Interaction between aluminium cans and beverages: Influence of catalytic ions, alloy and coating in the corrosion process

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ABSTRACT

This paper studies the interaction between aluminium cans and model solutions formulated to mimic beverages. Different levels of chloride and iron were studied in acid medium in relation to their potential to aluminium corrosion. The paper also evaluates the impact of packaging properties on aluminium corrosion. Among the evaluated concentrations of Cl and Fe, a critical combination to the aluminium alloy integrity was not identified. The apparently random occurrence of corrosion when exposing packaging specimens to the studied solutions was observed, which was attributed to the heterogeneity of the specimens. Three hypotheses were pointed out and discussed to describe the occurrence of corrosion, considering alloy composition and coating property parameters, proposing a new line of studies within this topic.

1. Introduction

Aluminium is a material used in various sectors, such as packaging of food, cosmetics, pharmaceuticals, household items, construction, as well as in aircraft manufacturing. Advantages for using it as food packaging are well known and documented, including basic requirements for food preservation such as protection to light and gas barriers, as well as versatility, post-consumer material recycling and corrosion resistance.

However, when exposed to certain conditions found in food and beverages, such as acid media containing chlorides (Soares, Anjos, Faria, & Dantas, 2016), corrosion resistance of aluminium alloys is modified, affecting their integrity (Jellesen, Rasmussen, & Hilbert, 2006; Solmaz, Kardas, Yazici, & Erbil, 2008). Other components normally found in water, food and beverages can also induce, catalyse or strengthen the aluminium packaging corrosion process. The presence of oxidizing agents in the product is one of the contributing factors for metal dissolution in food cans, and is included in this class of substances such as pigments and metallic ions such as iron (Khedr & Lashien, 1992; Perring & Basic-Dvorzak, 2002). Furthermore, the chloride ion is often considered as one of the main compounds that begins the localised corrosion process in aluminium alloys (Bakos & Szabó, 2008; Mayouf, Juhaiman, & Subaybani, 2008).

The first step in the initiation of the pit corrosion process involves the adsorption of chloride ions on the oxide layer surface (McCafferty,

1995). The corroded product is expected to be $Al(OH)_2Cl$ and the steps involved in the pitting corrosion is well described in the literature (Szklarska-Smialowska, 1999; Wong & Alkire, 1990).

Although some studies are available in literature describing anticorrosive substances (Xhanari & Finšgar, 2016), some of them naturally occurring in foods (Abiola & Tobun, 2010), there is a lack of studies focusing on the aluminium alloys used for food packaging (3104, 5182 and 8011, for instance).

Aluminium cans for beverages are made of two aluminium alloys. The 3104 alloy is used at the body (one-piece part that comprises the bottom and wall) of the can due to its ductility - property that allows the draw and wall ironing process to form the can. The 5182 alloy is used at the top (closure) of the can, has good corrosion resistance but is not ductile as the 3104 alloy, especially because the high amount of magnesium in its composition. According to Davis (1999), both alloys present good corrosion resistance, but the 5xxx series aluminium alloys are more resistant to corrosion than the 3xxx series alloys. Despite of its corrosion resistance, it is important to keep copper in low levels in the 3104 alloy (up to 0.15%) otherwise the tendency to corrosion becomes more pronounced.

In fact, the industry is still faced with corrosion in packaging during storage as a major recurring problem. In general, this problem is observed a few days (15–20 days) after beverage packaging. It still occurs in the industry, and it is rarely observed by the consumer. Pitting corrosion develops, in which its trajectory is traced towards the thickness

of the package, resulting in the perforation of cans and loss of the product.

In fact, this represents a real and important problem with environmental impact (material and electricity consumption for producing packaging and water for producing beverages - the latter being about 30% higher than the final beverage volume) and economic impact of the losses caused by the corrosion process, which are enormous. Another aggravating factor is food and drink waste. Therefore, the importance to understand this problem is highlighted, in order to solve it.

In a previous study, Soares, Dantas, and Anjos, (2017) demonstrated that the corrosion process in aluminium beverage cans is catalysed when the copper and chloride ions are found in the acid medium. Perring and Basic-Dvorzak (2002) described that substances such as anthocyanin and iron, compounds found in food and beverages, is one of the contributing factors for metal dissolution in food cans.

Even so, information on corrosion in aluminium food packaging is scarce in the literature, especially when considering corrosion catalyst found in food and beverages. Often, such compounds are found in food and beverages in amounts well below those observed in traditional corrosion studies (Niknahad, Moradian, & Mirabedini, 2010; Oliveira, Moraes, & Faez, 2009; Yazdzad, Shahrabi, & Hosseini, 2008). Therefore, it is important to study the interaction of this packaging with food and beverages to better understand the processes involved.

The main objective of this work was to study the influence of catalytic ions such as iron and chloride in acidic medium on the corrosion of aluminium packaging. The experiments were designed to study the behaviour of the 3104 aluminium alloy by polarization curves, as well as to evaluate the performance of aluminium cans when exposed to acidic medium with Fe and Cl ions. For this last experiment, two sample conditions were studied based on the porosity of the internal coating.

2. Material and methods

This study was carried out in three parts. In the first part, only the aluminium alloy (AA3104-H19) was evaluated, assessing the corrosion parameters of each component (iron and chloride) isolated or in combination. Then, in the second part, the coating layer was evaluated through the coating porosity in the real packages. Finally, in the third part, the interaction between the different products and the real package system (aluminium can coated with varnish) was evaluated in relation to corrosion, considering the aluminium release to the solution and different microscopic techniques. Based on the results, three hypotheses were formulated, evaluated and discussed to describe the observed behaviour.

2.1. Model solutions

This work was carried out using model solutions. Adopting this approach, the product composition and properties can be controlled in order to better understand the involved phenomena. Furthermore, it enables reproducible experiments to be conducted. The preparation of solutions was based on previous studies with different beverages, which were used to mimic real products through a simplified composition.

All model solutions were prepared by adding citric acid pentahydrate (Merck) to ultrapurified water (0.7195 g L^{-1}), resulting in a solution of pH 3, which corresponds to several beverages bottled in aluminium cans (Soares et al., 2016). This acidic solution without adding aggressive ions is referred below as "Control". NaCl (Merck) was used for the addition of chloride (studied concentrations: 50 mg L^{-1} and 100 mg L^{-1}), and for the addition of iron (studied concentrations: 25 μg L^{-1} and 100 μg L^{-1}) a standard solution containing metallic iron was used (TraceCERT® - Sigma-Aldrich).

Therefore, the following solutions were used for the interaction study: Control (citric acid pH3) and increased solutions of chloride (Cl, in mg L^{-1}) and iron ions (Fe, in μg L^{-1}). These solutions are identified in

this paper as: Control, $Cl_{50}Fe_{25}$, $Cl_{100}Fe_{25}$, $Cl_{50}Fe_{100}$, $Cl_{100}Fe_{100}$ – the numbers in subscript refer to the concentration of the compound in absolute value (each one in the corresponding units). The pH of all the studied solutions were set in 3.

2.2. Materials (Packaging)

In this study, a batch of aluminium cans, donated by a can manufacturer in Brazil and obtained from a regular lot commercialised by the beverage industry, was used. Consequently, the study was conducted with a real and representative sample. This package is a two-piece can with a nominal capacity of 350 mL (12 oz.), manufactured adopting the Draw and Wall Ironing (DWI) method with the AA3104-H19 alloy and internally coated with an organic coating.

The internal coating of the cans was 3 μm thick (determination made in Bruker profilometer, model DektatXT). It was identified directly analysing the coating film by means of infrared spectroscopy using a Perkin Elmer Spectrum 100 model, using the Attenuated Total Reflectance (ATR) spectroscopy technique (Dantas, Anjos, Segantini, & Gatti, 1996). The obtained spectra were compared with known spectra (standard library) for coating identification. The application of epoxy acrylate lacquer was identified in the aluminium cans.

The characterisation of the internal coating in 15 cans showed that the batch used in this study had a mean coating dry layer of 103.11 (± 3.74) mg/can and a mean porosity of 0.3 mA/can (maximum of 1.3 mA/can).

Therefore, all the cans used were in accordance with the specifications normally used by packaging and beverage producers.

All specimens used in the study were collected from the body's wall of the aluminium can, after removing the top and down parts and unwind the wall, to avoid the influence of the ironing process (manufacture of the can) over the metal physical properties.

2.3. Polarization measurements

The polarization curves of the AA3104-H19 alloy were plotted to associate them with the critical pitting formation potential in each model solution. The specimens with an area of approximately 1 cm^2 were collected from the aluminium can's wall, after removing the lithography and internal can coating by solvent (acetone p.a.), followed by surface polishing in metallographic sandpaper (200 to 1200 grit).

The determination was carried out using a potentiostat/galvanostat device (model PGSTAT 302 N, Autolab, and software NOVA version 2.1.1, developed by Metrohm Autolab B. V., Netherlands), using a system of three electrodes. Therefore, in addition to the working electrode (sample), a Saturated Calomel Electrode (SCE) was also used as a reference and a stainless-steel electrode was used as counter electrode.

The model solutions were bubbled for one hour with ultra-pure nitrogen gas before starting the assay, in order to remove residual oxygen. The cell was maintained with N_2 in the head-space during the run. The polarization curve was obtained by adopting the potentiodynamic method using a scanning rate of 1 mV s^{-1} and the kinetic parameters of the corrosion process were determined using the NOVA software. The pitting potential (Ep) was defined from the intersection of the lines before and after the abrupt increase of current in the working electrode (Wolynec, 2013). This assay was performed in 3 replicates.

2.4. Determination of the internal coating porosity

Metallic exposure through the internal coating, also known as porosity, was determined by electrochemical method using 1% NaCl (Merck) aqueous solution, applying a potential difference of 6.3 V for 4 s and measuring the current value (mA) that flows through the discontinuities of the coating.

This measurement was taken in several specimens in the same area that later came into contact with the model solutions during the

interaction period (Section 3.3). A potentiostat/galvanostat device (model PGSTAT 302 N, Autolab, Netherlands) was used and the results were expressed as mA cm^{-2}.

2.5. Model solution conditioning and packaging evaluation

To evaluate the interaction of the model solutions with the specimens from the aluminium cans (wall), a system consisting of a glass vial (120 mL) with a hole in its base ($\sim$ 1 cm^2) was assembled, and the specimens (collected from the aluminium cans' wall) were bonded with epoxy resin (with a thermal resistance up to 80 °C) and externally sealed with silicone.

The solutions were added to the described cell and conditioned for 60 days at 40 °C. During this period, the systems were monitored for any sign of corrosion (visually). Further, aluminium quantification was carried out in the model solutions after 15, 30 and 60 days of contact. Five specimens were evaluated for each model solution.

To quantify the aluminium concentration in the model solutions, an inductively coupled plasma atomic emission spectrometer (ICP OES, model OPTIMA 8300 DV, PerkinElmer, Waltham, USA) were used, considering a calibration curve appropriate for determinations prepared using an aluminium standard for ICP (TraceCERT®, Sigma-Aldrich).

Microscopic evaluations were conducted using an optical microscope (Leica, model M165C), scanning electron microscopes (SEM, Zeiss, model 904D and FEI, Quanta model 650 FEG) with microanalysis systems (Oxford Instruments) and an atomic force microscope (Bruker, FastScan Dimension model). Prior to the SEM analysis, the specimens were covered with gold (sputtering, model SDC050, Balzers).

3. Results and discussion

3.1. Corrosion parameters of AA3104-H19 aluminium alloy

The critical pitting potential values (E$_p$) were obtained from the intersection of the lines before and after the current increase. Fig. 1 was plotted separating the solutions based on the chloride concentration, to
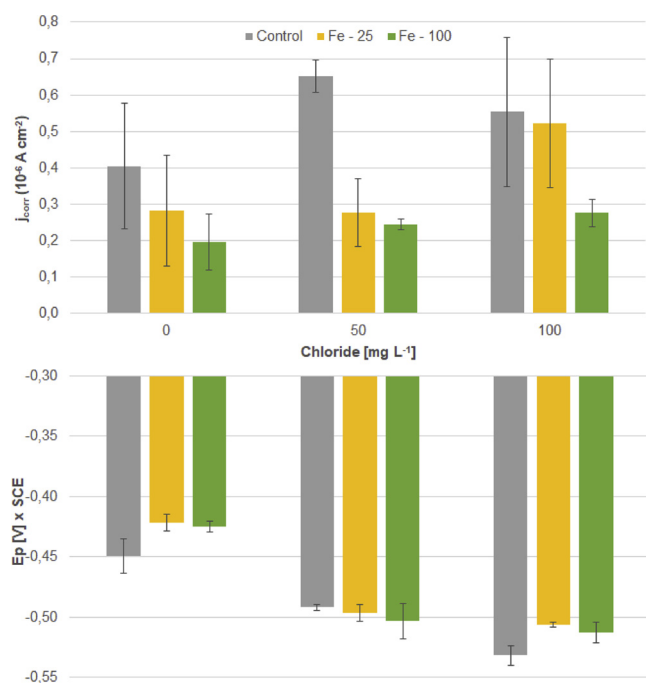

Fig. 1. Corrosion current density (j$_{corr}$) and critical pitting potential (E$_p$) of the AA3104-H19 alloy for citric acid solution - pH 3, as a function of the concentration of chloride (50 and 100 mg L^{-1}) and iron (Fe, 25 and 100 µg L^{-1}).

visualise the influence of this element on the critical pitting potential (E$_p$), as well as on the corrosion current density (j$_{corr}$). All Tafel parameters (b$_c$, b$_a$, E$_{corr}$, j$_{corr}$) and the critical pitting potential values (E$_p$) obtained from analysing the polarization curves are presented in the supplementary data material. The b$_c$ and b$_a$ slopes are related to the cathodic and anodic process occurring in the evaluated system (solution versus metal), as well as the E$_{corr}$, which represents the potential at the equilibrium reaction between the metal dissolution and the hydrogen reduction.

It was observed that the rise in chloride concentration in the solution increased the tendency of pitting in these systems (solutions and sample) due to a slight decrease in E$_p$. The small variation can be partially explained by the presence of citric acid and the pH.

The citric acid was used as acidulant in this study, and it was partially dissociated (pKa1 = 3.15, pKa2 = 4.77 and pKa3 = 6.40 – Atkins & Paula, 2011) in the solutions, resulting in the presence of citrate anions, which is a weak acid salt. According to Galvele (1976), weak acid salt anions such as benzoate, tartrate and acetate inhibit the occurrence of pitting by the elevation of E$_p$.

Fig. 1 shows a tendency to increase the corrosion current density (j$_{corr}$) following the increase of chloride in solution. However, for each chloride concentration studied, the increasing of iron ions in solution decreases j$_{corr}$. This is probably due to a combination of substances in medium (citrate, chloride and iron) resulting in less amount of aggressive ions to react on metal surface.

The Tafel b$_c$ slope value was similar in all solutions. As the medium was deaerated, the main cathodic reaction was that of the reduction of the hydrogen ions, whose calculated Tafel b$_c$ slope value is -0.118 V (Wolynec, 2013). Šeruga and Hasenay (2001) obtained values of E$_{corr}$ = -0.72 V, i$_{corr}$ = 0.73 µA cm^{-2}, b$_c$ = -235 mV and b$_a$ = 115 mV for a pure aluminium electrode in contact with deaerated citric acid solution (0.05 M) and pH 3. In acid pH and in the absence of oxygen in the studied cell, as well as of the electrochemical processes involved, the dissolution of aluminium is under electrochemical control, causing a reduction in hydrogen (cathodic process) and release of aluminium ions (anodic process).

The corrosion current (j$_{corr}$) is an indicative of the corrosion rate of the system. Higher values indicate greater dissolution of the aluminium. In the studied solutions, the corrosion current density is very low, i.e. in the order of 10^{-7} A cm^{-2}.

One reason for this is the concentration of the aggressive ions studied, especially chloride - an important corrosion catalyst for aluminium. Yazdzad et al. (2008) determined values of 3.8 µA cm^{-2} for the 3003 alloy in 0.5% NaCl solution. It corresponds to a chloride concentration 50 times higher than the one used in this study, whose maximum amount was 100 mg L^{-1} (0.01%). However, it should be mentioned that this study evaluated concentrations compatible with those found in food and beverages. The concentration of chloride in beverages, for example, is generally lower than 250 mg L^{-1} (Soares et al., 2016). In fact, in a previous work by this research group (Soares et al., 2017), it was observed that the corrosion current measured for the citric acid solution system (pH3, AA3104-H19 aluminium alloy) remained in the order of 10^{-7} A cm^{-2} and it was not influenced by the concentration of chlorides for values between 50 and 1000 mg L^{-1}.

Therefore, in the studied solutions, the corrosion current density was low, and the variations in the obtained values cannot identify a potentially more critical solution for the corrosion of the AA3104-H19 alloy.

3.2. Coating porosity

The basic principle of the coating porosity assay is to measure the electric current value that flows through the discontinuities of the coating. Therefore, higher values of current means that the coating presents more discontinuity, i.e., more pores that can be filled up with salt solution during the evaluation - then becoming a free way to the

contact between beverage (or model solutions) and the packaging metal substrate.

The maximum limit for porosity of the internal coating (or exposed metal) practiced on the market for 350 mL cans is 25 mA/can. This limit was used in this study as a reference. Consequently, the main differential of this work was ensured: the study of packaging in real conditions of use, unlike much of the literature that considers specimens and/or packaging developed with precision of research laboratories (and that therefore, do not have the imperfections and natural variations of industrial products).

By estimating the internal area of the can exposed to the electrolytic solution in the assay in approximately 250 cm², the direct ratio for the analysed specimens would be approximately 0.1 mA per specimen. Therefore, specimens with a response higher than 0.1 mA were considered equivalent to cans above the maximum accepted porosity value. Since the measured current response is proportional to the metal exposure area, it was assumed that the above approach would be valid for the study involving materials with different protection conditions of the metallic substrate.

Next, the specimens used in this study were divided into two groups: high metal exposure (HP, > 0.1 mA cm^{-2}) and low metal exposure (LP, < 0.01 mA cm^{-2}). The low metal exposure group, or low porosity, would be representative of cans with a response of up to 2.5 mA/can. This value is classified as acceptable by the packaging and beverage industries. The high porosity group would be representative of responses above 25 mA/can, i.e. above the maximum commercially acceptable value. Specimens with a response between 0.01 and 0.1 mA cm^{-2} were not analysed, as this response was maintained as a safety interval. Fig. 2a shows the results presented for the analysed samples, considering 420 measurements (35 cans).

Considering that 31% of the evaluated specimens presented a result ≥ 0.1 mA cm^{-2}, and extrapolating this result to the total area of the can, this would indicate that at least 30% of the cans would be out of specification. In practice, as well as demonstrated by the results obtained in the characterization of this lot (maximum measured value: 1.3 mA/can), values of metallic exposure above the maximum limit adopted are rarely observed in the evaluation of new and intact cans. Since the measured current is proportional to the exposed metallic area, the variability of the obtained results demonstrates that the metallic exposure (coating porosity) presents pores that are not homogeneously dispersed through the internal surface of the packaging.

3.3. Beverage / packaging interaction over the storage time: Aluminium migration

The release of aluminium from the coated packaging into the solutions is a key data to evaluate the interaction potential between the package and the solutions. The methodology used to quantify the aluminium concentration in solutions over the storage time by ICP OES had a lower limit of quantification (LQ) of 25 µg L^{-1}.

Two scenarios were considered, based on the metal exposure (porosity) of specimens: specimens with good coating condition, or low porosity (< 0.01 mA cm^{-2}), and specimens with inappropriate coating condition, or high porosity (> 0.1 mA cm^{-2}).

Many specimens remained unaltered throughout the storage period (60 days at 40 °C) having contact with all the studied solutions and in both coating conditions. However, in few specimens of both coating conditions, a huge concentration of aluminium was quantified, affecting the average value, as shown in Figs. 2b and 3 . The first conclusion of these results is that the coating condition based on metal exposure is not the key factor to predict aluminium release from metal package to the food or beverage – even though this is the standard assay in both industry and academia. The second conclusion is that there is an important difference among specimens, which makes it difficult to evaluate using average values. Furthermore, it also indicates that the performance of a packaging batch is dictated by a small number of

individuals, whose properties (such as local composition in the metal layer and/or local integrity in the varnish coating) are dominant over the corrosion conditions, as discussed in the next sections.

However, it is useful to observe the average values for a first evaluation.

Fig. 2b shows the average values for the aluminium concentration in the different model solutions over the storage time. Fig. 2b shows that the release process of aluminium is more intense at 60 days of storage at 40 °C. In this period, the packaged product is already in the distribution centres and at points of sale and the corrosive process should results in can perforation and loss of product. It represents a great waste to the food and beverage production and distribution chain.

Moreover, compared to the results of Fig. 3, another important piece of information is that the increase in aluminium concentration was measured in only a few specimens, which can be observed in the comparison between the average value (bar height) and higher value (label of green bars) in Fig. 2b, as well as in the individual assessment of Fig. 3.

However, the results presented in Fig. 2b show that aluminium migration was high in low porosity test specimens, sometimes even higher than in high porosity specimens. It was also observed that the high iron concentration in the solution resulted in the increase of the aluminium migration within the studied period, but high values of aluminium were also quantified in solutions containing low iron concentration.

By globally evaluating the interaction between the studied solutions (different compounds in an acidic environment) and the two samples (high and low porosity), it was observed failures in few specimens, i.e., interaction process which results in high aluminium values in the solutions leading to corrosion and perforation of the packaging.

In fact, most of the specimens have maintained values below the limit of quantification (LQ) during the 60 days of contact, highlighting the coating protective role. It is also observed that the failures occurred apparently randomly among the treatments studied (comparing the porosity condition versus the different solutions), although it reflects an increase in the concentration of aluminium in the solution mainly after 60 days of contact (T = 40 °C). Some data are not shown due to the early corrosion of the specimen (e.g. at 15 days).

The solution containing the Cl$_{50}$Fe$_{100}$ combination showed one of the highest corrosion current densities (0.487 µA cm^{-2}) when in contact with the aluminium alloy AA3104-H19 (without organic coating). Consequently, it is supposed to be one of the most aggressive for packaging among those studied. For this reason, it was expected that this system would be one presenting higher dissolution of aluminium for the solution, especially in the high porosity condition, given the higher rate of corrosion that it would be subject to.

However, the values of the aluminium quantification in the same solution showed no detectable migration during the contact period, when studying the high and low porosity coated specimens. In other words, even using the solution with one of the major corrosion potential, some of the samples showed no corrosion (visible or measurable by the aluminium quantification), indicating the absence of free contact between the solution and the metal surface. This demonstrates that other factors are involved in this process and need to be better understood, especially the role of lacquer used in the packaging. The influence of the coating on the specimens analysed in the interaction process seems to be the major factor in this study.

Therefore, some questions arise when the data is evaluated, such as: "Why do some specimens undergo changes before others?". It is important to mention that all the specimens were collected from cans of the same lot, which were new and donated by the manufacturer and separated from a regular lot in commercialisation with excellent specifications.

The results obtained confirmed the heterogeneity of the specimens. More importantly, the results indicate that the effect of possible coating imperfections and/or local metal composition in the alloy can overlap
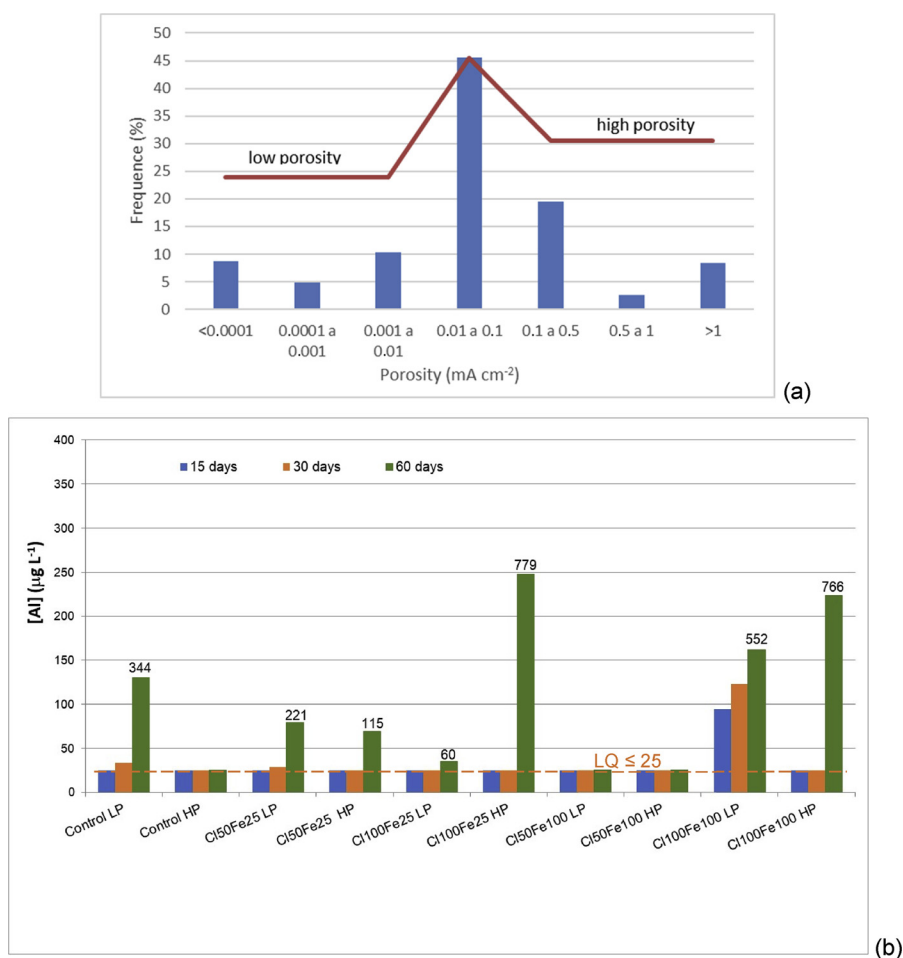
Fig. 2. (a) Histogram with the porosity response (exposed metal) of the evaluated specimens, divided into two groups: high and low porosity. The red line shows the total percentage of these two groups. (b) Average concentration of aluminium ($\mu g\ L^{-1}$) released to solutions studied as a function of the storage time at 40 °C. HP: high porosity and LP: low porosity. Labels indicate the highest values measured for each system (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

the effect of the model solution composition in the corrosive process.

4. Discussion: analysis of the factors that lead to the dissolution of aluminium

Based on the results obtained from the material evaluation by polarization curves, the polymeric coating porosity and the interaction process between packages specimens and solutions, three hypotheses were formulated, evaluated and discussed to describe the observed behaviour regarding aluminium dissolution into model solutions.

Once the metal matrix is the same and the responses obtained from the polarization curves do not indicate a potentially more aggressive solution to the metal matrix among the studied solutions, three possibilities can be considered to explain the problem:

i The local composition of the aluminium alloy presents variations in the ratio of metallic elements considering the average alloy composition. If these composition show elements that catalyses the corrosive process in regions of aluminium exposure to the solutions, the package will failure;

ii The coating has a specific performance in each specimen ; therefore, even though a whole lot can be approved after sampling, some packages can show specific problems in their coating, compromising the integrity;

iii The solutions can permeate the coating, reaching the metal surface and then promoting the corrosion.

These hypotheses are developed, as follows.

4.1. Hypothesis (1): local alloy composition influences the packaging corrosion

Aluminium alloys used to manufacture beverage packages have chemical elements such as iron (Fe) and copper (Cu) in their composition (The Aluminum Association, 2015), which should be kept at low levels to reduce the tendency towards aluminium pitting corrosion (Davis, 1999).

However, a small variation of local composition may result in the formation of galvanic microcells, which accelerate the corrosion of aluminium in the acid medium, such as that found in beverages. This problem becomes more relevant when it occurs in a metal exposure region, i.e. discontinuity in the polymeric coating resulting in pores.

Different performances among the studied systems, some of them with very high aluminium dissolution even in low porosity specimens (low metal exposure by the coating) show that the kinetics of corrosion is influenced by specific variations in the integrity/properties of the packaging. The local composition of the metal substrate, therefore, may be one of these factors.

In fact, this hypothesis is confirmed by the SEM-EDX analysis. Fig. 4 shows a region of one of the packages studied that presented corrosion. The image by the microanalysis identifies the presence of copper, which was estimated in a relative concentration of 5% in that position. This value is much higher than the average composition of the alloy. Since
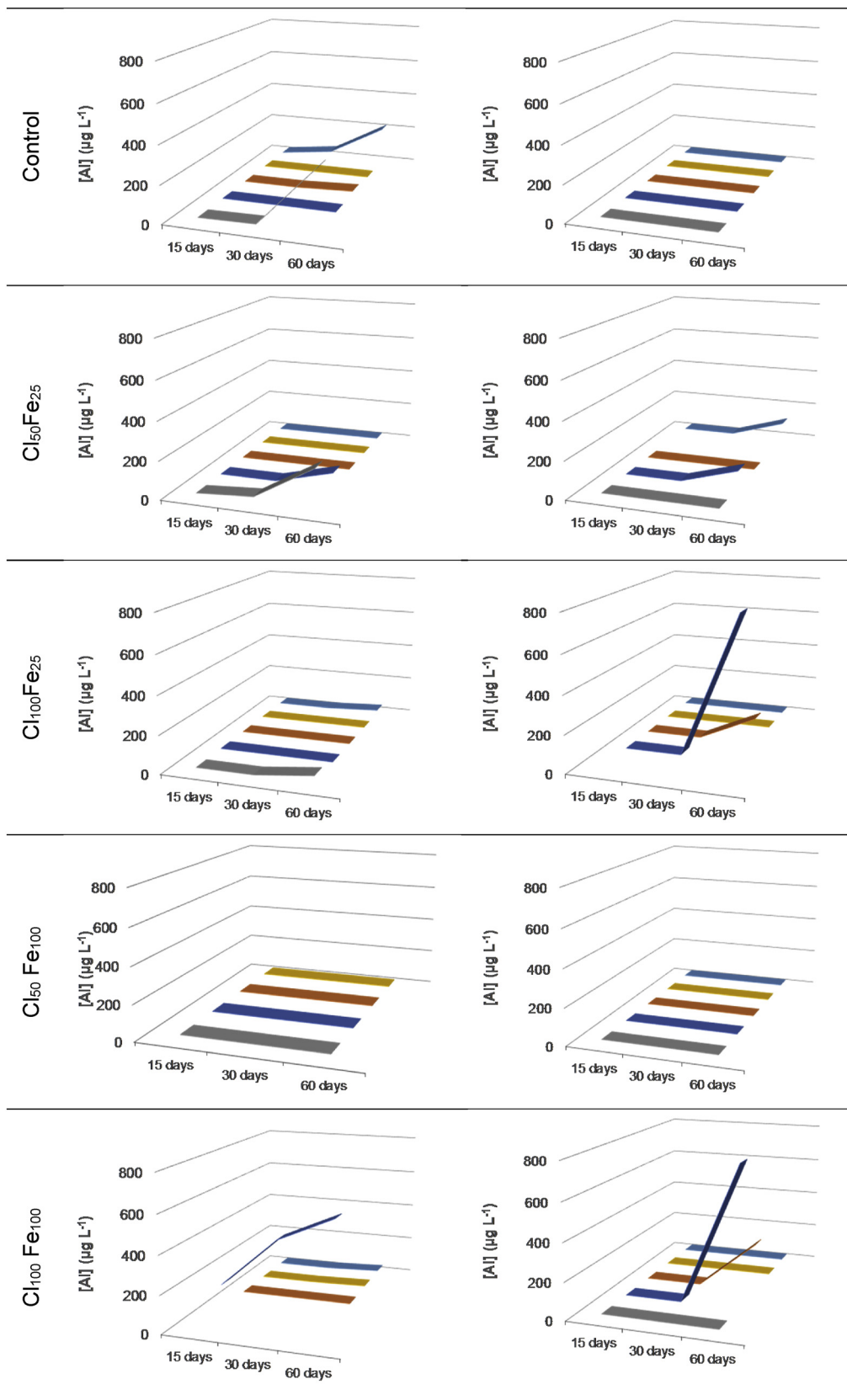
Fig. 3. Concentration of aluminium in the specimens studied as a function of the solution type, storage time and coating condition (left: low porosity specimens; right: high porosity specimens).
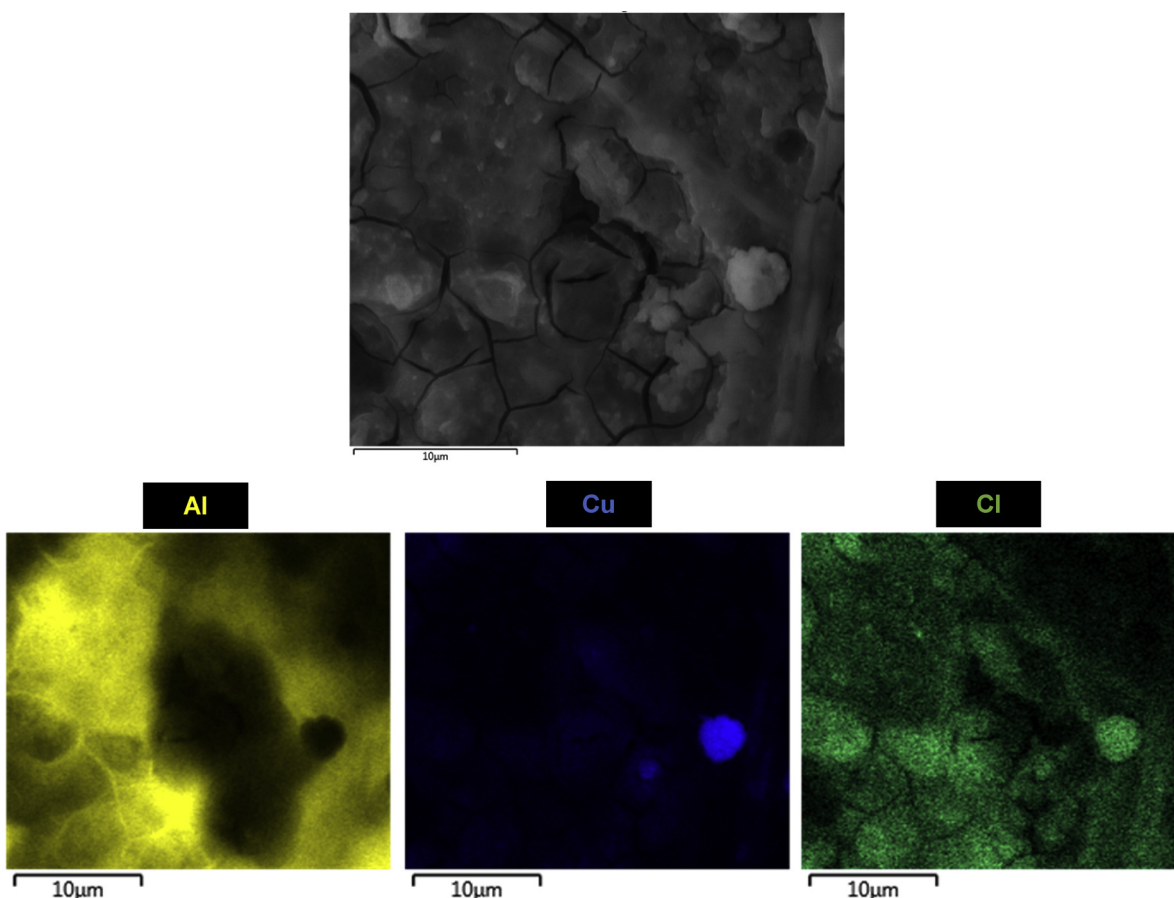
Fig. 4. Corrosion region identified by SEM (5 kV) after 60 days of contact at 40 °C. Up: topography image. Down: element mapping of Al, Cu and Cl.

the EDX technique used in the microanalysis identifies signals of only a few surface micrometres at the point of the electron beam's incidence, copper can be confirmed on the surface of the aluminium (inside the pit region) in contact with the studied solutions. To the best of our knowledge, this was firstly reported here.

Copper is present in the AA3104-H19 aluminium alloy at concentrations between 0.05 and 0.25% (The Aluminum Association, 2015), and it was quantified at 0.22% in the package sample used in this study (i.e. average value in the alloy evaluated). According to Davis (1999), the increase in the concentration of copper in the aluminium alloys of the 3xxx series, increases its tendency to corrosion, and this effect becomes more significant in concentration from 0.15%. Pitting takes place in copper-rich regions as a consequence of galvanic effects between inclusions or depositions and the metallic substrate, as reported in the literature (Xhanari & Finšgar, 2016; Soares et al., 2017).

Therefore, the identification of this element confirms the hypothesis of the influence of the local composition of the material on the corrosion process, resulting from the interaction of the package with the medium. Thus, a local variation of composition can accelerate corrosion of the aluminium in the acid medium. Even in small regions, this flaw is enough to affect the packaging, which may result in perforating it.

Although the local difference in the metal alloy composition may explain the observed failures, the contact of the metallic surface with the solution/beverage is only possible if there are problems in the coating performance. Therefore, two hypotheses (2 and 3) regarding the can inner polymeric coating are described and developed below, taking into account its performance and permeation.

4.2. Hypothesis (2): coating performance

The can inner coating has a very important function in metallic

packaging: to minimize the interaction between the content and the container. Once a high metal dissolution into the product is observed, a high interaction has taken place in the system and, therefore, the coating has partially lost its protective function.

For the studied systems, the coating performance can be better understood when assessing the high and low porosity results for the same solution, shown in Fig. 3.

From this comparison, it can be observed that the increase in metallic exposure does not necessarily result in an increase in the aluminium dissolution of the package for the model solutions. Once that the coating porosity response is related with the metallic exposure of the aluminium through the polymeric coating, it was expected to observe high aluminium concentration in solutions that had been in contact with the high porosity specimens. However, the obtained results demonstrate that each specimen has its own performance in the interaction process with the solutions. In some cases, even higher aluminium values are observed in the contact of the solution with the low porosity specimens.

It is thus confirmed that the internal coating condition of the packages is not fully homogeneous within the same production batch and that the classification of the samples in terms of porosity (or exposed metal) is not the determining (or more suitable) parameter for predicting if a sample will perform well during conditioning with model solutions or even commercial beverages. This conclusion is relevant when it is observed that the porosity analysis is a methodology currently used to measure the quality of internal coating in both the industry and academia.

To better understand the coating performance during its interaction with the beverage, the specimen's surfaces were studied by AFM before (Fig. 5a) and after (Fig. 5b) the contact with the solutions.

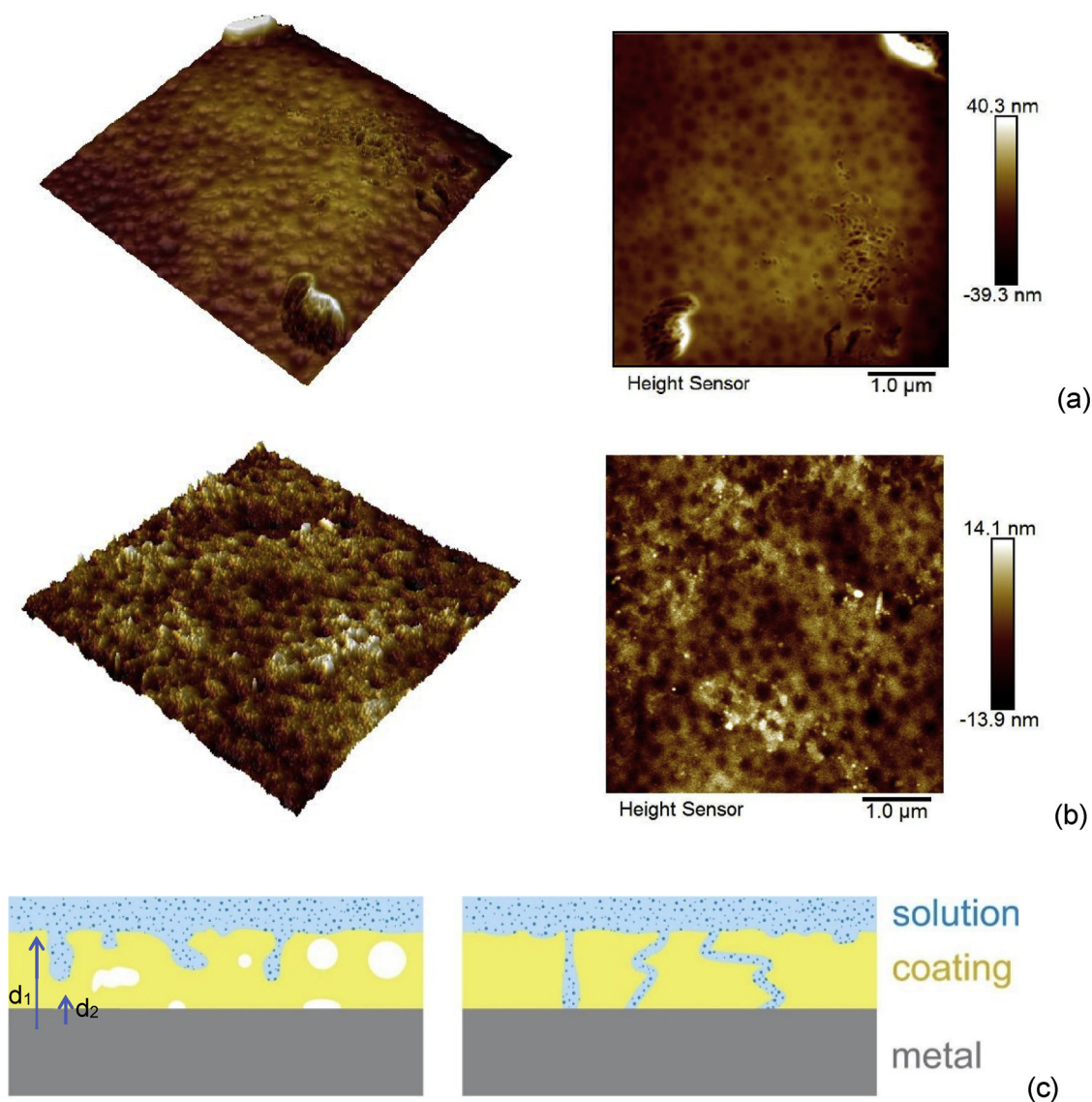It can be observed that the polymeric coating is not totally flat,

Fig. 5. Topography of the studied sample obtained in an atomic force microscope (AFM): (a) aluminium surface with coating and without use, (b) HP specimen after contact with the Control solution. (c) Representation of two coating conditions: on the left, porous coating without direct contact between electrolyte and metal; on the right, coating with discontinuity, allowing contact of the electrolyte with the metal. Not to scale.

presenting several regions of surface elevation and depression. It already exhibits small defects even before contact with the solutions. As the AFM is a high-resolution technique that observes the topography of the specimens on a nanometric scale, it could not confirm if the observed depressions reached the metal substrate. Therefore, given the physical limitations of the cantilever and the small area of exploration analysed (regions of ∼ 1.0 × 1.0 µm), the presence of complete porosity (or discontinuity) of the polymer layer could not be confirmed.

The principle of the metal exposure measurement using electrochemical testing is the current flows through the discontinuities of the coating, being its response proportional to the metal surface exposed through the polymer (coating). In this case, the method identifies situations where there is discontinuity of the internal coating (Dantas et al., 1996). However, this methodology does not evaluate other inadequate coating conditions, which do not result in the discontinuity of the coating. These conditions are related to situations such as inadequate curing (sub or super curing of the polymer), some dirt on the metal surface that results in the loss of local adhesion of the coating (showing the need for an efficient process of washing the cans before applying the coating) and applied layer control, among others. All these conditions may explain the failures observed in this study.

As the corrosion rate is very similar between the studied solutions and the metal substrate (due to similar values of corrosion current density), and as the polymer coating is the same (same chemical structure) under all conditions studied, the same chemical interaction in all specimens is expected. Therefore, the migration time may be affected by the influence of the local metal composition in the region of interaction of the electrolyte with the metal (hypothesis (1)), as well as due to a lower thickness in the polymer layer resulting from a local pseudo porosity of the coating (see indications in Fig. 5c).

Fig. 5c shows two coating conditions that can be considered as porous, but with different responses when the porosity analysis is used to measure the quality of the internal coating. The image on the left shows a region of the coating where there is no contact between the electrolyte and the metal. In this case, therefore, there is no current response in the test. The image on the right shows the pores reaching the metal surface, resulting in areas of discontinuity where the electrolyte will contact the metal and, consequently, there is current response. Therefore, new methodologies need to be adopted to predict the suitability of the internal metallic packaging coating in contact with food and beverages.

It can be observed, therefore, that lacquer and/or the quality of the

internal can coating is a limiting factor in the packaging performance, having a greater effect on the corrosion process regardless of the iron and chloride concentrations studied, considering the acidic aqueous medium.

4.3. Hypothesis (3): permeation of the solutions through the coating

The food and beverage storage is characterized by an interaction between the product and the packaging, which can be a slight or very intense process, depending on many factors. Regarding the metal packaging, the corrosion process is the one expected to occur, resulting in the dissolution of metal ions from packaging to food or beverage. Thus, the concentration of metal ions into the product is an indicative of the interaction process severity.

Based on the aluminium dissolution results, prior discussed in Section 3.3, another hypothesis concerning the role of the coating is pointed out: the solution can permeate through the polymer layer (coating), impacting the packaging performance.

A contact time is needed prior to the quantification of the metal ions from the corrosive process due to a permeation process. This "lag time" is followed by the beginning of the corrosive process on the metallic surface, through the diffusion of this metallic ion through the coating and ending with the dissolution in the interface polymer/solution and dispersion through the medium. These last three phases are characteristic of the migration process in food packaging (Catalá & Gavara, 2002).

This interpretation can explain the time required to quantify the aluminium in Fig. 3. Moreover, as described in the previous hypothesis, and presented in Fig. 5, differences in the coating performance would lead to different times of packaging failure.

In fact, evidence of this permeation was demonstrated in this study. As shown in Fig. 6, there was the occurrence of blister between the lacquer and the metal surface, without breaking the coating. However, it can be observed that the possible corrosion due to the permeation of the solution through the coating is of little relevance in this context, as even packages exposed to the aggressive solutions did not present aluminium quantification in the solution after 60 days at 40 °C.

However, if such permeation occurs in a region of critical composition of the metal alloy (hypothesis 1), and if it is associated with the discontinuity of the coating (hypothesis 2), the process becomes relevant, resulting in corrosion of the packaging.

In the case of specimens that showed metal exposure (classified in this study as HP) but did not result in the release of aluminium, one possibility is that this metal exposure occurs through very small discontinuities (microchannels), which require more time to be "filled" and "crossed" by the model solutions in order to initiate interaction with the metal surface. It can be assumed in this hypothesis that the identification of high porosity specimens may have been a consequence of a

region with many microchannels. In this case, the sum of measured current is high. However, from the point of view of interaction, they are still very small individual pores. Consequently, they result in a process similar to that described above, where the permeation process by the polymer coating overlaps the process velocity within the microchannels. It is also assumed that the dispersion step of the ions in the medium is very slow, given the small area of the pore in front of the path to be followed, delaying the time for dispersion of the ions in the medium. Furthermore, the permeation itself of the solution in the polymer could physically alter the polymer matrix (Oliveira et al., 2009), strangling the initial pores and not influencing the final result.

From the point of view of the porosity testing, the imposition of high electrical potential (6.3 V) combined with the test solution with high chloride concentration (1%) is sufficient to stress the material and result in an electric current measurement. However, the results show that under normal conditions of contact - without potential disturbance imposed to the study system - this exposure is not enough to alter the behaviour of the system. It shows again that the evaluation of the material in terms of only the coating porosity cannot predict its behaviour over time in contact with aqueous solutions as beverages.

4.4. Final remarks

Summarizing, three hypotheses were proposed to describe the observed behaviour in relation to the aluminium alloy corrosion parameters, the evaluation of coating porosity and the interaction among beverage and packaging over the storage time through aluminium migration.

The first hypothesis proposed that the local composition of the aluminium alloy can present variations in relation to the metallic average composition. If this composition shows elements that catalyses the corrosive process, the package will failure. In fact, this hypothesis was confirmed by the SEM-EDX analysis, demonstrating copper on the surface of the aluminium in a concentration much higher than the average composition of the alloy. To the best of our knowledge, this was firstly reported in this work. However, the solution must be in contact with the metal surface to initiate the corrosive process. Therefore, we assume that at least one of the next hypotheses should also be true in the packages with corrosion problems.

The second hypothesis proposed that some packages can show specific problems in their coating, compromising the integrity, even though approved in the standard porosity assay. We demonstrated that the polymeric coating is not totally flat, also presenting small defects. However, due to the technique limitations, we could not demonstrate if the observed depressions reached the metal substrate. Therefore, we could not confirm this hypothesis. Even so, we consider it plausible, suggesting further studies to evaluate it.

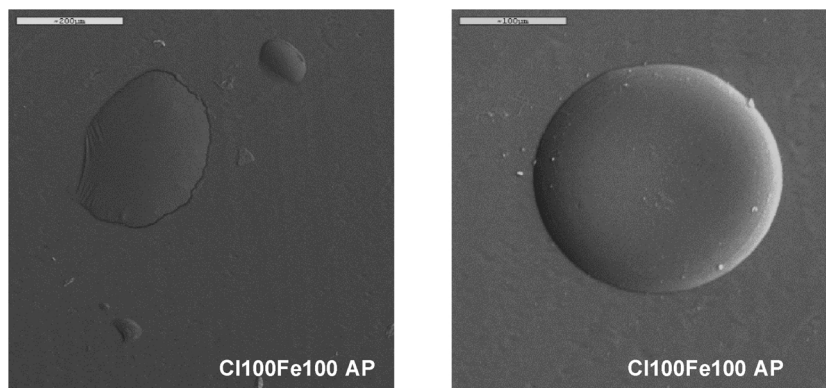Finally, the third hypothesis proposed that solutions can permeate

Fig. 6. Examples of specimens after contact with solution $Cl_{100}Fe_{100}$ evaluated by SEM (20 kV, 25 mm), in regions with blisters without evidence of coating breaking after 15 days of contact (40 °C).

the coating, reaching the metal surface and then promoting the corrosion. An evidence of this permeation was demonstrated by the occurrence of blister between the lacquer and the metal surface, without breaking the coating. Therefore, we consider this hypothesis plausible.

In conclusion, the observed corrosion process in aluminium packages seems to be a combination of possible defects, being necessary further studies with other solutions, coatings and conditions to elucidate the phenomena.

5. Conclusions

This research studied the influence of different iron and chloride contents in aqueous solution of citric acid (pH 3) in the interaction process with aluminium packaging. Both iron and chloride contents were evaluated in concentrations naturally found in food and beverages. Two internal coating conditions of aluminium cans (high and low porosity) were evaluated over 60 days at 40 °C. The obtained results enabled us to verify that, in practice, the most important variable in packaging performance is the material itself, i.e., the alloy composition and the condition of the polymer coating. Among the studied solutions, we did not identify more aggressive concentrations of each element, nor among its combinations. The segregation of specimens into high and low porosity groups demonstrated that this kind of evaluation is not suitable to predict if material will present low interaction with solution during the storage time. The occurrence of permeation through the organic coating and local differences in metal composition are evidenced in this work. The combination of possible defects, i.e., a local composition of the aluminium alloy benefitting corrosion development, as well as abnormalities in organic coating, suggests it is responsible for the failure of the package resulting in high aluminium concentration in solution, due to a localised and accelerated corrosion process. The need to work with alloys less prone to pitting corrosion, as well as developing new coatings less favourable to acidic aqueous solution permeation, and ways of applying and evaluating them, are guidelines for future research.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.fpsl.2018.11.012.

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