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DETERMINATION OF SOME POTENTIAL INTERACTIONS BETWEEN FOOD AND FOOD PACKAGING ADDITIVES BY RELATIVE COMPARISON OF THE SUPERFICIAL POLIMERIC FILM

Andreea Ioana ENACHE (BONTOȘ)[1], Marius Daniel BONTOȘ[2], Dănuț-Ionel VĂIREANU[3]

Lately the knowledge of the dissolution/diffusion/permeation processes of the packaging compounds through different organic coatings has become a very interesting issue due to the fact that, even if food manufacturers are mainly interested in extending the shelf-life of their products, they have also understood that food safety and consumers health should also be taken into account. This paper aims to present a novel method for testing the inside coating layers of food packaging, namely electrochemical impedance spectroscopy. Therefore from Nyquist diagrams, following a circular regression procedure, we are able to determine the charge transfer resistance, which shows if interactions occur between food and packaging.

Keywords: food packaging, electrochemical impedance spectroscopy, polymer films

1. Introduction

Food safety represents a continuously growing issue which stirs competent authorities and consumers interest. Lately, numerous irregularities concerning raw materials used for food processing were highlighted in the whole European Union imposing therefore a more thorough investigation of raw materials, processed foods as well as the economic and market issues.

Packaging materials plays a very important role when speaking about food due to the fact that it protects and preserves their intrinsic quality. Nowadays it is less likely to sell food without having it packaged. Therefore, food packaging industry has developed in the last years and new types of materials have been created in order to prevent aroma sorption or the transfer of undesirable flavors

[1] PhD eng., Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania
[2] PhD Lecturer, Department of Hydraulics, Hydraulic Machines and Environmental Protection, Faculty of Power Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: bontosmarius@gmail.com
[3] Prof., Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania

from packaging into foods. Even if efforts have been made regarding this issue, and so called “intelligent packaging” have been developed, there are still manufacturers who are more interested to prolong the shelf-life of their products even if this is detrimental to quality and safety of the products they are trading [1, 2].

Creating packaging materials which come in direct contact with food implies some basic rules that should be followed, such as: hazardous substances must not levigate from packaging into food and packaging should not affect composition or sensory properties of the food contained [3]. A quality packaging should meet environmental requirements (be environmentally friendly) and fulfill the conditions on the initial composition and auxiliary substances allowed to be added in order to achieve its production, while food manufacturers should take into account and analyze the toxicity limits of packaging components they use [4]. The chemical stability of the food contact materials must be analyzed to ensure that packaging contains only the allowed compounds. On the other hand, the products must be tested to evaluate possible migration of potentially toxic components, which can alter food quality and pose a health hazard to consumers [5].

In order to minimize the undesirable changes due to the chemical interactions that may occur between foods and packaging additives and to maximize the safety, the quality and the shelf-life of processed foods, one should analyze the polymer based materials used for food packaging which have a great impact on the mechanisms of food deterioration [1].

The corrosion phenomenon represents an electrochemical process based on simultaneous anodic and cathodic reactions. The main idea is that the less contact exists between the iron or aluminum packaging materials and the food content, the less likely that interaction may occur between them. That is why different organic coatings (polymer films), are being used to varnish the interior of the package. These organic coatings act as an inert barrier which blocks the migration of compounds due to the physico-chemical processes [6].

The aim of this study is to highlight that the electrochemical impedance spectroscopy is one of the valid applicable methods it can be used to reveal whether or not any interactions occur between the foods and/or food additives and the packaging materials, modifying the mechanical or the barrier properties of the packaging, causing a possible deterioration of food.

Brody et al. consider that the most common methods of mass transfer in food-packaging systems are: migration, off-flavors, selective permeability and the transfer of constituents between the heterogeneous parts of food product. [7]

2. Experimental Method

Nowadays, systematic studies are quite restrictive because testing packaging materials represents a time and money consuming activity.

Although there are many attempts which aim to simplify the methods for determining the migration of different compounds from packaging into food and to reduce them to mathematical models (theoretical approaches have been introduced by the application of predictive migration models for plastic materials), they are less effective and therefore searching for new methods that allow the assessment of these interactions to continue [8, 9].

Due to the complex and heterogeneous nature of foods it is quite difficult to isolate and to identify the migrating components from packaging materials into food products [6].

Until now, the usual method used to highlight the possible levigation of ions/atoms/molecules from the food packaging into food was represented by differential testing of food content. Through this method one may also investigate the attack of food components on packaging materials.

The basic idea discussed in this paper is how to test the superficial layer of packing material, often a polymeric film, using an electrochemical test procedure, such as electrochemical impedance spectroscopy [10**]**.

The electrochemical impedance spectroscopy provides an opportunity to obtain information on the state of metal surface, along with data regarding the properties of its non/conductive coatings – polymer films (thickness, weight, porosity, ionic conductivity, polarization resistance etc.) [11].

From the experimental point of view, a number of three experiments were performed for each considered sample. The experimental studies were accomplished initially and repeated after six months. It was calculated the average result obtained from data processing and were compared the results from the first batch with those from the second batch (analyzed after 6 months), namely the average of charge transfer resistance (R_2) from the first experimental batch with the average obtained for R_2 from the experiments performed six months later.

The experiments were accomplished on two different type of samples, both ferrous and non-ferrous cans (beer cans and fizzy soft drink cans), initially and six months afterwards.

The beer can (S_1) has a capacity of 500 mL, a height of 17 cm and a diameter of 5 cm. It contains a mixture of 50% unfiltered wheat beer and 50% grapefruit juice. Unfiltered wheat beer contains water, malted wheat, malted barley, hop extract, yeast, whereas the grapefruit juice contains water, 3% concentrate grapefruit juice, concentrate lemon juice, citric acid, carbon dioxide, sweeteners (sodium cyclamate, acesulfame-K, aspartame and saccharin sodium), natural grapefruit flavor, and other natural flavorings, stabilizers (locust bean gum, pectin), coloring agent E120. It contains a source of phenylalanine and carbon dioxide content of ca. 5.0 g / L.

The dose containing the fizzy soft drink (S_2) has a capacity of 330 mL, a height of 5 cm and a diameter of 11.5 cm. It contains: water, sugar, carbon dioxide, caramel coloring E150d, acidifying phosphoric acid, natural flavors, and caffeine.

It is also important to mention that the tested cans are from the same batch, the ones tested after six months have been stored at room temperature (about 22° Celsius) and each has been opened right before the experiments took place.

All the experiments were conducted using 3.5% NaCl solution at a constant temperature of 25° Celsius.

The investigated samples were cut as small disks and were fitted inside a specially constructed support acting as a working electrode having the surface of 0.283 cm^2. As reference electrode was used a saturated Ag/AgCl electrode and as auxiliary electrode a platinum disk with the surface of 1.13 cm^2 was used. For minimizing the noise, the reference electrode was connected through a capacitor with another platinum plate electrode (with the surface of 0.5 cm^2). These four electrodes have been placed into a 50 mL commercial thermostated electrochemical cell.

The experimental data were acquired using a Voltalab 40 PGZ301 system and the VoltaMaster software.

The results obtained during the experiments were processed by circular regression and the values of the charge transfer resistance (R_2), the most important characteristic parameter for the structural and compositional consistency of packaging materials, were recorded with Voltalab associated software – VoltaMaster. All acquired data were further processed with National Instruments – Labview graphical programming language for their representation as Nyquist diagrams in order to verify the results.

3. Results

The circular regression procedure applied to the Nyquist plots resulted from the electrochemical impedance spectroscopy, provides useful information regarding the ionic resistance (R_1), the charge transfer resistance (R_2), the ionic conductivity, capacitive behavior (C), and others. Nevertheless, in this paper, the most important parameter proved to be the charge transfer resistance (R_2), a characteristic element for compositional and also for structural consistency of the packaging, as its variation gives useful information regarding the possible interactions that might appear between food and/or food additives and the packaging materials.

Thus, if the charge transfers resistance (R_2) parameter remains constant or it registers only minor variations (up to 5%), it means that no structural changes have occurred to packaging or even if they appeared, they were insignificant. When the variations are greater than 5%, (between 5 and 10% - confirmed interactions, above 10% - significant interactions) it means that structural and compositional changes occurred in packaging and that this variation is not due to experimental errors, but to the interactions occurring between the food and the packaging materials.

Fig. 1 illustrates the Nyquist plot, corresponding to one of the three experiments performed on the first beer can, created with Labview software. In this case the packaging was made from iron foils and was coated on the inside with a polymer film.

Fig. 2 illustrates the Nyquist plot, created with Labview software, corresponding to one of the three experiments performed on the second beer can, six months afterwards.

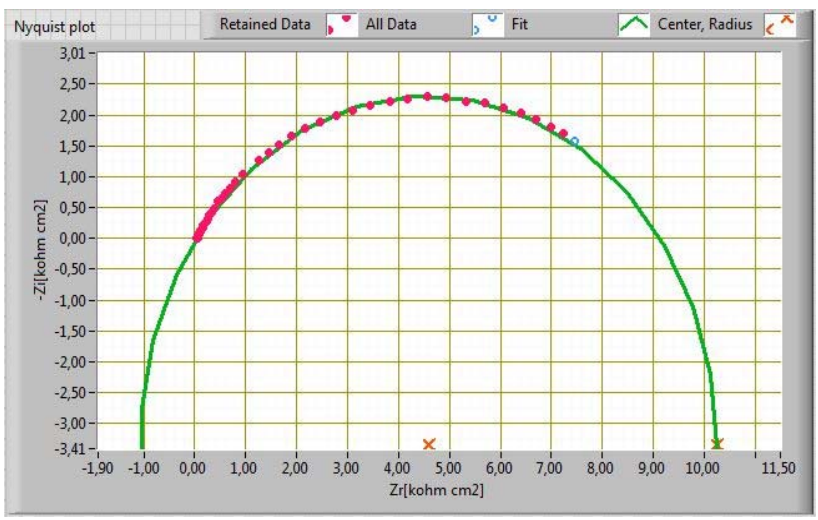

Fig.1. Nyquist plot initially for beer can 1

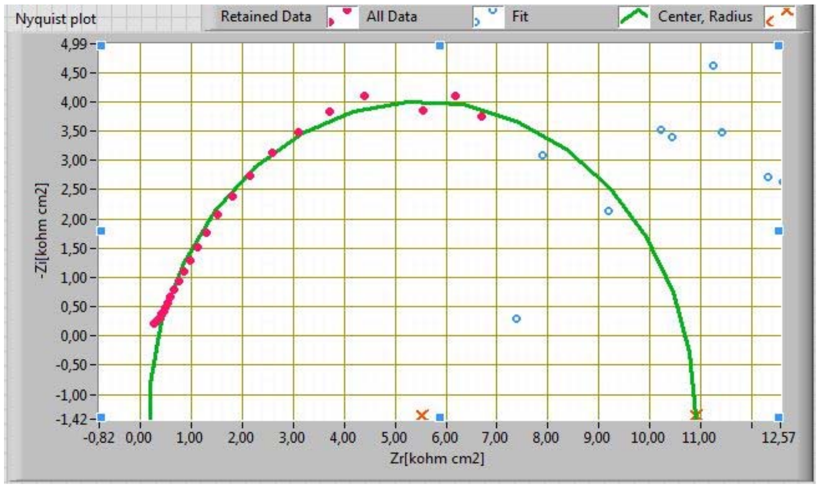

Fig. 2. Nyquist plot six months afterwards for beer can 2

Table 1 contains the most important parameters resulting from the circular regression performed following the initially experiment and also for the experiment conducted on the second beer can six months afterwards.

Table 1

Parameters values measured initially and after six months for beer can

Circular regression	20-09-2012, beer can 1	20-03-2013, beer can 2
Diameter	11.36 kohm×cm²	10.16 kohm×cm²
Coefficient	0.999	0.986
Depletion angle	-17.2 °	-6.28°
R_1	19.76 ohm×cm²	360.9 ohm×cm²
R_2	9.151 kohm×cm²	9.911 kohm×cm²
C	21.91 µF/cm²	32.11 nF/cm²

As one may see from the Table 1, the variation of R_2 is 8% (8.3%) higher after the six months period with respect to the sample from 20/09/2012 fact that leads to the conclusion of a confirmed interaction between the content and the packaging material. This is also substantiated when one compares also the average values. In the first set of experiments, conducted on the 20/09/2012, the average values obtained for the charge transfer resistance (R_2), was 8.761 kohm×cm^2. For the second set of experiments performed on 20/03/2013, the mean value of the charge transfer resistance (R_2) was 9.403 kohm×cm^2. Therefore it is found that the variation of the charge transfer resistance (R_2) value was 7.32 %, above 5% which corresponds also to the individual analysis. This can be explained by an adsorption process of some organic material on the surface of the polymeric coating leading to an increase in the charge transfer resistance.

As it was already mentioned above, the other experiments were performed on the fizzy soft drink cans. In this particular case, the packaging was made from aluminum foils and covered on the inside with a polymer layer.

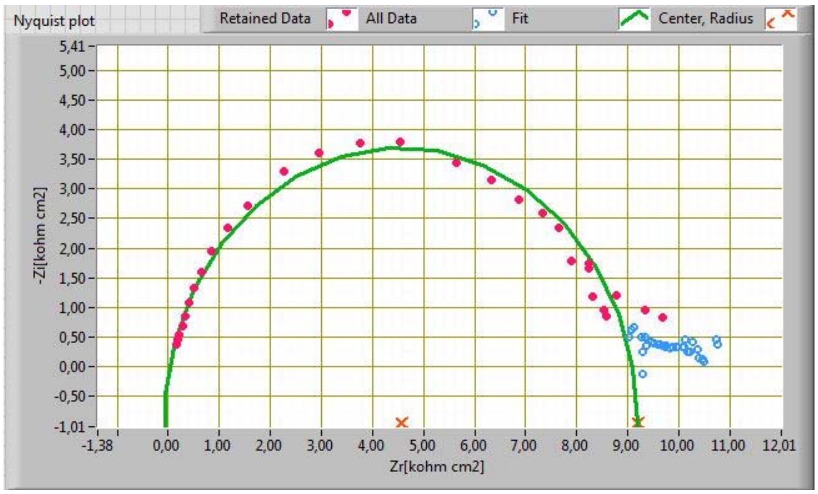

Fig. 3. Nyquist plot initially for fizzy soft drink can 1

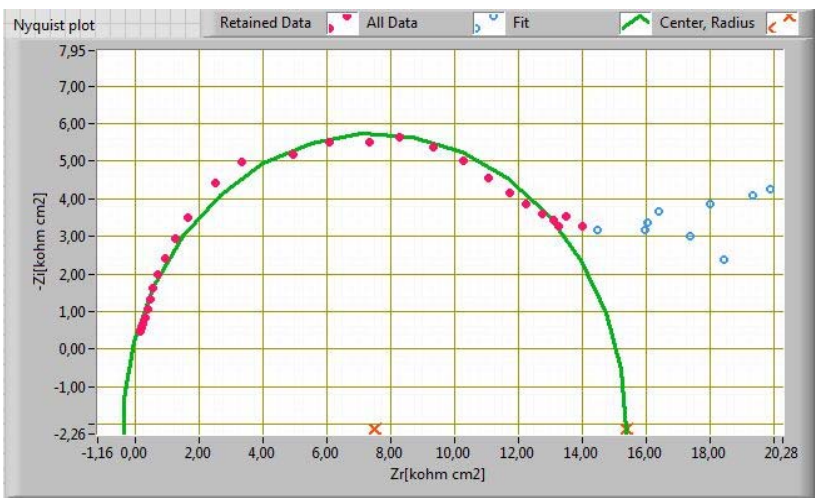

Fig. 4. Nyquist plot for fizzy soft drink can 2 six months afterwards

Fig. 3 illustrates the Nyquist plot, corresponding to one of the three experiments performed on the first fizzy soft drink can, created with Labview software.

Fig. 4 illustrates the Nyquist plot, created with Labview software corresponding to one of the three experiments performed on the second fizzy soft drink can after six months.

Table 2

Parameters values measured initially and after six months for fizzy soft drink can

Circular regression	25-09-2012, can 1	26-03-2013, can 2
Diameter	9.337 kohm×cm²	16.17 kohm×cm²
Coefficient	0.904	0.947
Depletion angle	-6.03 °	-8.39 °
R_1	2.521 ohm×cm²	-118 ohm×cm²
R_2	9.128 kohm×cm²	15.46 kohm×cm²
C	4.358 nF/cm²	3.252 nF/cm²

As one may see from Table 2, the variation of R_2 is 10% (namely 69.3%) higher after the 6 months period with respect to the sample from 25/09/2012 fact that leads to the conclusion of a confirmed interaction between the content and the packaging material. This is also substantiated when one compares also the average values. In the first set of experiments, conducted on the 25/09/2012, the average values obtained for the charge transfer resistance (R_2), was 9.113 kohm×cm^2. For the second set of experiments performed on 26/03/2013, the mean value of the charge transfer resistance (R_2) was 14.37 kohm×cm^2. Therefore it is found that the variation of the charge transfer resistance (R_2) value was 57.7 %, far above the considered limits of 10%, which corresponds also to the individual analysis. In this case one is able to say for sure that the interactions between the beverage and the packaging material were substantial, as the values of charge transfer resistance show major variations with reference to the initial point in time.

However, if the difference of the two compared charge transfer resistance has a negative values greater than 5%, here one may suspect the actual partial destruction of the coating layer by small cracks and pores (findings that may be proven by micrographic analysis).

Similar findings were discovered for other tested samples from different ferrous and non-ferrous packaging materials that were also coated on the interior surface with polymer films the results, excepting a limited number of high quality packaging materials, confirming the interactions between the food content and the packaging materials.

By circular fitting of the experimental data were also obtained other parameters like ionic conductivity ($R_{1)}$ and the capacitive behavior (C). R_1 is the component from which we can deduct ionic conductivity and its variations occur due to adsorption of components of ionic nature. The negative value of R_1 (from Table 2) is given by the circular regression model. However, these two parameters cannot be taken into consideration in this study, because it would be necessary to identify with certainty what ionic species are inside the beverages and the precise amount adsorbed.

4. Conclusions

Some acidity stabilizers and preservatives can cause corrosion phenomena on packaging without polymer film, causing loose of metal cations, which may have harmful effects on human health. This is the case of tin coated cans. In order to prevent such metal anodic dissolution, the manufacturers have resorted to polymer coatings. Although it is assumed that these are perfectly stable, under the harsh conditions (pressurized content, acidity stabilizers such as phosphoric and citric acid etc.) even such polymers, deposited as ultra-thin films may suffer degradation processes due to the above mentioned interactions.

The proposed method described above and based on comparing the variation in time of the charge transfer resistance may prove a valuable asset in determining if these interactions occur, their nature (deposits or structural deterioration of the coating layer) and their magnitude with respect to a reference point in time (e.g. fabrication date). If the charge transfer resistance (R_2) shows major changes, then one can say that the interactions between the packaging material and food content were substantial. On the other hand, if the charge transfer resistance (R_2) is relatively constant over time, one may say that the interactions are minor or even absent.

It is also worth to be mentioned that the results presented in this paper are part of a series of other experiments made on different types of packaging where we have achieved similar results.

Therefore, following the results obtained after testing different types of packaging materials, in this particular case the beer cans – made from iron and the fizzy soft drink cans made from aluminum, both covered on the inside with a polymer layer, one may conclude that none of both studied samples meet the quality requirements regarding the protective layers as the values obtained after data processing showed not only that the beverages interacted with the packaging materials but also that the interactions were substantial.

In conclusion, electrochemical impedance spectroscopy proved to be one of the valid applicable methods that can be used in order to reveal whether or not interactions occur between the foods and/or food additives and the packaging material

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