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ORIGINAL PAPER

# Electrochemical characterisation of protective organic coatings for food packaging

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**Abstract** A very common material for food packaging is steel, in the form of metallic containers (cans), in particular for beverage packaging. The corrosion degradation of the packaging must be carefully controlled, not only because the packaging integrity must be preserved, but also in order to avoid any significant contamination of the food or drink, compromising the flavour. In order to increase the coating performance and the food compatibility, new organic coatings are under development with very high protective properties, with the final aim to increase the shelf life of the product. An electrochemical characterisation is often used to study the protective performance of organic coatings on metal substrate for various applications. Some different coatings for food packaging were considered in the present study, including materials with different chemical composition and different pigments content. The protective properties were quantified using electrochemical impedance spectroscopy (EIS) measurements, comparing the electrochemical substrate activity with electrochemical noise (EN) and scanning Kelvin probe (SKP) measurements. The influence of mechanical deformations on the protective properties was also investigated. The results obtained on the studied coatings confirmed the validity of the electrochemical approach and showed that, in general, the coatings containing pigments ($TiO_2$) have better performance than clearcoats, while comparing the different polymers, epoxy–phenolic coatings have a better corrosion protection than epoxy–melamine coatings.

**Keywords** Electrochemical impedance spectroscopy · Scanning Kelvin probe · Electrochemical noise · Food packaging · Corrosion

## 1 Introduction

Metallic containers (cans) are often used for food, and in particular for beverage packaging [1]. The corrosion degradation of the packaging must be carefully controlled, not only because the packaging integrity must be preserved, but also in order to avoid any significant contamination of the food or drink, compromising the flavour. Even very low concentration of iron ions (0.5 ppm) can modify strongly the beverage perception [2].

The steel cans are generally obtained by mechanical deformation from tin plated steel sheets and coated with an organic lacquer in order to increase the corrosion protection [3].

In order to increase the coating performance and the food compatibility, new organic coatings with very high protective properties are under development, with the final aim to increase the shelf life of the product [4].

An electrochemical characterisation is often used to study the protective performance of organic coatings on metal substrate for various applications. Electrochemical impedance spectroscopy (EIS) is an experimental technique very useful for this aim [5–7], but recently also others electrochemical techniques, like electrochemical noise (EN) [8] and localised techniques like scanning Kelvin probe (SKP) [9] and scanning reference electrode (SRET) [10] have been used. Some examples are available in the literature also applied in the field of food packaging [11–13].

In the present study, some different coatings for food packaging, in particular for beverages, were considered,

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including materials with different chemical composition and different pigments content. The protective properties were quantified using EIS measurements, comparing the electrochemical substrate activity with EN and SKP measurements. The influence of mechanical deformations on the protective properties was also investigated.

## 2 Experimentals

Three different food-cans protective coating have been analysed, deposited on tin cans by spray deposition. The substrate composition is mild steel and the tin layer, obtained by dipping, is about 2 μm thick. Two coatings are based on a phenolic/epoxy resin and a third kind of coating is based on a melamine/epoxy resin.

The samples are summarised in Table 1. The idea is to compare materials with different coating formulation (pigments and composition). Pigments actually can play a very important role influencing the barrier and therefore the protective properties of the organic coating. All the coatings has a glass transition temperature around 115 °C.

The electrochemical measurements have been performed after samples immersion in a 0.35%wt NaCl solution at two different pH: 7 and 4 (obtained adding HCl). This last solution simulates the corrosion attack of acidic food, in order to better highlight the actual damage that can occur in real applications. The testing time was 120 h. The electrochemical cell consist of the can itself filled with the testing solution.

A classic three electrode electrochemical cell was utilised using Ag/AgCl (+207 mV SHE) as reference electrode and a platinum wire as counter electrode and the can itself as working electrode. An E.G&G 283 potentiostat and a FRA Solartron 1255 connected with a PC were used. The electrochemical impedance (EIS) measurements were carried out with a signal amplitude of 10 mV, in the frequency range of 10 kHz–10 mHz at free corrosion potential with a testing area of about 245 $cm^2$. The impedance data were fitted using Boukamp EQUIVCRT software to obtain the parameters values of the electrical equivalent circuit [14].

EN time records were obtained using an ACM Instrument controlled by means of the Sequencer program. This program was used in current and voltage time mode, in order to measure the current and the potential simultaneously. The EN data were recorded at 0.5 reading/s to supply consecutive time records of 2,048 points. The noise resistance as a function of the frequency was obtained from the noise data.

**Table 1** Materials

| Coating system | Symbol | Thickness (μm) |
|---|---|---|
| Epoxy/phenolic (unpigmented) | P | 29.0 |
| Epoxy/phenolic + $TiO_2$ + carbon black | PT | 29.2 |
| Epoxy/melamine + $TiO_2$ | MT | 31.0 |

After the EIS and EN characterisation some SKP measurements (SKP100E® system) have been performed at normal conditions of laboratory (in ambient atmosphere). The SKP samples were obtained cutting the bottom of the can in order to have a flat area. A tungsten electrode with a 500 μm diameter tip was used as the reference electrode and the air gap between probe and sample was kept at 70 μm. The vibration of the tip electrode was 30 μm and the scan area 25.5 × 19.0 $mm^2$. SKP data were recorded at 500 μm/s to produce consecutive spectra of 512 samples per line.

In order to better understand the influence of any mechanical deformation after the cans production, some samples were mechanical deformed following the mandrel bend test (following the ASTM D522 standard for the mechanical testing of the coatings) and the protective properties were characterized by EIS measurements after 24 h of immersion. Three different mandrel diameters were used: 4, 10 and 16 mm.

## 3 Results and discussion

### 3.1 Barrier properties

The barrier properties of the protective coatings are very important to define the quality of the packaging. With EIS measurements it is possible to quantify the coatings barrier properties towards ions and water penetration. An example of the EIS spectra is reported in Fig. 1, for the epoxy/phenolic clear coating immersed in the solution at pH 4. Two times constants are visible. The electrochemical data were therefore modelled using the typical equivalent electrical circuit (Fig. 2) which consists in a capacitance (the coating capacitance Qc) in parallel with a resistance (the coating resistance Rp) in series with the double layer capacitance Qdl and the charge transfer resistance Rct. The first time constant (Rp and Qc) describes the behaviour of the coating (barrier properties), while the second one (Qdl and Rct) is related to the electrochemical reactions occurring at the metal substrate surface and therefore it quantifies the corrosion reaction and the loss of adhesion.

The first property to be analysed is the barrier action. Figure 3 shows the coating resistance (Rp) as a function of the immersion time in the two solutions. The first plotted data are presented after two days of immersion, when the values appear to stabilize after an initial drop. The starting resistances are in the order of $10^{11}$ ohm $cm^2$ for all the samples. The values obtained in the neutral solution are

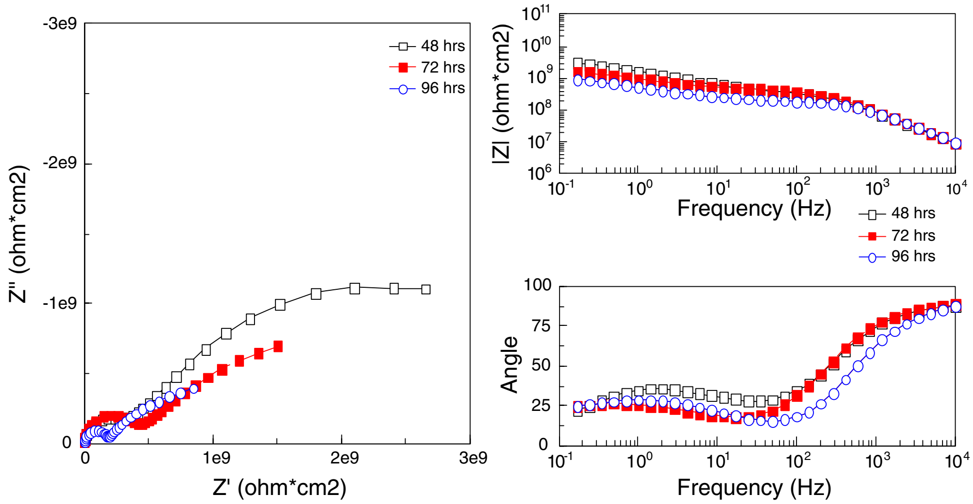

**Fig. 1** EIS results obtained on epoxy/phenolic (P) samples at pH 4 at different immersion time

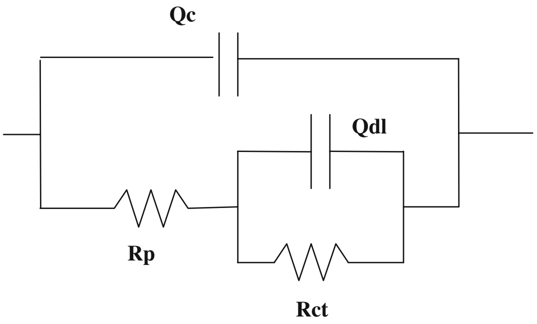

**Fig. 2** Equivalent electrical circuit (EEC)

very similar, proving a good stability of the studied coatings at pH 4. This result is not surprising because the coating barrier properties are not generally influenced by the pH, but only by the electrolyte ions concentration, except for the case of polymeric matrix degradation due to the high $H^+$ concentration in the solution which is clearly not the case for our samples (pH 4 is not aggressive enough to induce degradation for the studied polymeric materials).

The initial Rp values (reported after 48 h, when the values are stable and reliable) are quite high for all the materials, considering the limited coating thickness and the aggressive environment. All the materials show a progressive decrease, but after 120 h the values are still very high. However, different barrier properties are evident comparing the different materials: the highest values are related to the phenolic pigmented coating, followed by the phenolic clearcoat and finally the melamine one. It is generally assumed that the presence of pigments can increase the coating barrier properties, and therefore the better performances of the pigmented phenolic in comparison with the clearcoat one are not surprising. The worse barrier properties of melamine coating needs further investigation.

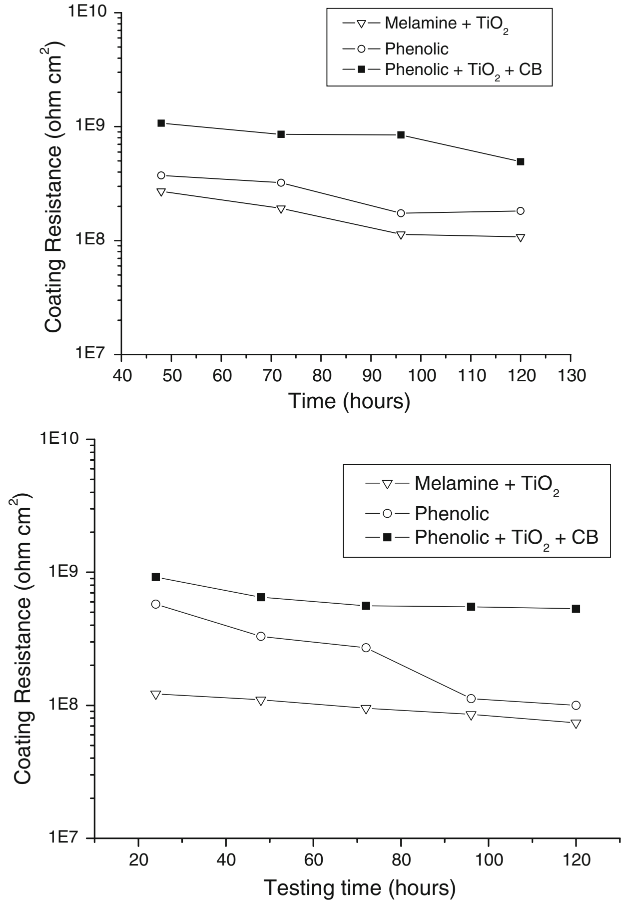

**Fig. 3** Coating resistance (Rp) evolution as a function of the immersion time in the testing solution at pH 4 (above) and pH 7 (below), for the different coatings

Also the coating capacitance can give important information about the barrier properties, being it influenced by the water penetration. The coating capacitance in the circuit of Fig. 2 was modelled using a constant phase element

(CPE). The value of the exponent $n$ was always very close to 1 (around 0.98), and therefore the fitted values can be assumed as true capacitance [15].

The water diffusion into the coating causes an increase of the coating capacitance values and therefore this parameter is an indication of the barrier properties against water penetration. Barrier property is a very important parameter for corrosion protection. It is possible to quantify the water volume fraction ($\phi_t$) diffused in the coating after the time $t$ from capacitance values using the Brasher–Kingsbury equation [16].

$$\phi_t = 100\ \log(Q_t/Q_o)/\log\ \varepsilon_w \qquad (1)$$

where $Q_t$ is the capacitance after the time $t$, $Q_o$ is the initial capacitance and $\varepsilon_w$ the water dielectric constant of water. The water uptake values obtained after 120 h of immersion (after saturation) are reported in Table 2 in the case of pH 7 and pH 4 solutions. The values, differently from the ions diffusion properties, are lower for the melamine coating and slightly higher for the phenolic coatings. However all the values should be considered low, proving good water barrier properties for all the materials. The small differences between the values measured at different pHs are not significant and they are inside the measurements accuracy. Again we can conclude that the different pH does not influence the coating barrier properties. However, the higher water barrier properties of melamine coatings cannot be the cause of the lower ionic barrier properties of this coating (Fig. 3), which have to be explained in a different way.

Food packaging can be accidentally deformed after production, during food transportation and therefore it is very important to check the barrier properties integrity after mechanical deformation. The food cans were deformed using a mandrel at different deformation values and the coating resistance was calculated from impedance data. Figure 4 shows the Rp values for the three materials at different deformation levels after 24 h of immersion in the acidic solution.

It is clear that the deformation causes a decrease of the ionic barrier properties. Considering a threshold limit of about $10^7$ ohm cm$^2$ (often considered the minimum acceptable value for a protective coating [17]), the 33% of deformation is too much for all the materials.

**Table 2** Water uptake values obtained after 120 h of immersion in the testing solution at pH 7

| | Water uptake (%) | | |
|---|---|---|---|
| | P | PT | MT |
| pH 7 | 5.21 | 4.72 | 2.06 |
| pH 4 | 5.64 | 4.91 | 1.85 |

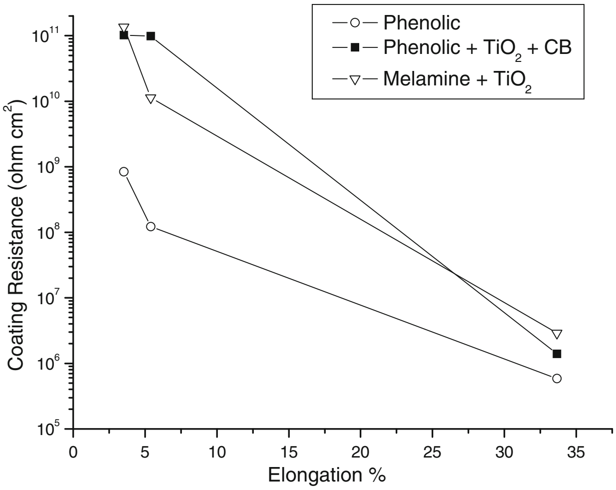

**Fig. 4** Coating resistance (Rp) as a function of the mechanical deformation after 24 h of immersion in the solution at pH 4, for the different coatings

Interpolating linearly the available data, it is possible to suppose that the maximum acceptable deformation could not exceed 10%. For the studied materials, the presence of pigments have a beneficial effect on the barrier properties after deformation. This result confirms the general conclusion that the pigmented coatings have better barrier properties. However after deformation the melamine coating and the phenolic pigmented coating behave in a similar way, in contrast with the results obtained without deformation (Fig. 3).

## 3.2 Corrosion reaction

The final aim of the protective coating is to limit the metal corrosion reaction and therefore it is very important to quantify the corrosion rate by evaluating the charge transfer resistance (Rct) which is inversely proportional to the corrosion rate.

Figure 5 shows the charge transfer resistance evolution for the studied samples during the immersion in the testing solution at pH 7. Obviously all the samples show a Rct decrease increasing the immersion time, because of the activation of the corrosion reaction. The Rct values however are quite large, indicating a limited metal degradation. At the end of the test, the higher Rct values are measured for the phenolic sample containing pigments (PT) followed by the phenolic clearcoat and finally the larger corrosion rate is measured in the case of melamine coating (MT). This ranking is exactly the same previously measured for the barrier properties (Fig. 3) demonstrating that the corrosion protection action is mainly due to the coating barrier properties, because the studied materials do not contain any active corrosion inhibitor.

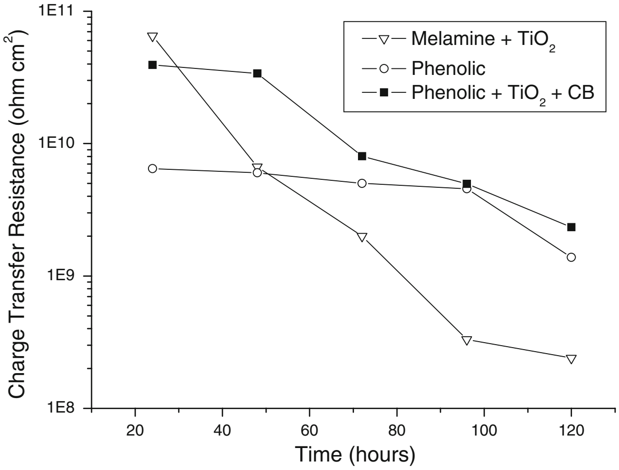

**Fig. 5** Charge transfer resistance (Rct) as a function of the immersion time in the testing solution at pH 7, for the different coatings

This is not actually the ranking for short immersion time, when the melamine coating is the best one. This fact allows us to better understand the behaviour of this material. The lower ionic barrier properties (Fig. 3), and lower water uptake (Table 2) can be explained considering a coating with intrinsic good barrier properties, but with a larger presence of defects (cracks or pores which are preferential paths of ions diffusion). In fact the presence of defects can remarkably reduce the Rp values, but it does not influence the capacitance values (and therefore water uptake). For short immersion time (Fig. 5) the lower water uptake of melamine coating delays the corrosion reaction, being water essential for the corrosion reaction, but later, during the test, because of the larger presence of defects previously described, the MT coating is not able any more to protect the substrate from the corrosion reactions as the less defective phenolic coatings. This mechanism is also consistent with the results obtained after mechanical deformation. In fact the deformation induces in general new defects and the behaviour is dominated by the deformation effects (limited by the presence of pigments and by the mechanical properties of the polymeric matrix), more than by the initial status of the coatings.

The Rct values measured during testing in the pH 4 solution are remarkably lower (Fig. 6), proving an activation of the corrosion reaction due to the acidic pH. Again we have a confirmation that the solution pH influences the corrosion reaction, but it is not influent for the barrier properties. However the values appear more stable during testing, even if a general decreasing trend is visible for samples MT and P. At pH 4, the lower corrosion rate is again measured on PT samples, while the unpigmented coating (P) is in this case the worse. Two aspects can be considered for explaining this result: first it is probable that the water uptake kinetics is more important in the acidic conditions, and therefore the melamine coating, with lower water uptake, performs better than in the case of neutral pH. Moreover the presence of pigments can play a different role in acidic and neutral solution, increasing the barrier properties at pH 4 and explaining the worse behaviour of the clearcoat P.

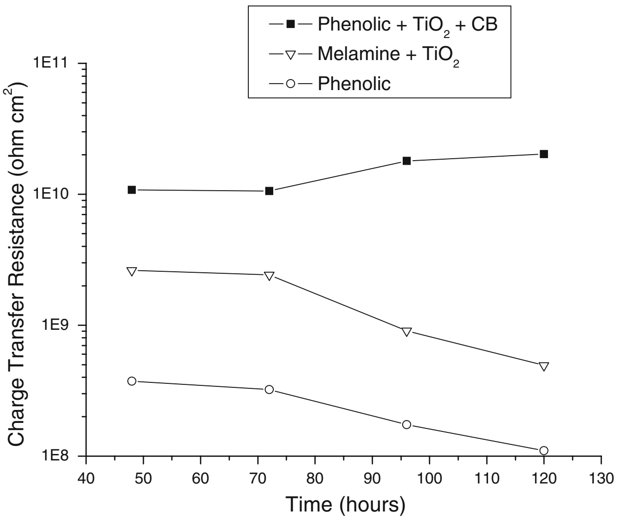

**Fig. 6** Charge transfer resistance (Rct) as a function of the immersion time in the testing solution at pH 4, for the different coatings

All the discussed measurements are related to average properties of the coatings (the impedance values are obtained on a few square centimetres area). In order to confirm the proposed protection mechanisms and the different presence of defects it is very interesting also try to study the coating properties on a different scale by local electrochemical techniques like SKP measurements. Figure 7a shows a work function map of melamine coated sample before the continuous immersion (MT). It is possible to observe some defects on the surface represented by high and localized work function variations, compared with the average value all over the surface (1 deV, with standard deviation of 0.21). Figure 8a presents the SKP map of the phenolic polymer coated steel (PT) before immersion in the electrolytic solution. Comparing this mapping with the previous (Fig. 7a) it is clear that except the marginal zones, the total area is more homogeneous than the corresponding melamine coating. The average value for phenolic before continuous immersion is 0.4 deV with standard deviation 0.3. The different presence of defects in the coating can modify the work function measured on the metal surface. In fact, SKP measurements are able to defect the electrochemical conditions of the metal surface under the organic coating and not the defects in the coating itself. However, the presence of defects in the organic coating (both pores and loss of adhesion) influences the metal work function.

The higher presence of defects in melamine coating MT has been therefore proved independently with a different technique, and the results are in good agreement with the

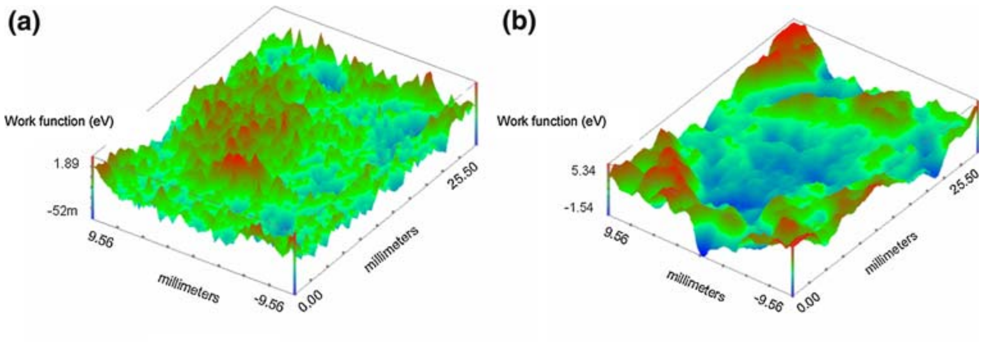

**Fig. 7** Work function map for melamine coating (MT) before immersion (**a**) and after 120 h of immersion in the testing solution at pH 4 (**b**)

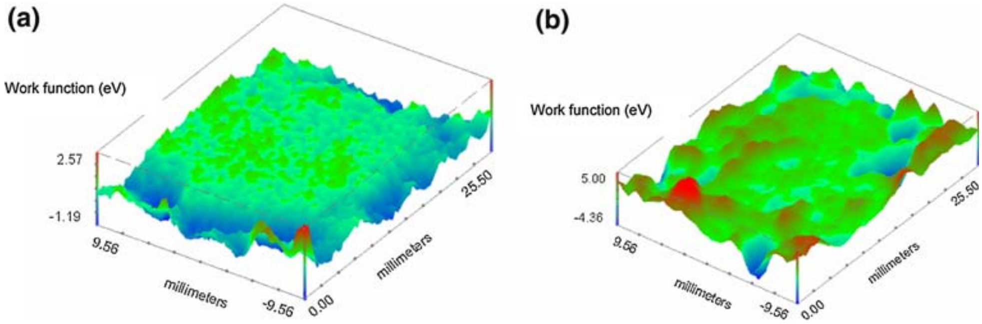

**Fig. 8** Work function map for phenolic pigmented coating (PT) before immersion (**a**) and after 120 h of immersion in the testing solution at pH 4 (**b**)

ionic barrier properties of the coating reported in Fig. 3 and the proposed mechanism.

Figure 7b shows the SKP scan of the melamine coated after continuous immersion for 120 h in the testing solution at pH 4. The average work function difference is 2 deV with standard deviation 0.62. It is possible to observe that the coating surface is damaged by the chloride ions generating some defects. The influence of the solution is evident.

Figure 8b exhibits the phenolic coated surface after the immersion in the solution. Its work function average value is 1.1 deV and standard deviation is 0.98.

With these results it is possible to observe higher changes on the melamine surface compared to phenolic one, proving lower ionic barrier properties of sample MT in comparison with PT and showing the increase of the corrosion reaction starting from the initial defects. Note that after the immersion time the two coatings were very similar by visual observation and there was no evident remarkable differences between the two.

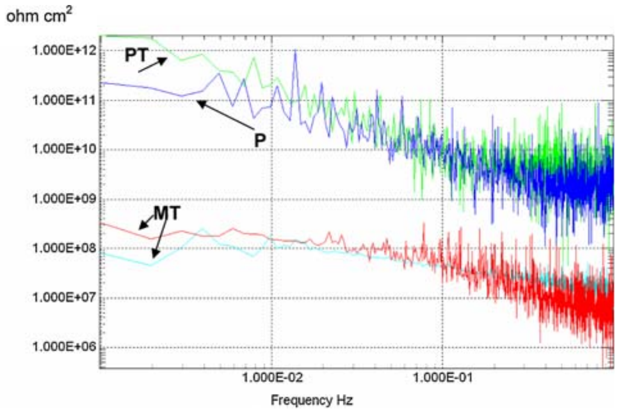

**Fig. 9** Impedance noise of the studied samples, after 120 h of immersion in the testing solution at pH 7

Figure 9 shows the impedance noise obtained after 120 h of immersion in the testing solution at neutral pH. The impedance noise was obtained by the ratio of the fast fourier transform (FFT) potential values of each frequency divided by the equivalent FFT current values [18]. The impedance noise at low frequency can be considered equivalent to the total resistance evaluated by EIS (Rp + Rct), which is in our case dominated by the charge transfer resistance Rct. Comparing the low frequency impedance noise values at low frequency for the different samples it is possible to get the same ranking obtained comparing the charge transfer resistance values, but the absolute impedance values are in good agreement with Rct only for the melamine MT coating (Fig. 9 shows two equivalent measurements), while the values for both the phenolic coatings (P and PT) are remarkably higher. It is not unusual to find in the literature such a differences in EN and EIS values [19]. In our case we can suppose that the values are very similar when the coating is defective enough (like in case of MT) to have a stable current signal during noise measurements, even at the very low noise potential fluctuations. When the coating impedance is higher (P and PT), a quite high signal amplitude like in the case of EIS measurements (10 mV), induce a easily measurable current, while in the case of noise measurements (low potential fluctuation and higher impedance) the current is very low, affecting the apparent noise resistance. Similar results were obtained for the samples tested in the solution at pH 4.

## 4 Conclusions

Electrochemical techniques are an useful tool for developing new materials for an important industrial sector like the food packaging. In particular the synergic information which it is possible to obtain from traditional electrochemical techniques, like EIS, and new experimental methods with spatial resolution are very interesting.

The results obtained on the studied coatings showed that, in general, the coatings containing pigments ($TiO_2$) have better performance than clearcoats, in particular after mechanical deformations.

Comparing the different polymers, epoxy–phenolic coatings have a better corrosion protection than epoxy–melamine coatings because this last kind of coating, despite the better water barrier properties, shows more coatings defects inducing the metal corrosion reaction.

The different studied environments (pH 4 and 7) are not affecting the coating barrier properties, but they influence the metal substrates corrosion.

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