

Effect of uniaxial strain on the protective properties of coil-coatings

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Abstract

The effect of uniaxial deformation on coil-coated galvanised steel was investigated. Samples with several degrees of uniaxial elongation were exposed to a corrosive solution and the loss of protective properties was monitored by electrochemical impedance spectroscopy (EIS). Protection rapidly decreased with the degree of elongation. After 16% the coating degradation introduced by elongation was so high that EIS was not able to distinguish different strained samples. The loss of protection was interpreted in terms of the morphological changes experienced by the coated system as a consequence of strain, supported by scanning electron microscopy (SEM) observations.

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1. Introduction

Coil-coatings are widely used for roof and wall elements in the building industry, casings for household appliances and internal parts or bodywork structures for the automotive industry. The use of this technology is increasing due to its advantages such as the reproducible manufacturing process, lower cost and reduced environmental impact. These are materials with a finished surface, therefore the various processing procedures such as cutting, punching, parting, perforating, bending, drawing and deep-drawing are executed with the organic coating already applied to the metal surface. To avoid damaging the paint, the tools used need to be in very good condition and extreme care must be taken during the processing work. Nevertheless, the final shaped object will have areas that were subjected to distinct forces during manufacture, and different strain conditions will be present in those regions. This is particularly true in the cases of bending and deep-drawing. The areas with higher deformation are expected to be prone to faster coating degradation and early corrosion of the metal substrate.

Electrochemical impedance spectroscopy (EIS) is an efficient technique for assessing the performance of organic coatings [1–5]. Determination of the various parameters can be used for comparing the performance of coatings. In fact,

the barrier protection against corrodants, such as water, ions and gases is evaluated by the film resistance. Water absorption can be measured by the film capacitance variation, since the capacitance increases with the amount of water absorbed. Paint delamination can be assessed by the double layer capacitance; the absence, or late appearance of the double layer capacitance and its slow increase corresponds to good paint adhesion. Finally, the charge transfer resistance can be taken as a measure of the corrosion rate since the two are inversely proportional.

Not many studies can be found in the literature concerning the influence of metal forming on the anticorrosive properties of organic coatings [6–10]. In a study using the Erichsen dome test, a tendency was observed for strained coatings to significantly increase their capacitance due to an increased water uptake when compared to the unstrained samples [8]. By the use of EIS, it was also possible to determine how that process could be accelerated by the weathering of the coating previously to deformation. In a recent study, an attempt to correlate uniaxial strain with the bending mandrel test method made on silicone polyester has shown that the coating resistance decreased with the strain, whereas the double layer capacitance, i.e., the delaminated area, increased [10].

This work presents results of a study on the performance of pre-painted electrogalvanised steel deformed by uniaxial stress of various magnitudes. EIS was used for monitoring the coating corrosion protective properties and scanning electron microscopy (SEM) allowed inspection of the samples.

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2. Experimental

2.1. Samples

The coil-coated electrogalvanised steel consisted of a steel sheet 800 μm thick, covered by an electrodeposited zinc layer of 7 μm thickness, a pre-treatment consisting of phosphating followed by a chromate rinse and the paint. The paint system was a 5 μm polyester primer plus a 15 μm polyurethane intercoat. No topcoat was applied, in order to accelerate the corrosive process. The steel used was ST14

type, very ductile, adequate for deep-drawing work. Samples of 30 mm \times 250 mm were submitted to various uniaxial traction forces, resulting in various degrees of elongation: 0, 9, 11, 16, 19 and 23%. The elongation is given by the expression:

$$\varepsilon (\%) = \frac{l - l_0}{l_0} \times 100 \quad (1)$$

where l_0 and l are, respectively, the distance between marks before and after deformation. The marks were positioned with a separation of 80 mm, in the central part of the panel

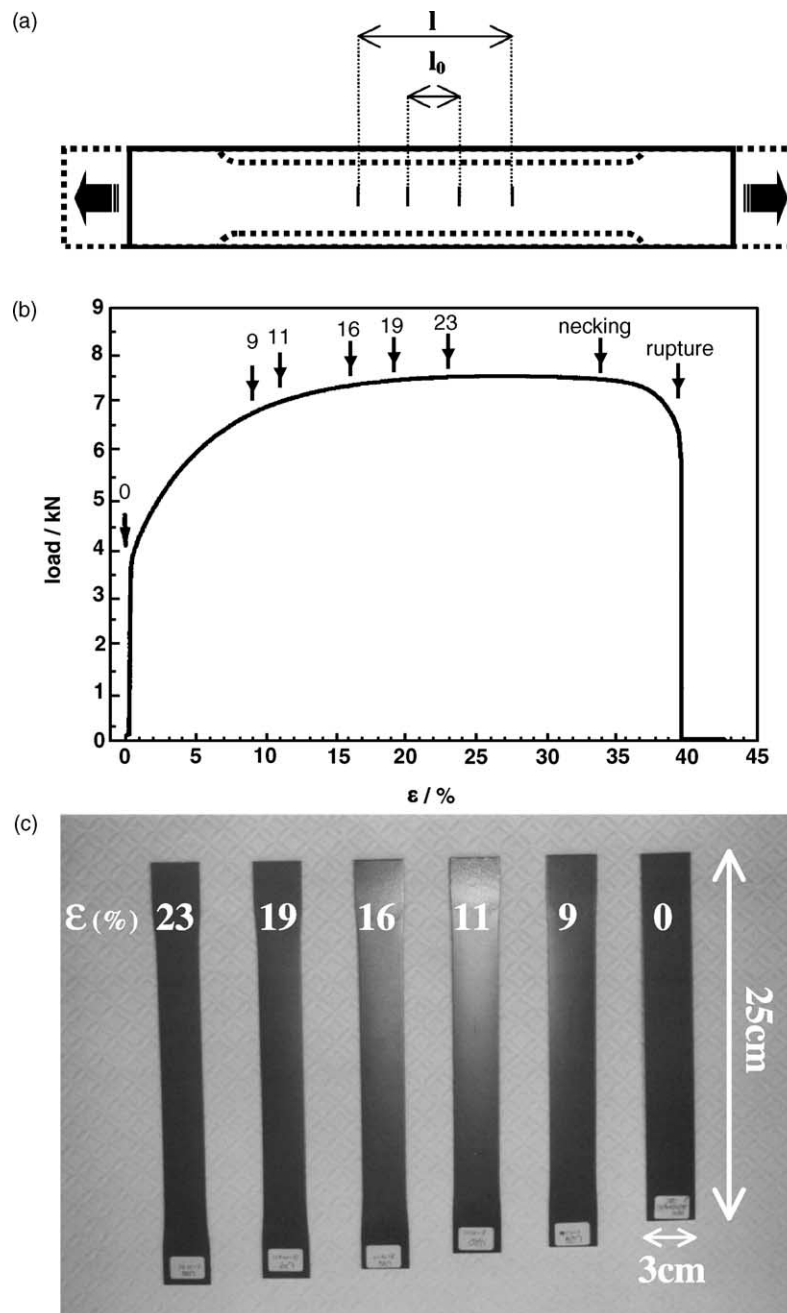


Fig. 1. (a) Scheme of the uniaxial deformation; (b) load–elongation diagram of the coil-coating under study; (c) a set of elongated samples used.

(Fig. 1(a)). Fig. 1(b) shows the complete load–elongation curve and Fig. 1(c) shows a set of the samples used. With the elongations used, reduction in the coating thickness does not exceed 10%.

2.2. Electrochemical impedance measurements

The electrochemical cells were prepared by gluing PMMA tubes to the samples surface. The tubes, delimiting an area of 3.8 cm^2 were filled with 5 wt.% NaCl (Merck p.a.) aqueous solution. A three-electrode arrangement was used, with a saturated calomel electrode as reference, a platinum counter electrode and the exposed sample area acting as working electrode. The cells were connected to a Gamry FAS1 Femtostat + PC4 Controller Board and all the measurements were performed at room temperature in a Faraday cage. Impedance measurements were made at the open circuit potential, in the frequency range 50 kHz–5 mHz with seven points per decade, logarithmically distributed; the sinusoidal perturbation had 10 mV r.m.s. of amplitude. A minimum of four samples was tested for each type of elongation, with good reproducibility. Fitting of the spectra was made using the EQUIVCRT software [11].

2.3. Scanning electron microscopy

Two different microscopes were used. A Hitachi S-2400 scanning microscope (15–25 kV) with a Rontec energy

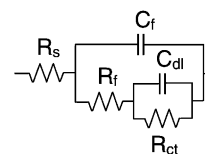


Fig. 3. Equivalent circuit used to mimic coated systems with delamination.

dispersion spectrometer (EDS) standard Si(Li) detector for X-ray microanalysis and a Jeol JSM-6301F scanning microscope (10–15 kV) with a Noran Voyager EDS. The micrographs were acquired digitally and stored in the controlling PC hard-drive.

3. Results and discussion

The impedance spectra were typically as illustrated in Fig. 2 for samples with 0 and 19% of elongation. Interpretation is made by describing the impedance response of the coated system with the equivalent circuit shown in Fig. 3, where R_s is the uncompensated resistance between reference electrode and working electrode, R_f the coating film resistance, C_f the film capacitance, C_{dl} the double layer capacitance and R_{ct} the charge transfer resistance. In general, the impedance response obtained in the first instants of immersion was fully capacitive. For the unstrained samples ($\varepsilon = 0\%$), this behaviour was maintained for several days and only

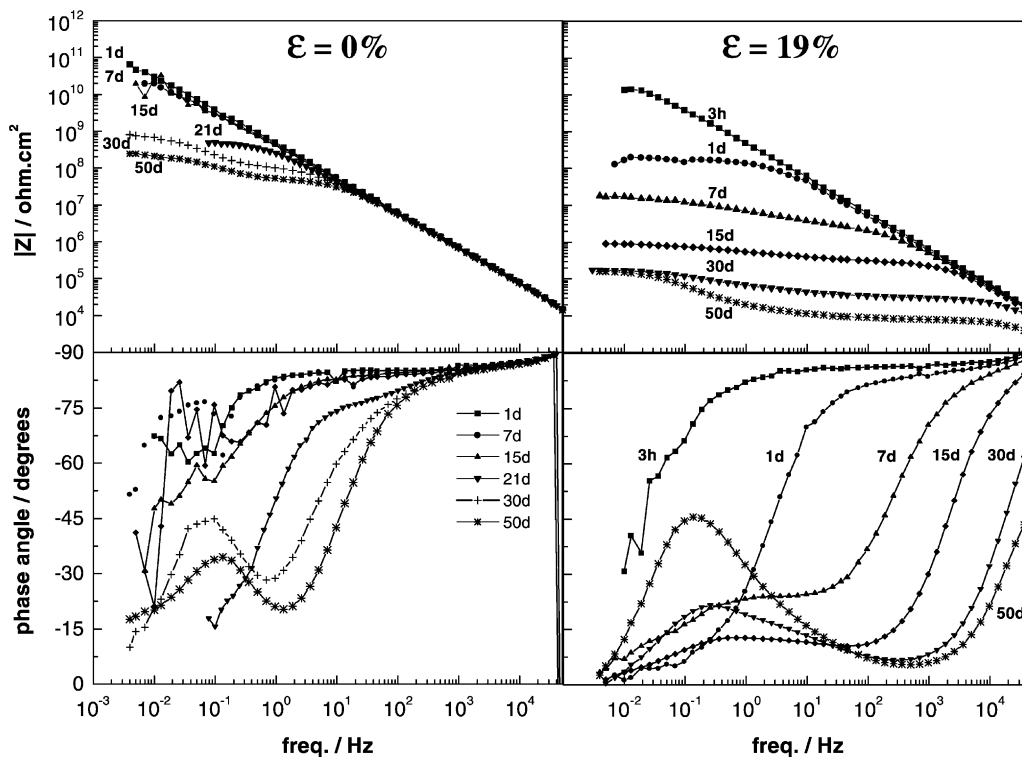


Fig. 2. Bode plots of the impedance measurements on a sample without strain and a sample with elongation of $\varepsilon = 19\%$ during immersion in a NaCl aqueous solution.

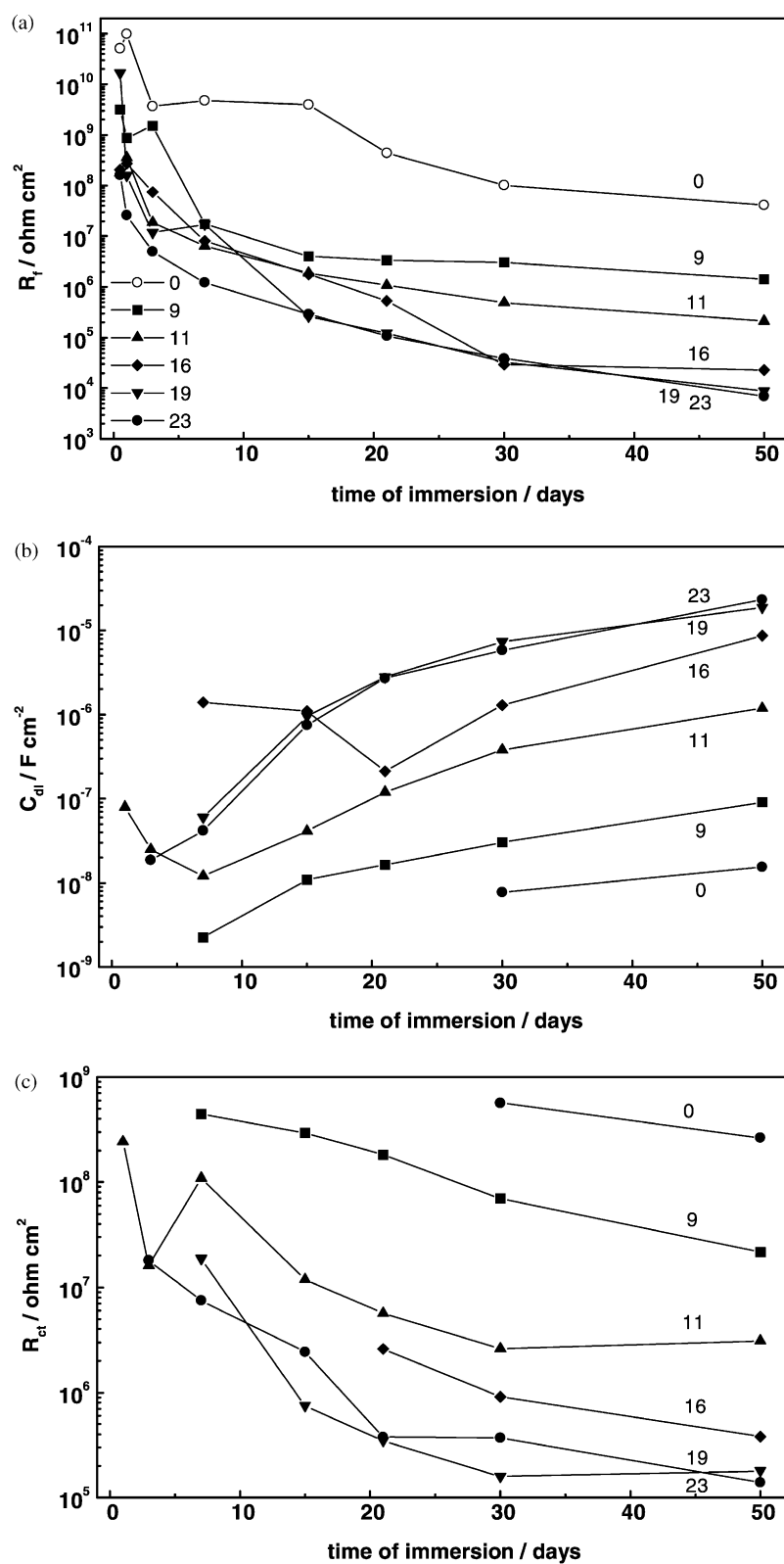


Fig. 4. (a) Film resistance, (b) double layer capacitance and (c) charge transfer resistance evolution with time of immersion for uniaxially strained samples. Degrees of elongation from 0 to 23%, as indicated in the figures.

after 1 month of immersion a clear definition of the charge transfer process was observed at ~ 0.1 Hz. For the samples with higher strain ($\varepsilon = 19$ and 23%), the low frequency behaviour became resistive after only 1 day of exposure to the salt solution, revealing a significant loss of protective properties. The coating resistance gradually decreased with time, by a total of six orders of magnitude, during the exposure period. All samples showed a similar behaviour but with different rates, faster for those with larger elongation. The film resistance, the double layer capacitance and the charge transfer resistance obtained by numerical fitting are plotted in Fig. 4 as a function of the time of immersion. The film resistance has a very high value, near $10^{10} \Omega \text{ cm}^2$, at the instant of immersion and irrespective of the strain, decreasing rapidly in the first 10 days and then in a smoother way until the end of experiment. The rate at which resistance decays is clearly dependent upon the degree of elongation, up to 16% . Above that and up to the maximum elongation tested (23%) the systems resistance levelled out.

The initiation of the corrosion process is associated with a drop of the coating resistance. The value of $10^6 \Omega \text{ cm}^2$ is sometimes suggested as that critical value [1], although in this case, signs of corrosion were detected for coating resistances in the order of $10^7 \Omega \text{ cm}^2$. The time for corrosion initiation, here defined as the time necessary to the formation of a detectable double layer capacitance, decreased with increasing strain for elongation below 11% , but above that strain a correlation could not be observed. The double layer capacitance increased with elongation between 9 and 19% and no further increase was observed for 23% . For the most severely formed samples the capacitance attained the range $10^{-5} \text{ F cm}^{-2}$, corresponding to extensive delamination. In some cases C_{dl} started at values in the range 10^{-5} to $10^{-6} \text{ F cm}^{-2}$, decreasing one or two orders of magnitude and then slowly increasing with time. The initial high capacitance and its rapid decrease apparently corresponds to a contact with metallic surface followed by a decrease in the

area undergoing corrosion, possibly due to the accumulation of the first corrosion products with the aid of chromate ions from the pre-treatment. This unusual C_{dl} evolution can be explained by the existence of defects or interfacial voids created during the deformation process that expose the metal and become easily filled with solution.

Signals from charge transfer resistance appear at the same time as the double layer and are associated to the onset of electrochemical processes at the metal interface. As stated before, R_{ct} is inversely proportional to the corrosion rate. For $\varepsilon = 11\%$ and above, corrosion evolution increases faster during the first 30 days and then maintains its rate. For samples with lower elongation, corrosion started after longer exposure times and increased at a lower rate, as evaluated by the charge transfer resistance and the double layer capacitance.

Of the parameters monitored, the one that had the most regular variation, and thus the one that best characterised the loss of protective properties due to mechanical deformation was the film resistance. In Fig. 5 the film resistance is re-plotted, as a function of elongation for 1, 7, 15, 30 and 50 days of immersion. The plot reveals an approximately logarithmic decrease of R_f with elongation, except for the two higher values of elongation, 19 and 23% , which reveal a similar coating resistance. This observation suggests that a critical strain was attained, beyond which coating degradation may occur via a different mechanism. Using a criteria for good protection, values of R_f above $10^6 \Omega \text{ cm}^2$ and values of C_{dl} below $10^{-6} \text{ F cm}^{-2}$ then, at the end of the experiment (50 days of immersion), only the samples with 0 and 9% of elongation would be acceptable with the 11% sample being near the threshold values.

Although the resistance is proportional to the coating thickness, this effect is of minor importance, since the coating resistance decreases by several orders of magnitude, largely exceeding the small thickness reduction involved in the test. Therefore, some other effect is responsible for the resistance decay.

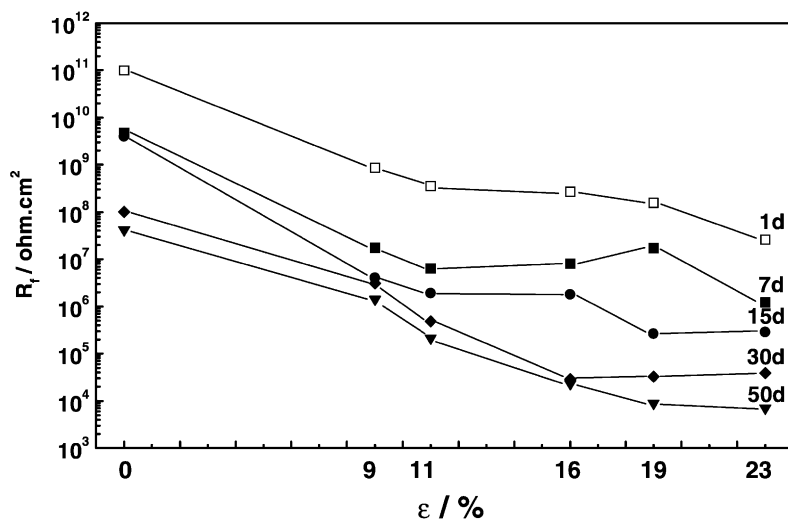


Fig. 5. Film resistance vs. elongation for various immersion periods (1–50 days).

SEM of the coating showed increasing roughness with increasing elongation (Fig. 6) possibly as a result of relaxation and rupture of polymer chains as well as some movements of the pigment particles. Samples strained to rupture also showed curling on the coating and many holes on the surface. These holes were always observed adjacent to a solid particle, either of pigments or of extenders or fillers like barite or calcite (Fig. 7). It was not clear whether the defects appeared in the bulk of the coating or just at the surface;

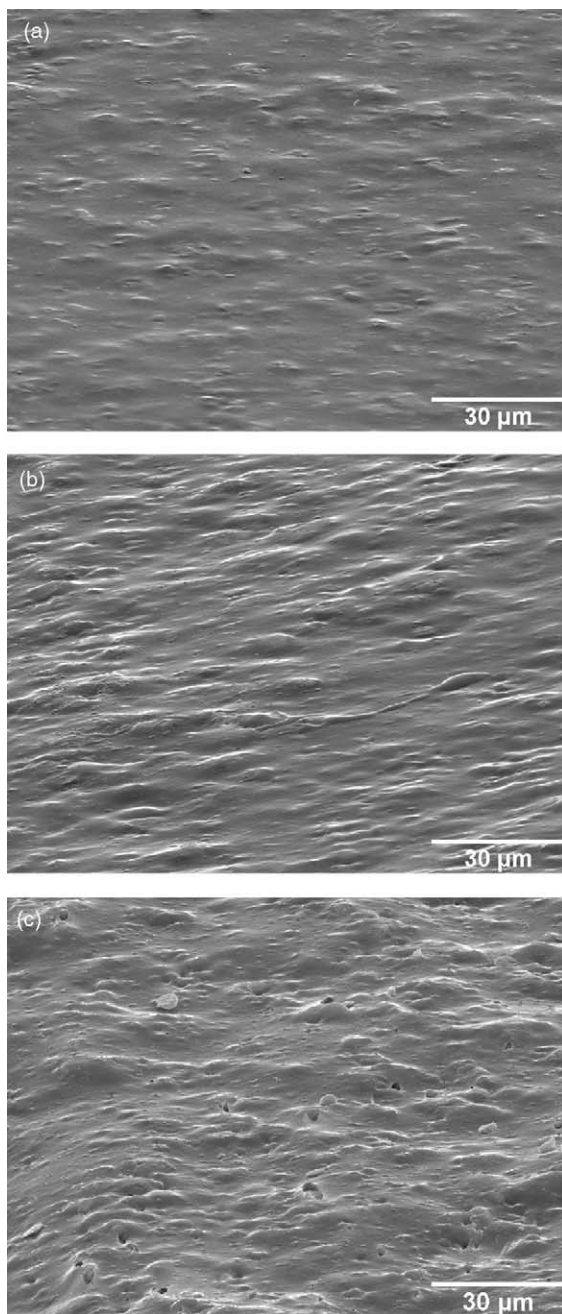


Fig. 6. SEM micrographs of organic coating surfaces with no elongation (a), 23% of elongation (b) and elongation until rupture (c). Surfaces are 70° tilted.

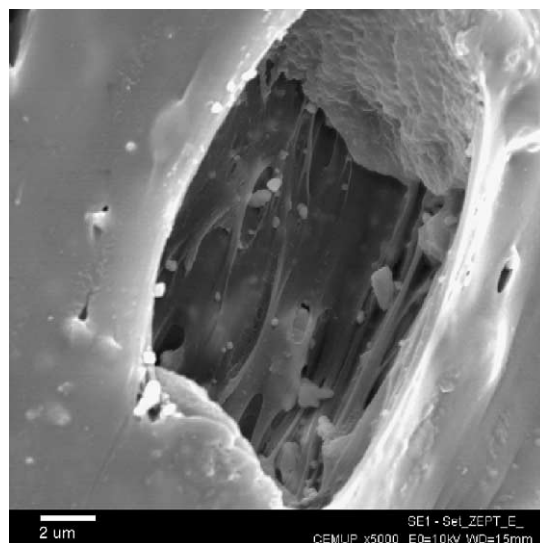


Fig. 7. Electron microscopy detail of defects on a sample elongated up to rupture.

however, smaller holes were observed at the inner walls of the larger holes (Fig. 8).

The same observations were made comparing a pigmented coating with a clear coat. In both systems it was possible to observe some roughness that increased with strain, possibly as a consequence of the effect of strain on the substrate. No holes were observed for pigmented samples with elongation up to 23%, but they were present in the samples strained up to rupture. The clear coat showed holes and other defects in the region near the fracture where the film was lacerated by the phosphate grains from the surface pre-treatment. Away from the fracture, some defects were encountered but scarce and coincident with heterogeneities present in the matrix. Fig. 9 shows that the defects are a consequence of strain and originated by heterogeneities in the matrix, which, in the

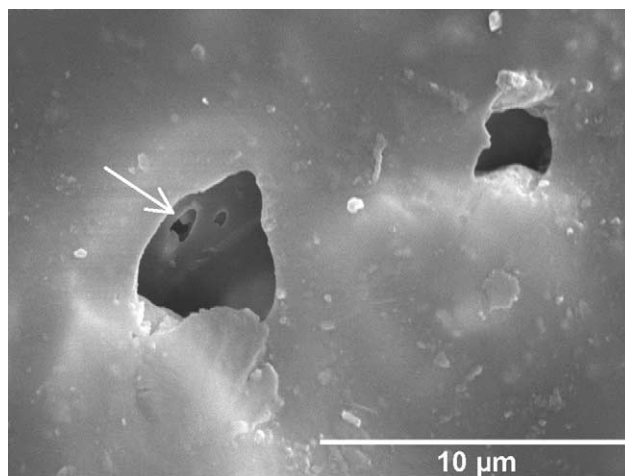


Fig. 8. Detail of a pore, showing smaller defects at the inner surface (as indicated).

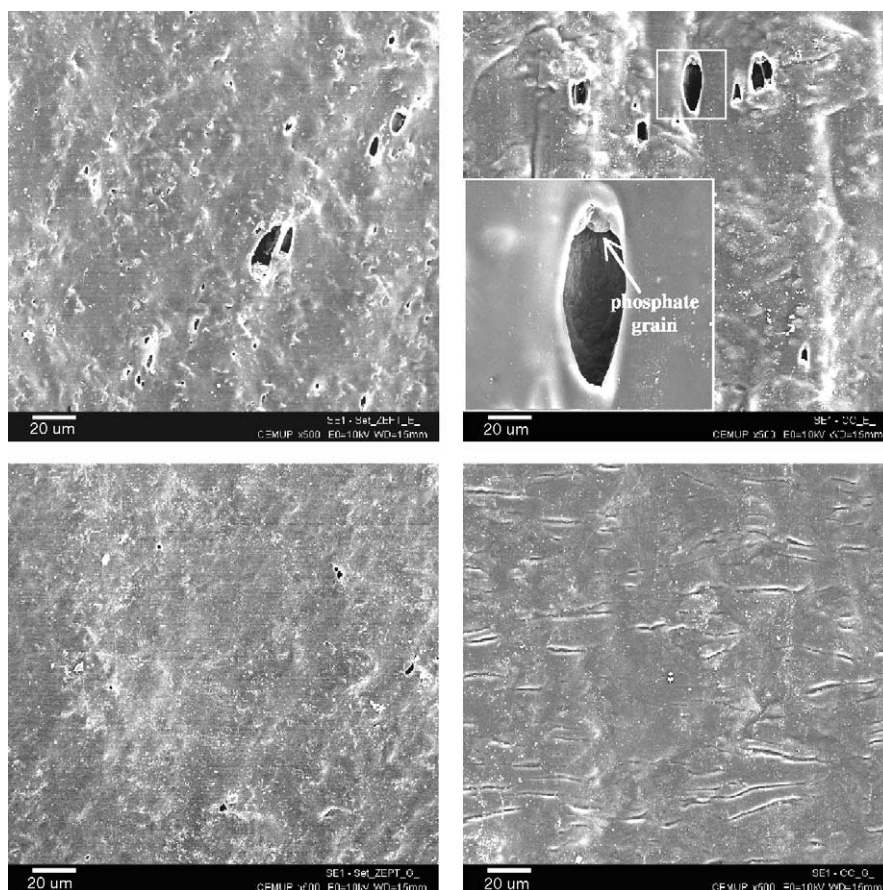


Fig. 9. Surface of pigmented samples (left) and clear coats (right) after rupture. Top: micrographs taken in the vicinity of the fracture. Bottom: micrographs taken 6 cm from the fracture.

case of paints, are largely present in the form of pigments. These defects can be responsible for the rapid decrease of film resistance with strain. The effect is gradual: when a disrupted sample's surface is observed, the presence of small defects is observed, with their number and size gradually increasing towards the fracture. For samples with $\varepsilon = 23\%$ no defects were observed as a direct consequence of deformation. However, after immersion many holes were present

on the surface, apparently due to loss of pigments. In contrast, the sample without strain had its surface practically unaffected after immersion (Fig. 10). The explanation for this difference can be due to some disbonding at the polymer/pigment interface. In the samples that were strained up to rupture, this effect was greater, leading to the development of defects (holes) to the surface. In the samples with lower strain, this weakening of the bonds was not detected

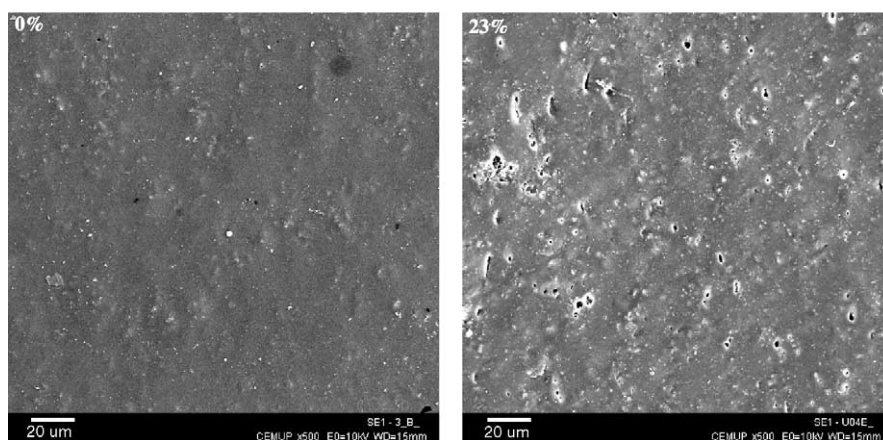


Fig. 10. SEM micrographs of coated surfaces after 100 days of immersion, on samples with no deformation (left) and with 23% of elongation (right).

before immersion, but the cooperative effect of water may lead to swelling with relaxation of the matrix, facilitating the pigment release from surface. Besides, water intrusion at the polymer/pigment surface may interact with the chemical bonding between the two phases.

EIS has thus shown that the barrier properties of the coating decrease with increasing strain and SEM was able to explain those results morphologically. A relatively high saline concentration, as well as the absence of a topcoat was chosen in order to accelerate the corrosion process. The primer and the mid-coat had a total thickness of 20 μm , and pigments with relative large dimensions were used in their formulations. Thus, extrapolation to different systems should be done with care. Usually a topcoat means a thicker layer of paint and also the presence of small round-shaped pigments, combined with a lower pigment concentration. These factors should lead to a slighter effect of the strain. Moreover, the results are dependent of the polymer mechanical properties since harder polymers will more easily become fractured, while softer ones would survive higher elongation.

4. Conclusions

EIS and SEM were used to achieve valuable information regarding the effect of uniaxial strain in the barrier properties of coil-coatings. The anticorrosive protection was assessed by the resistance of the organic coating, the capacitance of the double layer and the charge transfer resistance, which were determined from the electrochemical impedance data. All the parameters were sensitive to the induced strain. The coating resistance and the charge transfer resistance decreased with the elongation, whereas the double layer capacitance increased, all revealing a loss of barrier properties with the mechanical deformation. From the parameters tested, the coating resistance was the one that gave the most

regular dependence with the strain. A correlation between induced strain and loss of protective properties was clear until $\varepsilon = 16\%$; for higher strains (19 and 23%), but below film rupture, further degradation was not observed. Based on the microscopic inspection of the coating, it was concluded that strain created defects at the vicinity of pigments. The strain is believed to reduce the polymer–pigment interactions so that subsequent electrolyte intrusion can degrade film quality.

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