods. The procedure of the surface treatment of the samples was done by anodizing followed by sealing in a solution containing the inhibitor. Essays of potentiostatic polarization and electrochemical impedance spectroscopy were done to evaluate the inhibitor effect. The mechanical analyses were performed on anodized samples to evaluate the influence of the thickness of anodization on the mechanical resistance of the samples. The potentiostatic essays indicated that a cathodic inhibitor effect occurs only in non-anodized samples and that the anodic effect of the inhibitor not appears on the anodized samples. The calculated efficiency of the inhibitor was 96 %. The EIS results indicated that the higher values of polarization resistance (16 kΩ) occur on anodized samples containing inhibitor after 72 hours of immersion in NaCl 3%wt. The mechanical essays indicated a non – significant difference between anodized and non – anodized samples.

Introduction

Aluminum is an abundant, lightweight, non-toxic, malleable element and has good corrosion resistance, so it is widely used in food packaging. However, this material can degrade when exposed to aggressive environments such as those containing chloride in the composition [1-6]. Such degradation might be minimized by the anodizing process, which involves the creation of an oxide film on the metal surface and improves the adherence of the protective coating [1-7].

The package passes through a washing procedure before and after be filled by the product during the food processing. The hot water of the washing procedure can induce to the formation of defects on the coating of the package. This factor might induce to the corrosion processes of the package and thus contaminate the product in contact with the environment (food) that can have lower pH. In order to prevent such degradation, corrosion inhibitors have been used in several studies [1, 8-12].

Although many synthetic compounds show good anti-corrosion activity, most of them are highly toxic to humans and to the environment. The use of green inhibitors to control corrosion in metals and its alloys are highlighted in studies focusing the application in the food industry, once they do not contain heavy metals or other toxic compounds [13,14]. Extracts from plants may be sources of ingredients, which are highly efficient as corrosion inhibitors. They are environmentally friendly, readily available, renewable, low-cost, bringing ecological concern of food industry to fulfill the social and environmental demand [14-18].

Considering environmental issues, the concern about the toxicity risk and the most serious problem caused by the corrosion of aluminum packaging in the food industry, this study seeks to develop a surface treatment of aluminum using anodizing and natural corrosion inhibitors for application as coatings for food packaging. In order to evaluate the performance of the treatment, electrochemical studies by potentiostatic polarization and EIS were conducted to evaluate the corrosion resistance. The DMA was performed to analyze possible changes in the mechanical strength of the system.

Materials and Methods

Preparation of samples. Aluminum packages for soft drinks from the same batch were cut in sheet form, mechanically polished with silicon carbide emery paper 200 to 600 mesh, cut into rectangular samples with dimensions of 4 x 3 cm and maintained in a desiccator prior to the use. To perform the DMA, the samples were cut into dimensions of 3.5 x 1.4 cm.

Anodizing. The samples were cleaned using alkaline attack and acid activation with NaOH 0.5 %v. (CAS 1310-73-2) (Proquímicos) at 50 °C for 2 min and a solution of HNO₃ 2.5 %v. (CAS 7697-37-2) (Aldrich) at room temperature for 2 min, respectively. The samples were anodized, during 15 minutes, with controlled current 0.12 A in a solution of H₂SO₄ 1.5 %V (CAS 9664-93-9) (Aldrich) with the addition of 15 g/L of aluminum powder. The cleaning process and anodizing were performed twice to each sample, in order to form an oxide as uniform as possible. Subsequently, the samples were sealed in boiling water for 5 min. The use of anodizing on this work is due to the increase of the roughness of the surface that would improve adsorption of the inhibitor.

Selection and preparation of plant extract. In previous studies [19], types of natural plant extracts were analyzed as corrosion inhibitors, and the extract of *Solidago chilensis* showed better results. The specimens of *Solidago chilensis* were collected in the Pampa biome in the city of Bagé, Rio Grande do Sul, Brazil, in August, 2012. The plants were dried and milled at room temperature in an analytical mill. The extract was prepared by maceration with methanol at room temperature for four consecutive times and each extraction was performed for a period of four days. This concentrated extract was subjected to a rotary evaporator to give a crude extract of *Solidago chilensis*.

Electrolyte solution. NaCl 3 %wt. (CAS 7647-14-5) (Aldrich) was acidified until pH reach 2.7 with HCl (CAS 7647-01-0) (Aldrich). To evaluate the corrosion inhibitor effect, 150 mg of extract of *Solidago chilensis* were dissolved in 10 mL of methanol and added to 50 mL of NaCl 3 %wt. solution.

Potentiostatic polarization. The polarization tests were performed in the cited electrolyte solution, with and without inhibitor addition. The cell used was a conventional three electrodes where the metal was the working electrode, the counter electrode was a spiral platinum wire, and the reference electrode was Ag/AgCl (197.2 mV, KCl saturated). The electrochemical study was conducted using the Potentiostat Gamry™ 3000 on samples with 3.49 cm². The open circuit potential was measured for hundred seconds. The test was performed in triplicate.

Electrochemical Impedance Spectroscopy (EIS). The EIS tests were performed applying 0 V DC voltage versus the open circuit potential over the course of 216 hours of immersion in NaCl 3 %wt with and without inhibitor addition using the same three electrode cell of the potentiostatic polarization essays. The initial frequency was 100 kHz and final frequency was 0.1 Hz. The AC amplitude was 10 mV. The test was performed in triplicate.

Dynamic Mechanical Analysis (DMA). The analysis was performed with simple bending tests on TA Instruments Q800™ equipment, when the samples were fixed in one extremity and bent on the other. To perform this test, the force controlled mode was used to obtain a stress-strain curve. The ramp force initiated in 3 N/min until 18 N.

Results and discussion

Polarization. The potentiostatic polarization curves indicated that the behavior of the corrosion potential and current density of blank and anodized samples, with and without inhibitor immersed in NaCl 3%wt. solution had no significant differences between them. But the corrosion potential shifted to more positive values in anodized samples.

In Fig. 1 it is shown the polarization curves that compare the behavior of corrosion potential and current of the blank and anodized samples, in the NaCl 3 %wt. solution with and without inhibitor.

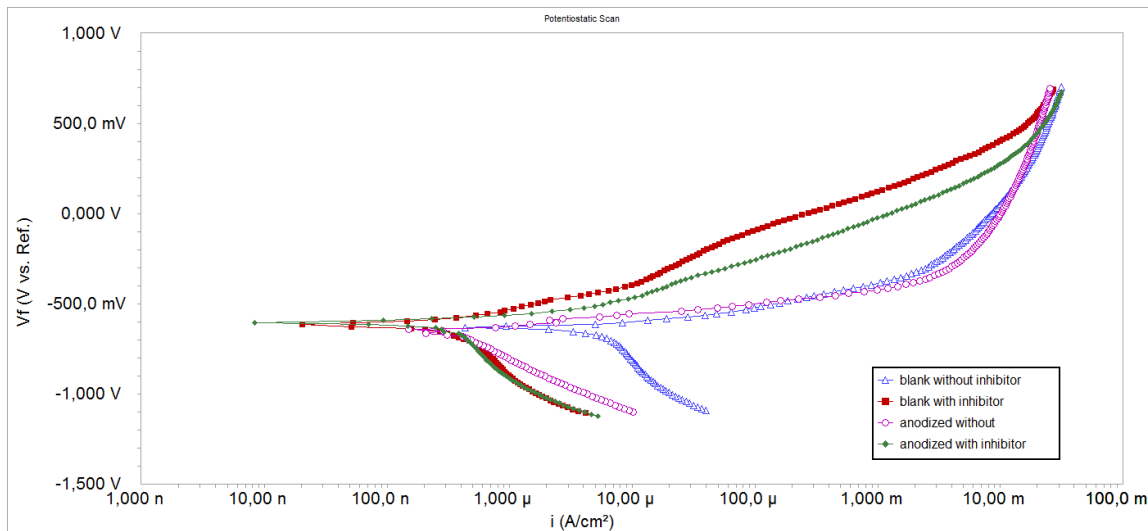


Fig. 1 – Polarization curves of the blank sample and sample anodized with and without inhibitor.

The corrosion potential shifted to more positive values for the anodized samples with inhibitor. In regards to the current, a decrease can be noted for the anodized sample with inhibitor compared with other samples. The coincidence of plots indicates that the anodic effect of the inhibitor not appears on the anodized samples and the current increase with the addition of it is observed. But, the inhibitor effect on blank samples is observed, as a cathodic effect. The displacement curves in the anodic and cathodic regions could indicate the adsorption of the inhibitor, forming a film [20].

Tafel extrapolation measurements were taken and the efficiency value was calculated by Eq. 1.

$$\eta\% = \frac{I_{ocorr} - I_{corr}}{I_{ocorr}} \cdot 100 \quad (1)$$

The better result of inhibition efficiency to all samples with inhibitor was approximately 96 %.

EIS. The EIS essays indicate that the behavior of the polarization resistance (R_p) of the anodized samples without inhibitor is higher than blank samples without inhibitor. And, comparing The R_p of anodized samples it was possible observe that they were similar between them.

In Fig. 2 it is shown the Bode diagrams, where is possible to see curves of phase angle and Z_{mod} versus frequency for the first 0.5h in immersion in NaCl 3 %wt. solution with and without inhibitor of blank and anodized samples. It is possible observe that the Z_{mod} of the samples anodized in solution without inhibitor show values approximately 10 times higher (in the low frequencies range) than the blank samples in the same solution. However, the anodized samples presented similar results in both solutions (with and without inhibitor).

The effect of the inhibitor was higher on blank samples than anodized samples, probably because of the structural changes caused by the anodizing procedure that reduced the adsorption of the inhibitor on the surface of the samples.

One depressed capacitive loop was observed at the higher frequency range followed by an inductive loop in the lower frequency region. The impedance spectra for different Bode diagrams were analyzed by fitting the experimental data to the equivalent circuit model presented in Fig. 3 [21].

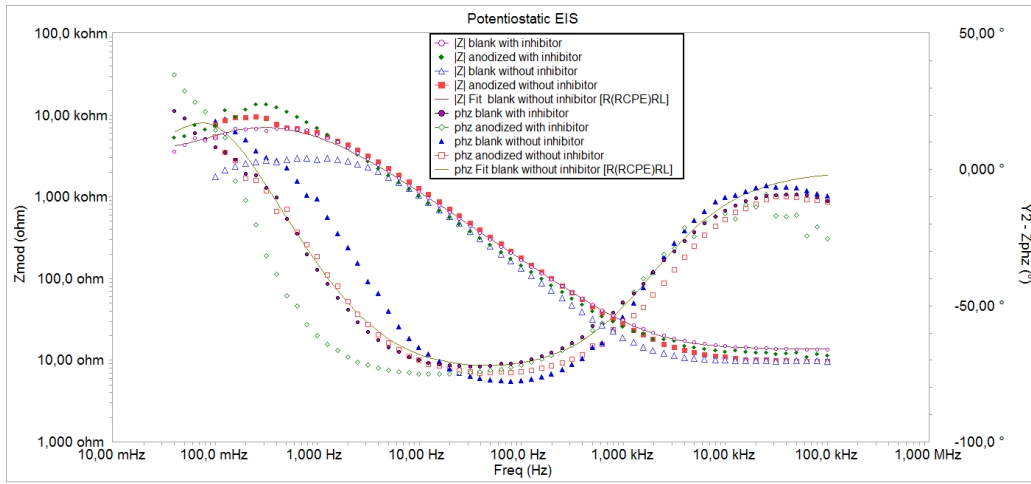


Fig. 2 – Bode diagram for the first 0.5 h in immersion in NaCl 3 %wt. solution, with and without inhibitor of blank and anodized samples.

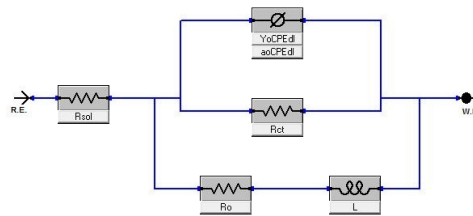


Fig. 3 – Equivalent electrical circuit model used to fit the experimental data of the impedance spectra for different Bode diagrams.

A good fit with this model was obtained with the experimental data. It was observed that the fitted data match the experimental ones. It corresponds to the parallel connection of the charge-transfer resistance with series connection of the resistance R_o and inductance L . The presence of the inductive loop may be attributed to the relaxation process obtained by adsorption specimens like Cl_{ads}^- and Na_{ads}^+ on the electrode surface. The constant phase element, CPE, was introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit. R_s represent the solution resistance. The values of R_{ct} e R_o were determined by EIS measurements and the values of R_p determined by Eq. 2 [21].

$$R_p = \frac{R_{ct} R_o}{R_{ct} + R_o} \tag{2}$$

Fig. 4 shows the behavior of the calculated values of R_p during 216 hours of immersion.

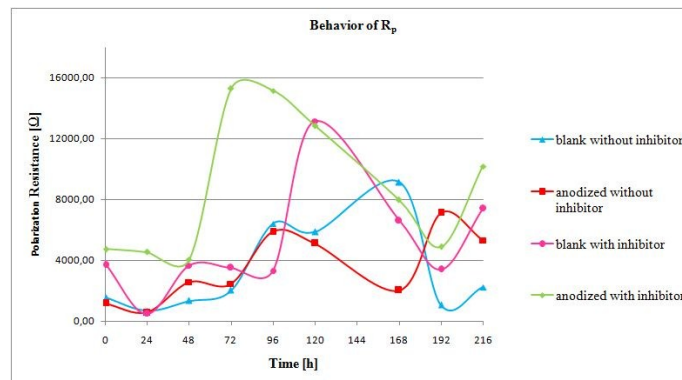


Fig. 4 – The behavior of the calculated values of R_p for blank and anodized samples with and without inhibitor.

It was observed that at 0.5 and 216 hours of immersion, the samples immersed in the solution without inhibitor show lower values of R_p than the samples immersed in the solution containing inhibitor. The analysis of variance (ANOVA) determined that there were no significant differences,

$p \leq 0.05$, for the values of R_p of the samples during 216 hours of immersion. The t-student test determined that there are significant differences, $p \leq 0.05$, between all samples with exception of the blank and anodized samples in the solution containing inhibitor probably because of the data series of means used. T-test compares the means between two groups (blank and anodized) and ANOVA compares the means between the 4 groups. Moreover, the anodized samples immersed in solution with corrosion inhibitor presented the best results.

Dynamic Mechanical Analysis (DMA). Typical curves of simple bending test for blank and anodized samples are shown in Fig. 5.

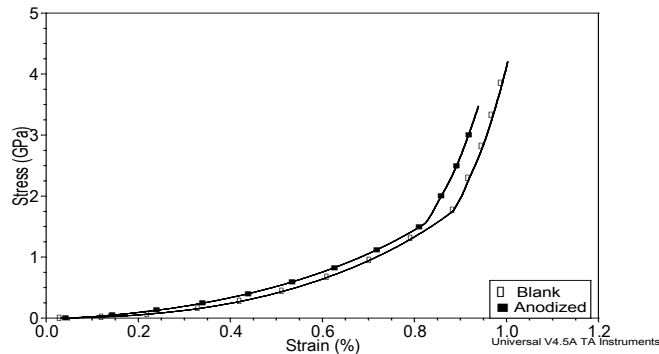


Fig. 5 – Typical curves of simple bending test for blank and anodized samples.

The elastic modulus of the samples calculated by ASTM D-5934 [22], had no significant differences with respect to the anodizing according to ANOVA and t-student test, $p \leq 0.05$. This result shows that the anodizing had no significant effect on the *elastic moduli* of the metal-oxide, considering the precision of the accuracy of the equipment.

Conclusions

The potentiostatic polarization essays indicated that anodized samples present higher corrosion potential and lower current density in both used solutions.

The EIS results presented the higher R_p for the anodized samples in the solution with inhibitor.

The DMA measurements indicated that there are no significant differences between the anodized blank samples on the *elastic moduli*.

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