Application of Electrochemical Impedance Spectroscopy Technique in the Performance Evaluation of Internal Lacquer of the Can/Simulant System

Bianca de O. Pelici[a], Maria Teresa de A. Freire[b], Gelson A. Conceição[b], Eliana S. Kamimura[b] and Célia Marina de A. Freire[a]

[a] *Faculdade de Engenharia Mecânica, Universidade de Campinas - UNICAMP, Campinas, SP, Brazil*
[b] *Faculdade de Zootecnia e Engenharia de Alimentos, Universidade de São Paulo – USP, Pirassununga, SP, Brazil*
e-mail: biancapelici@gmail.com

Introduction

Tin-plate cans represent most of the cans for canned food. Since they are not inert, during the storage period, interaction occurs with the product and metal dissolution can occur, especially when it is acid food. To minimize this interaction it is used organic coatings, and epoxy-phenolic resin is the most used. As the foods are complex biochemical systems, in most of the studies related to the interaction product/package simulants are used, that are organic substances that are analogous to the diffusive properties of food and have simpler composition. These substances are used in the tests to replace the food, to facilitate, speed up and reduce costs in analytical procedures. The choice of simulating is made according to the physico-chemical properties of the food, which follows the classification determined by the legislation. For acidic aqueous food the proposed simulant is acetic acid 3% (w / v). This work aimed to evaluate the performance in cans with nominal layer of tin 2.0 g/m^2 coated with lacquer-type epoxy phenolic (double inner layer) when in contact with simulant solutions. The technique of electrochemical impedance spectroscopy (EIS) was used to monitor the degradation of organic coating and to characterize their barrier properties over time as corrosion resistance Also images were also obtained of the sample surfaces by Scanning Electron Microscopy (SEM) after the electrochemical tests to complement the characterization of the film.

Experimental

Tin-plate with tin layer E = 2.0 g/m^2, coated internally and externally with epoxy fenólic lacquer, with the inner face with double coating, were used for the analyzes. The storage solutions were prepared with distilled water and organic acids (acetic, citric and malic), with a concentration of 0.5 M and pH = 2.8. To achieve the desired pH value was used sodium hydroxide. EIS tests were carried out using a circular 36,0 cm^2 surface of the samples. A potentiostat coupled to a frequency analyzer system, a glass corrosion cell kit with a platinum counter-electrode and a calomel electrode (SCE) were used. As the electrolyte, solution under the same conditions of storage solutions was used. The potential amplitude was set to 10 mV; peak-to-peak (AC signal) in open-circuit, with six point per decade and the frequency range was set from 10 mHz to 10 kHz. The tests were performed in triplicate and monitored over time. On the 200th day SEM imaged were made.

Results and Discussion

Figure 1 shows the experimental EIS plots for the samples immersed in solutions of acetic, citric and malic acids for 1 and 150 days. It is observed that there was a decrease in the value of the module of the impedance and in the diameter of the capacitive arcs over time, indicating that the coating used was losing its protective barrier characteristics. That is, there was decrease in film strength, which is associated with possible failures, in which would be occurring metal corrosion. Note also that for the acetic acid solution the values of $|Z|$ and the capacitive arches were superior than those obtained with the other acids, indicating a less aggressive environment, where the lacquer exhibited better response against corrosion. Between citric and malic acids the behavior were similar.

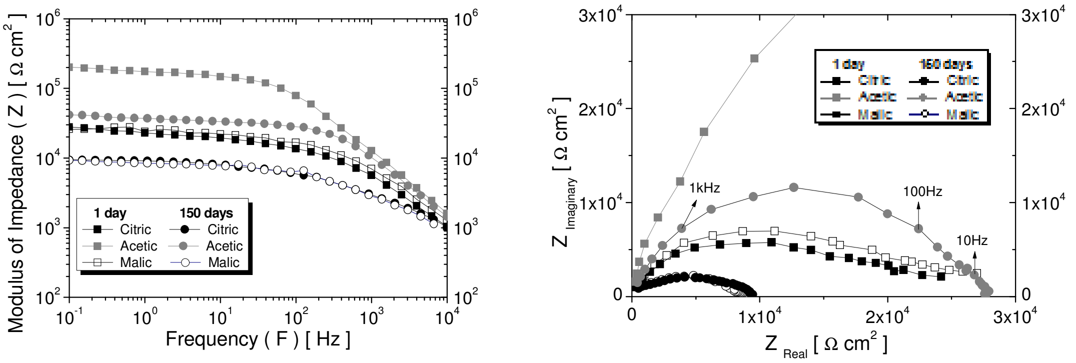

Figure 1 – (a) Bode and (b) Nyquist plots to the samples immersed in solutions of acetic, citric and malic acid

The EIS results were adjusted by the equivalent electrical circuit in which the interfaces metal / coating / simulant are represented by capacitive and resistive elements and constitutes a form of representing the system under study. The circuits were constructed with ZView ® software and the values obtained for the resistance of the coating are shown in Table 1.

Table 1 – Resistance values of coating (Rco) obtained by adjusting the equivalent electrical circuit

	R_{co} (Ω cm^2)		
	Acetic Ac.	**Citric Ac.**	**Malic Ac.**
1 day	$1.6x10^6$	$1.4x10^5$	$1.6x10^5$
150 days	$2.2x10^4$	$1.9x10^3$	$1.0x10^3$

With the data from Table 1 it was confirmed the interpretation of the EIE graphics. The resistance of the coating decreases for the three acids, which may be related to the hydration and migration processes that occur into the polymer film. Faced with acetic acid the coating showed greater resistance. To complete the characterization of the lacquer, images was obtained by the technique of SEM, as shown in Figure 2, in the end of storage period in order to evaluate the effect of corrosion process at the surface appearance of the coating. It is observed that in all situations the lacquer layer showed signs of imperfections such as holes and bubbles, indicating that the coating has suffered degradation process. These images confirm the results obtained by EIE, since the surface that was in contact with the solution of acetic acid showed less degradation.

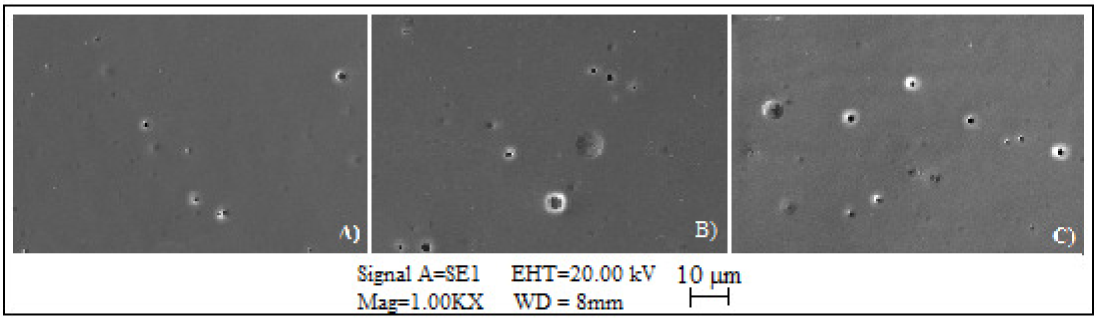

Figure 2 - Scanning Electronic Micrography of the sample of tin-plate immersed in solution of A) acetic acid, B) citric acid and C) malic acid

Conclusions

Through electrochemical impedance technique could be evaluated the system metal / coating / simulant in the study of the characteristics of the interaction packaging / simulant. The EIS technique along with the SEM and analysis of experimental and simulated data obtained with the equivalent circuits led us to conclude that the coating has suffered degradation over time, allowing the permeation of the electrolyte and contact with the metal substrate, causing corrosion process on metal. Furthermore, the film presented better corrosion resistance when exposed to solution of acetic acid. The difference in the behavior of the coating for corrosion when in contact with the different acids may be related to processes that occur between the complexation of organic acid anion and metal ion components of tin-plate because according to complexing anions present, the potential of the constituent metals of the packaging assume different relative positions, thus conditioning the mechanism of internal corrosion of the package.

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