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Electrochemical Corrosion study via linear polarization in peas can

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Abstract
The aim of this work is to study the corrosion of tinplate can for peas. Firstly, the characterization of canning solution was made. The values of pH, conductivity, Brix, viscosity, density and content of Fe were, respectively, 5.88; 32.6 mS/cm; 6.6%; 3,42cP; 1.026 g/ml; 12.05 mg/kg. The corrosion rate in the cans was determined by linear polarization technique. The electrodes with and without varnish were analyzed in the first and fifth day of the experiment for the 3 parts of the can. The corrosion rate increased significantly when the coating was removed and the body showed a higher corrosion rate, reaching 1.7 mm/year in the absence of varnish. The microstructure of the samples was evaluated by scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS). The increase of iron on the surface, evidenced by energy dispersive spectroscopy (EDS) may have contributed to the corrosion in the samples without varnish.
Keywords: corrosion, tinplate cans, linear polarization, peas

Introduction

The packaging play a key role in the food industry. They are very important in conservation, maintaining quality and safety, acting as a barrier against chemical, physical and microbiological deterioration of the foods. Among many types of packaging, metal packaging is still widely used due to its impermeability to light and gases, moisture sealing, mechanical, and thermal resistance (Calderón & Buitrago, 2007; Jorge, 2013). The more common metal packaging consists of the mild steel base, a $FeSn_2$ layer, a Sn layer, and a passivating Sn oxide layer(Jorge, 2013). Also, it is applied an organic coating to prevent the metal base corrosion. When this coating is damaged, metals such as Fe and Sn, coming from corrosion reaction, can contaminate the food content. The Sn is considered the priority contaminant by the Codex Alimnetarys Comission (Codex alimentarius commission, 2010) . The possible dissolution of metal package is influenced by food matrix, oxygen concentration, pH, time, temperature of storage, and presence of oxidizing reagents (Perring & Dvorzak, 2002).

When the oxidation of Sn to $Sn(OH)_2$ occurs due to food substances (Blunden & Wallace, 2003), it is also generated in bulk solution, acids, alcohols, esters and organics acids that affect food properties and their pH reducing its shelf life (Gayoum & Rahman, 2015; Weber, 1997). High level of Sn can damage human health. According to Brazilian law (ABIA,1992), the maximum concentrations of Sn and Cr are 250 $mg.kg^{-1}$ and 0.10 $mg.kg^{-1}$, respectively. Canned foods represent the main source of contamination by Sn (Knápek *et al,* 2006). On the other hand, it does not set limits for the Fe (ABIA, 1992). However the iron content should be reviewed as, according to Dantas 1998, iron concentrations above 40 $mg.kg^{-1}$ can cause changes in the taste of peas canned and the iron is related to base metal corrosion (DANTAS, 1998).

Thus, it has increased researches about corrosion of canned food once that, package oxidation is related to decreasing of shelf life and

economic losses in the food industry (Esteves *et al,* 2014; DANTAS *et al,*1999; Esteves *et al,* 2014). Despite this, there are few papers using the electrochemical techniques to evaluate the electrochemical corrosion, and subsequently, the shelf life of the packed food ((Esteves *et al,* 2014; Xia *et al, 2012;* Jena, 2012; Pournaras, *et al.,*2008; Catalá *et al*, 1998; Katemann *et al.,*2003; Bastidas *et al.,* 1990). Among these techniques, stands out Linear polarization that has advantages: low cost, non-destructive technique, fast, reliable and requires a small amount of sample.

In this sense, the aim of this study is to evaluate the electrochemical corrosion of peas can (*Pisum sativum L*) by linear polarization (DANTAS *et al., 2011*). The corrosion was evaluated varying the exposing time for different parts of the can (lid, body and bottom) in the canned peas. The characterization of can surface was made by scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) with and without varnish.

Methods

List of symbols

L-V1: can lid with varnish in the first day of experiment
L-V5: can lid with varnish in the fifth day of experiment
L-U1: can lid unvarnished in the first day of experiment
L-U5: can lid unvarnished in the fifth day of experiment
BD-V1: can body with varnish in the first day of experiment
BD-U1: can body unvarnished in the first day of experiment
BD-U5: can body unvarnished in the fifth day of experiment
BT-V1: can botton with varnish in the first day of experiment
BT-V5: can botton with varnish in the fifth day of experiment
BT-U1: can botton unvarnished in the first day of experiment
BT-U5: Can botton unvarnished in the fifth day of experiment
SEM: scanning electron microscopy
EDS: energy dispersive spectroscopy

Characterization of the canning solution of the peas

The multiparameter Hanna HI2020 edge® equipment was used to measure the conductivity and the pH of the canning solution of the peas. For the determination of soluble solids it has been used an Aaker Q-767B refractometer.

The determination of metals (iron) in the solution was quantified by atomic absorption spectroscopy using in an AAS model AA-1275A from Intralab. The analysis was done in the first and fifth day of the experiment for the three parts of cans: lid (L), body (BD) and Botton (BT).

Electrochemical analysis and fabrication of the electrodes

Electrochemical measurements were performed using an IVIUM P15537 and Ivium Software. The working electrode was made of tin plate can and it was prepared as a rectangular foil with geometric area of 1.0 cm^2. The samples were sanded with 600-grit sandpaper for removing the varnish and washed with distilled water and acetone.

The electrochemical measurement was done using electrodes with and without varnish. The auxiliary electrode, was made of platinum with an area of 3.7 cm^2. A saturated Ag/AgCl was used with reference electrode. The electrochemical measurements were performed without solution agitation, at 25 ^oC in the absence of air, for 5 days in the canned peas electrolyte. In the potentiodynamic measurements the initial and final potential polarization were −0.50 and −1.00 V. The potential scan rate was of 1.00 mV s^{-1}.

Characterization of the tinplate cans electrodes

The characterization of tinplate can electrode surface was made by scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) on a Hitach microscope. The electrodes were analyzed with and without varnish in the first and in the last day of the experiment.

Results and discussion

Chemical physical properties of the canning solution

The peas are leguminous plants that, in some cases, are packed in acidified Picklemidium which is aggressive to the metal material, due to the presence of acids and chlorides, which requires an appropriate specification of the internal varnishing packing (DANTAS *et al, 2011*). Then the corrosion control will be insured by varnish layer and in this work the possible migration metals to the solution was verified. Table 1 shows the results of Brix degree, pH, conductivity, density and viscosity of the canning solution of the peas.

Table 1: Physicochemical parameters of canning solution of the peas

Parameters	Results
pH	5.88
Conductivity (mS/cm)	32.6
Density (g/mL)	1.03
ºBrix (%)	6.6
Viscosity (cP)	3.4

Iron concentrations in the first and fifth day of experiment for the lid (L), body (BD) and Botton (BT) of cans with varnish (V) and unvarnished (UV) in the first and fifth day of the experiment are showed in table 2.

Iron concentration was higher on the last day of the experiment for the unvarnish sample that showed a bigger corrosion process, which could be verified in the electrochemical measurements. However, the iron concentrations found in the sample with varnish was not a concern since this amount can reach 20 mg / kg (DANTAS *et al, 2011*).

The concentration of iron found in the pickling may vary according to the type of varnish used in the tinplate can and to its storage time. Dantas found 19.41 $mg.kg^{-1}$ and 18.07 $mg.kg^{-1}$ for

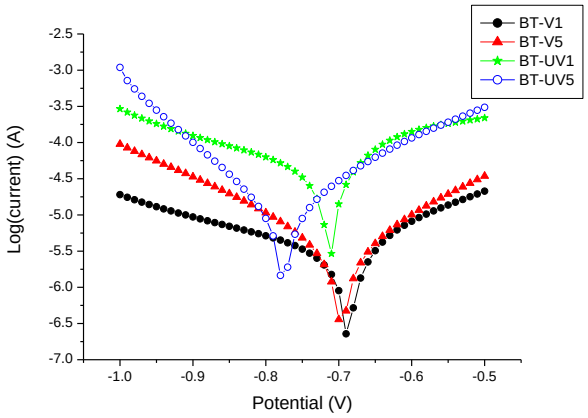
the can with the epoxy-amine and for epoxy-urea coatings, respectively, both after 365 days of storage at 35 °C (DANTAS, 1998).

Table 2: Fe concentration for different parts of can

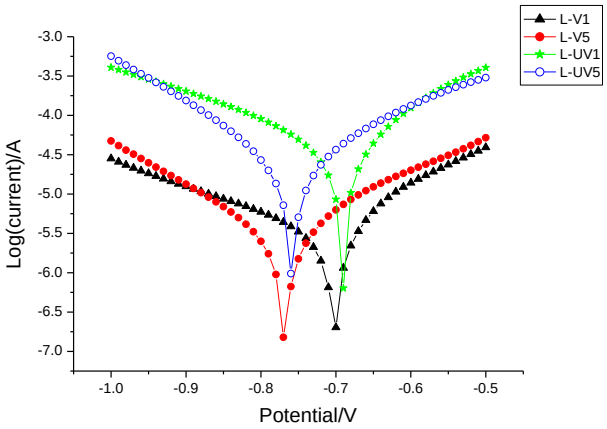
Sample	Fe (mg/kg)*
L-V1	7.2±2,4
L-V5	4.9±2,4
L-U1	6.6±2,4
L-U5	18.5±2,4
BD-V1	7.5±2,4
BD-V5	8.9±2,4
BD-U1	6.6±2,3
BD-U5	12.5 ±2,3
BT-V1	5.5 ±2,3
BT-V5	5.5 ±2,3
BT-U1	9.0 ±2,3
BT-U5	13.0±2,3

Linear polarization

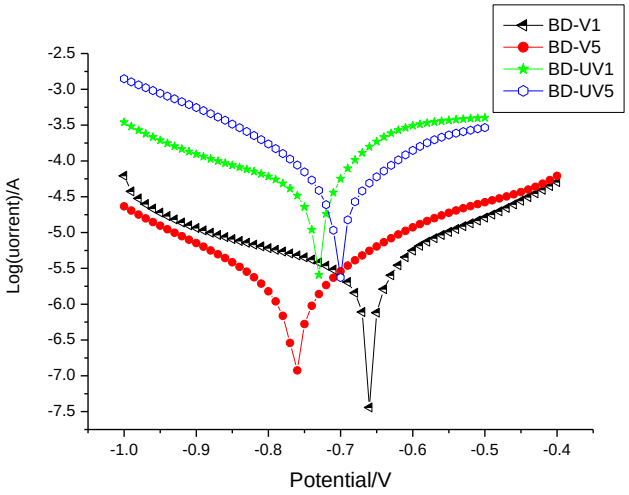
According to the Tafel curves in figure 1, in all cases, the corrosion is higher when the varnish layer is removed. However, the body is the part of the tinplates can which showed a more pronounced corrosion, as shown in figures 1 and 2. The varnish protects at least four times when compared with unvarnish cans in all cases. Then it becomes important that the varnish layer is intact to purchase the product. In all cases the corrosion potential is more negative with time for unvarnished samples. This information proceeds to the body and the lid of the tin with the varnish. However for the bottom the time did not influence the corrosion potential value.



(a)



(b)



(c)

Figure 1: Tafel curve, versus Ag/AgCl electrode reference of : (a) Lide can (LI) (b) Botton can (BT) and (c) Body (BD) can for the varnish(V) and unvarnish (UV) sample in the first (1) and fifth (5) day of experiment

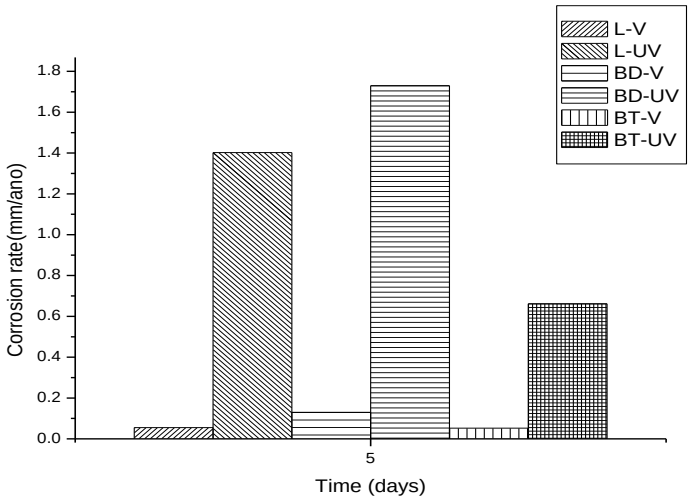


Figure 2: Corrosion rate for the three parts of the can in the fifth day of the experiment

Corrosion rates can vary with time and temperature storage, pH or even the manufacturer or with the parts of the can. These parties may change the surface in terms of thickness and porosity of varnishes layer and with the presence of risk and "defects" in the surface and this also affects corrosion. Because of this, the different parts of the can show distinct corrosion rate results as showed in figure 02. In this study we can see that the body (BD) tinplates can corrode more than the top and bottom in the presence and absence of varnish. This was expected, since the can body is in closer contact with canned peas and because it probably has different properties in relation to other parts. In the absence of varnish, the corrosion rate for the body is higher, reaching 1.7 mm/year. From the point of view of protection against corrosive processes, the can side-welding region is critical and may be a critical factor during the storage.

The five days of analysis in this study was not enough to check the decrease of corrosion resistance, but it was enough to associate factors to corrosion and to identify the parts most attacked by the electrolyte.

Morphology characterization

According to micrographs in figure 03 it is obvious that the unvarnished samples show an increase in the corrosion if compared with the varnish samples on the fifth day of the experiment.

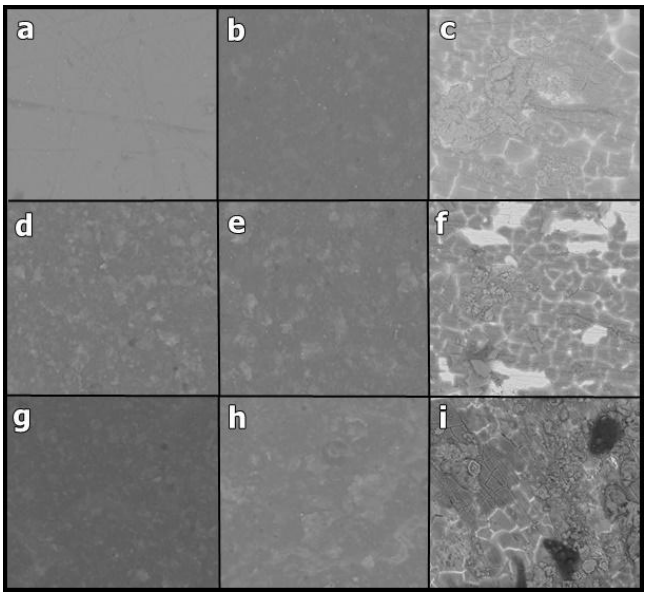


Figure 3: SEM surface morphology of (a) LI*; (b) LI- V5 (c) LI-UV5 (d) BD (e) BD-V5 (f) BD-UV5 (g) BT (h) BT – V5 (i) BT-UV5

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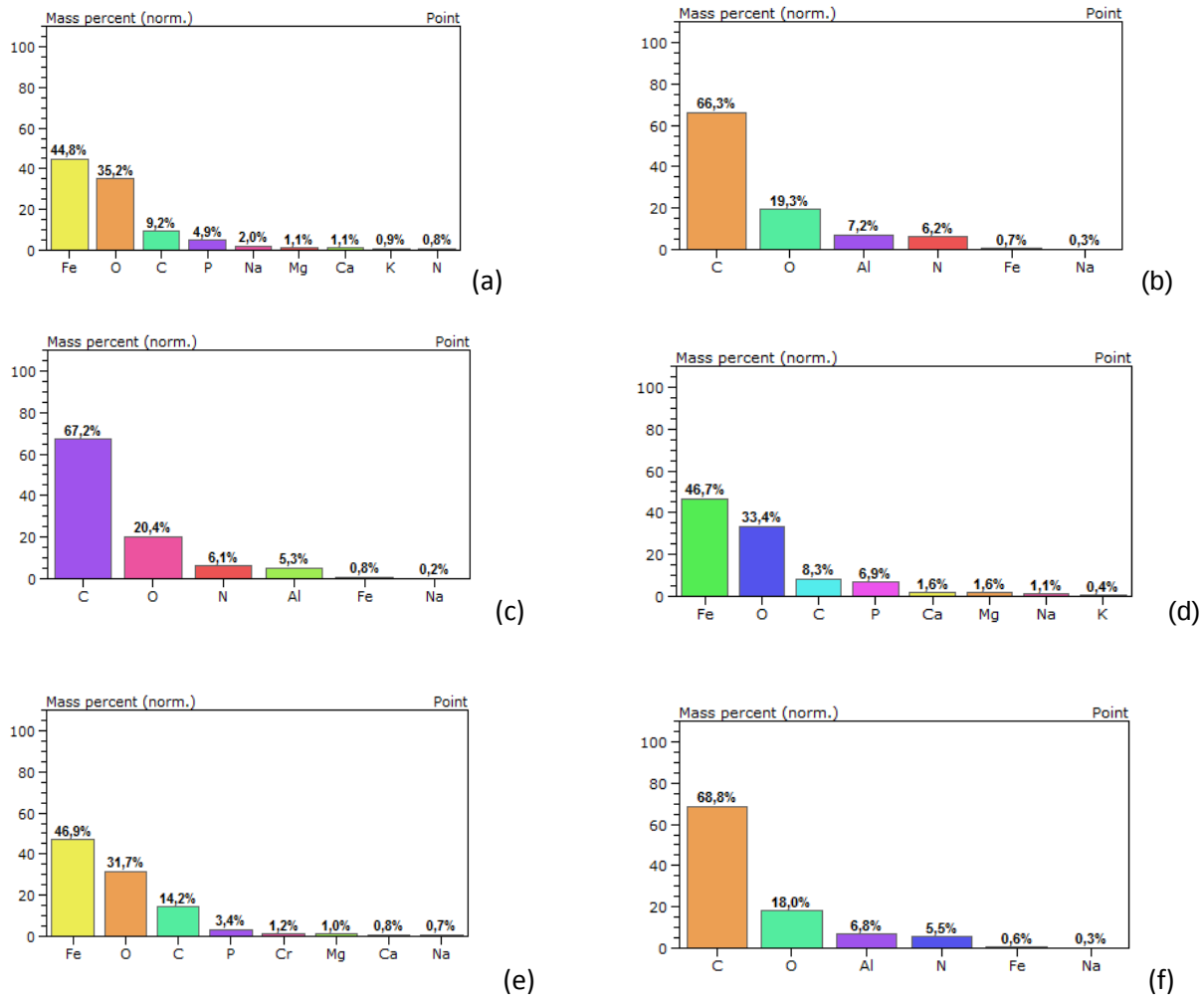

Figure 4: Chemical composition of electrodes EDS analysis, in the fifth day of experiment: (a) LI-V (b) LI- UV (c) BD-V (d) BD-UV (e) BT- V (f) BT-UV

Figure 4 shows the surface chemical composition of the tinplate in the first and fifth day of the experiment. The mass percentages of the elements were obtained from EDS analysis for each sample. It is possible to observe that samples with varnish have a higher carbon composition and lower iron showing an effective coating

The concentration of carbon is greater for the background, according to figure 04. This happens because in spite of doing the same procedure to remove the varnish, this was not enough to remove the entire bottom layer. Probably in this region the varnish layer is thicker. The fact of containing 4% more carbon was one of the reasons for reducing the corrosion rate by half. This content of 4% more carbon was one of the factors responsible for reducing the corrosion rate in a half.

The presence of chlorine, as indicated in the EDS spectrum, is probably due to the NaCl in the pickle. The NaCl has influenced the corrosion process, but its concentration remained constant until the end of the experiment for the varnished and unvarnished samples.

In the fifth day of the experiment, the unpolished samples showed a lower concentration of aluminum and carbon and a high concentration of iron indicating the beginning of the corrosive process. However five days of experiments were not enough to observe an effective increase in the corrosion current, and it does not affect the quality of the product.

Conclusions

The varnish presence is essential to limit corrosion, as a small tear can compromise the quality of food. In the analysis time, it was not observed a significant increase in corrosion rate. However it was possible to show that the varnish

protects the metal surface four times more. Thus it is important to get the canned foods without damage in the packaging. For the different parts of peas tinplate cans, the body showed higher corrosion rate (1.7 mm/year) on the fifth day of the experiment. The exhaustion from corrosion was also observed by OM and SEM.

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