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Use of impedance spectroscopy techniques in the study of corrosion resistance of peel-off aluminum foil lids for the packaging of pureed food

Chiara Zurlini*, Angela Montanari

Stazione Sperimentale per l'Industria delle Conserve Alimentari, Viale F. Tanara, 31/A, 43121 Parma, Italy

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ABSTRACT

This work examines the *chemical and morphological properties* of the different types of aluminum foil lids used for packaging pureed fruit and vegetables (thickness, porosity and type of lacquer applied), their *resistance to corrosion* when in contact with simulant solutions and influence of the *presence of residual air* inside food packages.

Resistance to corrosion was studied using electrochemical impedance spectroscopy (EIS). In an initial approach focused on quality, this technique was used to determine the protective power of the different types of lacquers and to observe changes in the electrode system over time (storage at 37 °C for three days) with respect to permeability to electrolytes, occurrence of porosity and onset of a corrosive peeling process in the metal substrate.

The results of the first accelerated tests carried out in electrochemical cells in air with saline solution, provided a quick, complete feedback on the corrosive behavior of peel-off lids and made it possible to determine the effectiveness of the different lacquering systems considered and the corrosion mechanisms at play.

Electrochemical impedance measurements were also carried out in electrochemical cells, which enable the system to be kept in an oxygen-less environment for some time, in order to reproduce the physico-chemical conditions that are observed in food packages and in a citric simulant solution with pH 4.0. The cells were stored at a temperature of 37 °C and observed over time for up to 14 days of contact. On the one hand, the results obtained confirmed the different corrodibility of the lid groups examined; on the other hand, they provided information on the commercial life of the packages made with materials that have a good degree of protection.

The electrochemical impedance measurements performed with both electrochemical cells show how the value for resistance Rp and capacity Cc registered in the initial phases of the test are fundamental for predicting the corrosion resistance of materials.

In conclusion, from the results obtained it was possible to define key physicochemical and electrochemical parameters, such as nature and porosity of the lacquer or presence of additives, to be taken into account in the production of peel-off lids for which aluminum protection is of fundamental importance. The electrochemical tests have provided information on the impedance values needed to ensure the required shelf life for this type of products, recently introduced on the market.

1. Introduction

The selection of a food-grade metal package must take into account the physicochemical characteristics of the product to be packaged (pH, saline concentration, chemical composition of the food, expected shelf life), filling method (product temperature during packaging, thermal stabilization treatment, storage conditions) and the package closure system.

It is important to evaluate and to be able to determine the chemical resistance of a package to one or more of the compounds present in the food, to prevent corrosion phenomena that can lead to sensory and physicochemical changes in the product content (oxidation, rancidity, taste, bacterial contamination) [1,5].

* Corresponding author.
E-mail addresses: chiara.zurlini@ssica.it (C. Zurlini), angela.montanari@ssica.it (A. Montanari).

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To increase their protective characteristics, metal packaging materials can be coated with protective lacquer or laminated with a polymer film.

The pureed fruit and vegetables on the market are packaged in semi-rigid aluminum containers, sealed with peel-off lids made of the same material. These acid products are corrosive for aluminum (pH ≤ 4.0), making it necessary to protect the metal base with a suitable chemically resistant lacquer. The commercial life of these products is one year.

Over the last few years, there have been several cases of early failure of these packages, due to rapid corrosion of the peel-off aluminum lid, sometimes resulting in perforation. A few months after filling, the packages swelled up due to hydrogen formation from corrosion, leading to high concentration of aluminum in the product, up to 90 mg/kg.

In order to identify the ***causes of intense corrosion*** and a technological solution to the problem, an experimental work was carried out, which consisted of three stages:

- Study of the *physicochemical and morphological properties* of the different groups of peel-off lids, some of which are critical for the corrosion phenomena observed;
- Design of a specific electrochemical method to quickly evaluate and predict the *corrosion resistance* of the lids examined;
- Identifying an analytical method that will provide information about shelf life, taking into account the characteristics of the packaged product as well as filling, packaging and storage methods.

The work examined eleven different types of lacquered peel-off aluminum lids from different suppliers.

2. Materials and methods

2.1. Materials

It was carried out on eleven types of peel-off lids from different industrial lines, with special focus on three types of lids, with particular physicochemical differences and respectively coded as *"First group", "Second group"* and *"Third group"*.

All the lids were made with soft-alloy aluminum foil, with 72 mm diameter and thickness between 50 and 60 μm and lacquered internally with a heat-sealing lacquer, for standard 100 g aluminum trays and external lithography. In all three groups, the surface of the lids was embossed with fine knurling.

2.2. Methods

2.2.1. Chemical and morphological characterization of lids

The morphological properties of the surface were studied using a Vision Engineering Lynx stereo microscope and an electronic microscope combined with Cambridge Stereoscan 200 x-ray microanalysis. The chemical nature of the organic coating applied on the internal side of the lids was identified using an FTIR Perkin Elmer Spectrum One™ spectrometer. The FTIR spectra of the coatings were obtained both by simple reflection and by micro-ATR technique.

The weight of the lacquer on the lids was determined by weight difference using a SSICA in-house method. The results are expressed in g/m^2.

2.2.2. Electrochemical *impedance spectroscopy (EIS)*

Resistance to corrosion was studied using electrochemical impedance spectroscopy (EIS), a technique which provides indications on the insulating power of an organic coating and on the different phenomena that determine the overall corrosion process [2–4,6–10]. Impedance measurements were carried out at free corrosion potential, with the application of 10 mV sinusoidal voltage, in a frequency range from 100 KHz to 10 mHz.

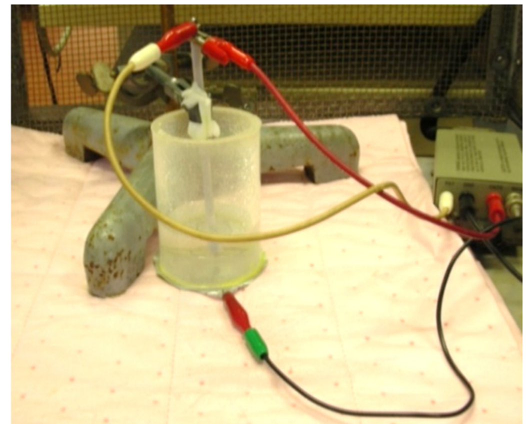

Fig. 1. "Open" electrochemical cells for the electrochemical tests (EIS technique).

The electrochemical tests used Parstat 2273 potentiostat/galvanostat/FRA by Princeton Applied Research. ZView™ software was used to generate the impedance curves. The analysis of the results was based on the Bode and Nyquist diagrams as well as on the following parameters:

Rp (Resistance of the electrolyte in pores, indicative of coating porosity), Rct (Charge transfer resistance, indicative of resistance to under-film corrosion), R'ct (Resistance to transfer of under-film charge), Cc (Capacity of intact coating, indicative of insulating power), Cdl (Double layer capacity, indicative of resistance to under-film corrosion) and C'dl (Under-film charge transfer capacity).

Measurements of corrosion resistance were carried out in two conditions: "open" electrochemical cells for the study of corrodibility of the different materials and "closed" electrochemical cells to obtain information on the shelf life of packaged food products.

For the preparation of the "open" electrochemical cells, Plexiglas cylinders with an area of 28 cm^2 were used, glued directly onto the internal surface of the peel-off lids. The electrolyte used was an aerated solution of 1% sodium chloride and the measurement of electrochemical impedance was carried out with two electrodes, platinum as counter electrode and the analysis area as working electrode (Fig. 1). The cells were hot filled (T = 70 °C) and the measurement was made in the presence of oxygen. The cells were heat sealed at 37 °C and the measurements were carried out at preset times, after 1 h, 1, 2, and 3 days of contact.

For the "closed" electrochemical cells the electrolyte used was a deaerated citric solution at pH 4.0 and the impedance measurement was 3-electrode, SCE as reference electrode, platinum as counter electrode and 20 cm^2 analysis area (Fig. 2). The cells were filled at 70 °C in the absence of oxygen. The cells were stored at 37 °C and measurements carried out at the preset times, after up to a maximum of 14 days of contact.

3. Results and discussion

3.1. Surface properties

3.1.1. Surface morphology of the lids

Under an optical microscope, the internal surface of all the lids examined revealed a "globular" kind of embossing, more marked in the "third group" than in the other two groups. The surface of the "third group" lids appeared shinier than the other lids, while the "second group" was more opaque.