

Influence of the stress generated during an ageing cycle on the barrier properties of cataphoretic coatings

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ARTICLE INFO

Article history:

Received 19 June 2007

Received in revised form 22 January 2008

Accepted 29 January 2008

Keywords:

EIS

Stress

Electrocoating

Barrier properties

Water uptake

ABSTRACT

The ageing of organic coatings is generally associated with an increase of stresses leading to a coating degradation: loss of adherence, increase of the porosity and irreversible changes during exposure to climatic parameters such as humidity and temperature.

In this work, electrochemical impedance spectroscopy (EIS) and the cantilever method (stressmeter) were used to establish a correlation between the loss of barrier properties and the increase of the stress of electrocoated paints. The stress was generated during hygrothermal ageing cycles in a climatic chamber (20 h at 55 °C–84% RH and 4 h at 23 °C–40% RH).

Phosphatised steel plates were used for the electrochemical measurements and calibrated steel strips for the stress measurements. Two electrocoated paints differing by their composition were tested. For both electrocoatings, the plates and the calibrated steel strips were submitted to 0, 1, 2 and 4 hygrothermal cycles in the climatic chamber. The generated stress was determined after each cycle. The strong influence of humidity on the stress was underlined during humidity cycles at ambient temperature. The sensitivity of the organic coatings to humidity increases with the number of humidity cycles and finally induces an irreversibility of the system. The barrier properties were evaluated after the different hygrothermal cycles and after 0, 2, 7, 14 and 21 days of immersion in 0.5 M NaCl electrolyte solution by EIS on the electrocoated steel samples. The stress generated during ageing increases with the number of cycles and at the same time a decrease of the barrier properties is observed. For the electrocoating whose stress evolution is more sensitive to humidity, a good correlation is observed between the increase of the internal stress and the increase of the coating capacitance due to water uptake by the coating.

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1. Introduction

Cathodic electrocoating is widely used as a primary layer coating in the automotive industry. This deposition technique has many advantages including high throw power, good corrosion protection and adhesion, low permeability, high coating utilization (>95%) and low level of pollution (aqueous system). Due to the excellent behaviour of these organic coatings, short-term test methods must be developed to evaluate the corrosion resistance of the paint/metal systems and decide which coating will be designed for long-term durability. The principle of climatic accelerated tests is the application of climatic conditions (temperature, humidity, salts and UV lights) at higher levels than in natural exposure to produce accelerated ageing. A few papers [1–6] showed that thermal ageing can be

used to reproduce and accelerate some of the degradation phenomena occurring in the real exposure. These tests induce physical and chemical ageing of the coating and affect the coating durability. In several papers, the thermal ageing is coupled with electrochemical spectroscopy to assess properties of organic coatings. The EIS technique allows to follow the changes in the organic coatings such as porosity, water uptake, delaminated area during the thermal ageing. If chemical changes in coating composition due to the action of moisture and temperature are important factors in the degradation of most of organic coatings, the stresses arising in coatings are also playing an important role [7–11]. Without mechanical impacts, the main causes of stress formation in a coating are: film formation, variation of temperature (T) and variation of relative humidity (RH).

The aim of this paper is to establish a correlation between the loss of the barrier properties and the increase of the stress generated during hygrothermal ageing cycles of electrocoated paints by using electrochemical impedance spectroscopy (EIS) and the cantilever method.

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2. Experimental

2.1. Materials

Two anticorrosive cathaphoretic epoxy electrocoatings (A and C) containing no toxic pigments such as lead compounds were supplied by PPG Industries-France and tested. For the stress measurements, the electrocoatings were applied with a constant voltage method on calibrated carbon steel substrates (282 mm × 12.6 mm × 0.1 mm) degreased with acetone.

For the electrochemical impedance spectroscopy tests, both electrocoatings were applied on phosphatised steel samples (100 mm × 100 mm × 1 mm) supplied by Etalon. To obtain a thickness of 15 μm, the applied voltage was 100 V (the distance between the electrodes is 6 cm and the ratio cathode area/anode area is 6.3) and 150 V (the distance between the electrodes is 3 cm and the ratio cathode area/anode area is 4) for calibrate substrates and phosphatised steel samples respectively. The bath temperature was 30 °C and all samples were coated for 2 min 30 s, rinsed and cured at 175 °C (if not specified).

After curing, the film thicknesses were measured by a 456 Elcometer thickness gauge.

2.2. Hygrothermal ageing test

The samples were placed in a humidity chamber and submitted to the following hygrothermal ageing:

Step 1: 55 °C–84% RH during 20 h

Step 2: 23 °C–40% RH during 4 h

The total cycle duration was 24 h.

The stress and electrochemical impedance spectroscopy measurements were carried out for the samples submitted to 0, 1, 2 and 4 cycles.

2.3. Stress measurements

2.3.1. Stress interpretation

The three main causes of stress development in an organic coating are: the film formation, the variations in temperature and in relative humidity (RH) [7–11]. The stresses arising are known as film formation (S^F), thermal (S^T) and hygroscopic (S^H), respectively. The thermal and hygroscopic stresses are often referred to as hygrothermal stresses. The total stress is defined by the following equation:

$$S = S^F \pm S^T \pm S^H \quad (1)$$

For coatings that can contract or expand only through their thickness, Eq. (2) represents the simplified general equation describing the stress arising in a coating:

$$S = \frac{E\varepsilon}{1-\nu} \quad (2)$$

One can also write that

$$S^F = \int_{V_S}^{V_t} \frac{E\varepsilon}{1-\nu} \frac{1}{3V_S} dV \quad (3)$$

where S is the stress (N/m²), ε the strain, ν the Poisson's ratio, E the elastic modulus (N/m²) and V_S and V_t are the volumes of the coating at vitrification and at time t after vitrification, respectively.

When coated substrates are exposed to variations in temperature and humidity, dimensional changes are induced. If the thermal and hygroscopic expansion coefficients of the coating (α_F^T and α_F^H) and the substrate (α_S^T and α_S^H) are different, which is usually the

case, thermal and hygroscopic stresses (S^T and S^H) will develop in the coating [7–10].

$$S^T = \int_{T_1}^{T_2} \frac{E}{1-\nu} (\alpha_F^T - \alpha_S^T) dT \quad (4)$$

$$S^H = \int_{RH_1}^{RH_2} \frac{E}{1-\nu} (\alpha_F^H - \alpha_S^H) dRH \quad (5)$$

In practice, these stresses act together. The positive sign denotes a coating tendency to contract (tensile stress) and the negative sign a coating tendency to expand (compressive stress). S^F is practically always positive.

Two climatic conditions can provoke high stress in a coating:

1. Low temperatures and RHs induce high tensile stresses;
2. High temperatures and RHs induce high compressive stresses.

2.3.2. Method

The method used to measure the stress is based on the works by Perera and Schutyser [7–10]. They proposed to use the cantilever or beam method. This method is based on the fact that for a coating under stress applied on a substrate, the coated substrate will deflect in the direction which relieves the stress. Since the deflection can be measured and the elastic properties of the substrate are known from separate determinations, the stress can be calculated.

The mathematical equation proposed in the literature to calculate the stress is as follow:

$$S = \frac{4d'E_s e^3}{3l^2 d(e+d)(1-\nu_s)} + \frac{4d'E_c(e+d)}{l^2(1-\nu_c)} \quad (6)$$

where d' is the deflection in the middle of the substrate (m), E_s the elastic modulus of the substrate (N/m²), E_c the elastic modulus of the coating (N/m²), ν_s the Poisson's ratio of the substrate, ν_c the Poisson's ratio of the coating, e the thickness of the substrate (m), d the thickness of the coating (m) and l is the distance between the two knives edges (m)

Eq. (6) assumes a good adhesion between the coating and the substrate, isotropic elastic properties of the coating and the substrate. It also assumes that the elastic limit of the substrate is not exceeded and that the stress is constant throughout the coating thickness.

The second term in Eq. (6), which contains a number of coating properties difficult to determine, can be neglected since in that case $E_s \gg E_c$ and $e \gg d$.

A commercial equipment, the CoRI-Stressmeter was used to measure the deflection in the middle of the substrate. This apparatus enables to measure the internal stress which developed in organic coatings from –40 °C to about 200 °C under a variety of RH. The stress evolution of an uncoated substrate, used as reference, is always subtracted from data obtained with a coated one.

For each condition, the measurements were repeated three times.

2.4. EIS measurements

2.4.1. Method and equipment

A conventional three-electrode cell was used for the EIS measurements. The working electrode was the investigated sample (exposed area of 4.5 cm²). The counter electrode was a platinum plate and all potentials were measured with respect to an Ag/AgCl reference electrode. The cell was filled with NaCl 0.5 M solution and placed in a Faraday cage in order to minimize external interference on the system.

The impedance spectra were obtained at the open circuit potential using a frequency response detector EG&G 1025 coupled with an EG&G 283 potentiostat. Both devices were computer controlled

using Powersuite® software. The impedance measurements were carried out over frequencies ranging from 100 kHz to 10 mHz using a 20 mV rms amplitude signal voltage.

The impedance measurements were made at ambient temperature on the samples submitted at 0, 1, 2 and 4 hydrothermal ageing tests and after 1 h, 2, 7, 14, 21 days of immersion in aerated NaCl 0.5 M solution.

2.4.2. EIS interpretation

The loss of the barrier properties of the film was determined after different hydrothermal ageing tests and different immersion times by following the changes of impedance values at low frequency (10 mHz) and the coating capacitance determined from impedance values obtained at high frequencies [12,13].

The impedance values at the lowest frequency represent the total resistance of the system including pore resistance and polarisation resistance. The changes of low frequency modulus are mainly due to the decrease of the pore resistance and to the loss of barrier properties of the film. The values are related to the number of pores or capillary channels perpendicular to the substrate through which the electrolyte reaches the interface. The coating capacitance C_c is generally assumed to be a measurement of water absorption by the coating. The coating capacitance is defined by:

$$C_c = \frac{\varepsilon \varepsilon_0 A}{d} \quad (7)$$

where ε is the dielectric constant of the coating, ε_0 the permittivity of the vacuum, A the area of the coating and d its thickness. The dielectric constant of water is about 20 times greater than that of a typical coating, so the penetration of water through the coating is generally accompanied by an increase of C_c . The amount of water absorbed by the coating can be estimated from the capacitance data by using the empirical formula derived by Brasher and Kingsbury [14]:

$$X_v = \frac{\log(C_c/C_0)}{\log 80} \quad (8)$$

where X_v is the volume fraction of water absorbed by the coating, C_0 the coating capacitance at the beginning of exposure (dry film capacitance) and 80 is the dielectric constant of water.

3. Results and discussion

3.1. Stress

3.1.1. Determination of T_g

In this work, the evolution of the stress as a function of temperature was used to determine the values of the glass transition for both electrocoatings cured at 175 °C. The sample was placed in the stressmeter and submitted to the following thermal conditions: from 40 to 130 °C with a slope of 1 °C/min.

Fig. 1 gives $S=f(T)$ for both electrocoatings (A and C) 24 h after electrodeposition and curing. During the measurement, the relative humidity was very low (15% RH) and constant during the thermal cycle so that for each system only the thermal stress changed during the test.

The glass transition can be determined from the interpretation of the $S=f(T)$ curves since the elastic modulus E , the expansion coefficient α_S^T and the Poisson's ratio ν show a profound change at T_g . Below T_g , the coating is in the glassy state, while above T_g , the coating is in the rubbery state. The linear dependence of S on temperature in the glassy state greatly facilitates the determination of T_g . This linearity is due to the fact that in this region E , α_S^T and ν are practically independent of temperature [15]. The T_g temperature was obtained from the intersection between the straight lines

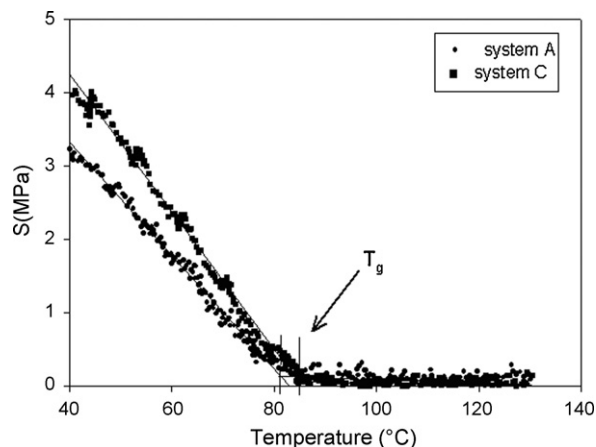


Fig. 1. Stress as a function of temperature for the systems A and C.

extrapolated from the linear parts at low and high temperatures of the $S=f(T)$ curves.

The value of the glass transition depends on the method used to determine it and in the present case, the transition detected is due to changes of the mechanical properties.

The T_g of the systems determined by this method with a thermal slope of 1 °C/min are 81 ± 1 and 83 ± 2 °C for A and C respectively. The values supplied by PPG and determined by DSC with a thermal slope of 20 °C/min are 92 °C for A and 94 °C for C. For $T < T_g$, the stresses are higher for coating C. At 40 °C and 15% RH, the stress is 3.2 ± 0.2 and 4.2 ± 0.3 MPa for coatings A and C respectively. This difference is probably due to a higher film formation stress for coating C.

3.1.2. Influence of the humidity

The influence of humidity on the generated stress was determined on samples cured at 175 °C during 25 min. These samples were placed in the stressmeter at 25 °C and a humidity cycle composed of four steps was performed. The humidity changes (1) from 40 to 85% RH during 30 min, (2) from 85 to 40% RH during 30 min, (3) from 40 to 20% RH for 30 min and (4) finally from 20 to 40% RH for 30 min as shown in Fig. 2. The stress was measured each 10 s.

The temperature is maintained at 25 °C and so, only the hygroscopic stress changed during this measurement.

During the high humidity period, water adsorption occurs and induces a compressive stress. In the opposite, during the low

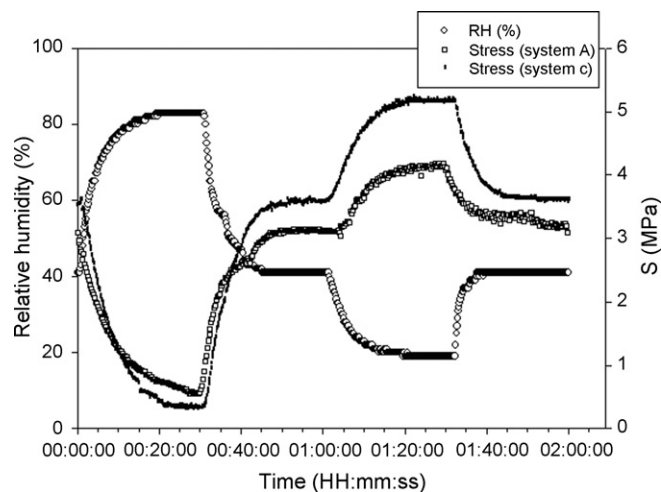


Fig. 2. Influence of humidity on the stress at 25 °C for the systems A and C.

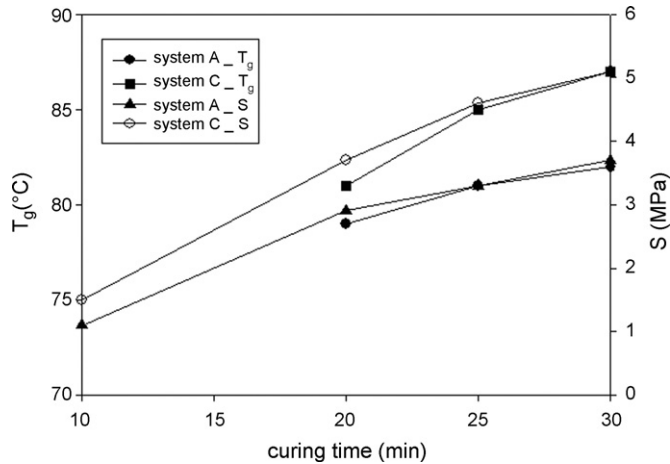


Fig. 3. Influence of curing time on the stress measured at 40 °C and 15% RH for the systems A and C cured at 175 °C.

humidity period, the water desorption generates a tensile stress in the coating. The behaviour of both coatings is reversible. The final stress measured at the end of the cycle is the same as at the beginning in the same conditions of temperature and humidity (25 °C and 40% RH). However, coating C is more sensitive to humidity than coating A. The stresses gap obtained between 20 and 85% RH is higher for the system C (about 5.2 MPa) than for A one (about 3.4 MPa).

3.1.3. Influence of curing temperature and time

The influence of the curing temperature (155, 165, 175 and 185 °C), the time of curing (10, 20, 25 and 30 min) on the stress (at 40 °C) and T_g were evaluated at 15% HR. During these measurements, the hygrothermal stress is constant and only the internal stress is changed.

Fig. 3 shows the evolution of the stress and T_g as a function of curing time for both electrocoatings. Due to an increase of the reticulation rate, the internal stress and T_g increase with the time of curing. This increase is practically linear between 10 and 25 min and stabilizes between 25 and 30 min. For each curing time, the stress and T_g values are higher for C coating.

Fig. 4 illustrates the stress and T_g values as a function of the curing temperature for coating A. A higher curing temperature increases T_g and the stress. The T_g value rises a little between 175 and 185 °C but a high increase of the internal stress can be observed

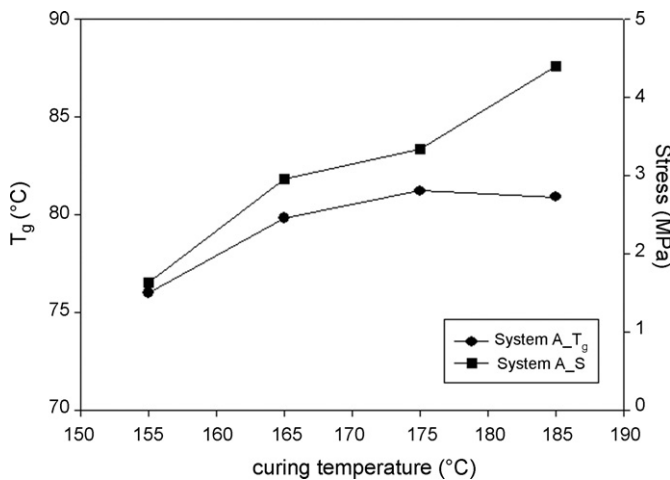


Fig. 4. Influence of curing temperature on the stress measured at 40 °C and 15% RH for the system A cured for 25 min.

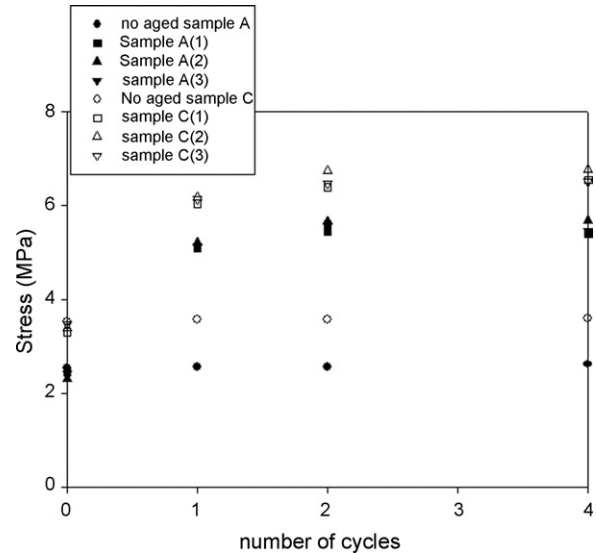


Fig. 5. Stress (at 23 °C–50% RH) as a function of number of hygrothermal cycles for systems A and C.

leading probably to a more brittle layer. These curves can be used to optimize the values of T_g , formation stress and thus reticulation ratio. For example, the best compromise between a high value of T_g and a quite low stress was obtained for a curing of the system A at 175 °C for 25 min.

3.1.4. Influence of the hygrothermal ageing test

To evaluate the stress development (at 23 °C and 50% RH) during ageing, the samples A and C cured at 175 °C during 25 min were submitted to 0, 1, 2 and 4 hygrothermal ageing cycles. Each cycle is composed of a long period (20 h) at 55 °C–84% RH followed by a period (4 h) at 23 °C–40% RH before stress measurements. As explained, these conditions induce a high level of hygrothermal stress in the layer. Many degradation mechanisms have threshold activation energy. This threshold corresponds to the temperature level at which a sequence of events will be initiated. When the energy activation exceeds this threshold, the deterioration produced is significantly different from that at the lower temperature. If the temperature is too low, the rate of change is slow and the deterioration is not enough severe. In the opposite, if the temperature is too high, the degradation will proceed too quickly and the effect will be too severe and not consistent with the natural mechanisms of degradation. In this test, the temperature did not exceed 55 °C to respect this condition.

Fig. 5 shows the evolution of the stress measured at room conditions for coatings A and C as a function of the number of cycles. As shown on the figure, the measurements are reproducible for both systems. The stress of the samples not submitted to thermal cycles was measured after 24, 48, 72 and 96 h at ambient temperature (23 °C, 50% RH). The stress was constant (2.5 MPa for A and 3.5 MPa for C) and no changes are observed with time. For samples submitted to one thermal cycle, a significant increase of the stress can be observed for both systems (from 2.5 up to 5.1 MPa for A and from 3.5 up to 6.1 MPa for C). Between 1 and 2 cycles, a slight increase of the stress can be observed. The stress reaches 5.5 MPa for A and 6.5 MPa for C. After four cycles, the stress is stabilized showing that physical and chemical irreversible changes in the layer are mainly provoked during the first thermal ageing test. In order to emphasize this irreversibility, a humidity cycle was performed on the samples A submitted to four thermal cycles and compared with the behaviour of the same samples without ageing test (Fig. 6).

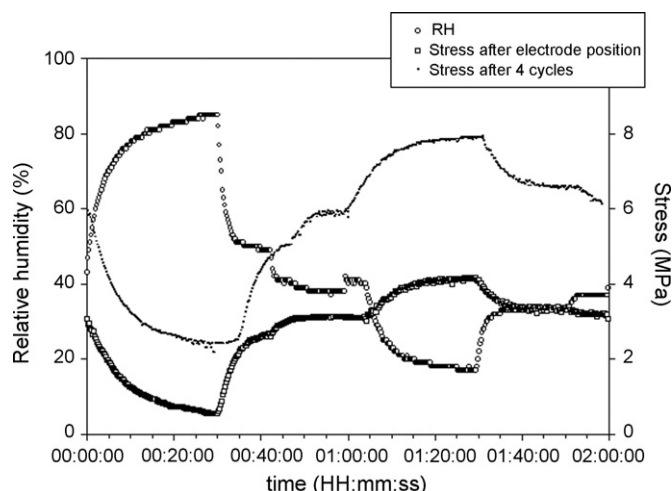


Fig. 6. Influence of relative humidity on samples A 24 h after electrodeposition and after four thermal ageing cycles.

The aged layer becomes more sensitive to high and low humidity. The difference between the minimal value S_{\min} (at 85% RH) and the maximal value (at 15% RH) increases from 3.6 MPa for 0 ageing cycle to 5.6 MPa for four cycles. The water uptake and desorption are higher than for a layer which was not submitted to thermal cycles but is reversible during a humidity cycle at ambient temperature.

3.2. EIS

Fig. 7 shows the evolution of the Bode-plot (logarithm of impedance modulus vs. logarithm frequency) as a function of the immersion time in NaCl solution.

For samples A not submitted to the ageing test, the behaviour is still purely capacitive after 21 immersion days in NaCl solution. The coating remains intact, keeps its barrier properties and the porosity does not change. For the samples A, Fig. 8a illustrates the behaviour obtained for samples aged with 0, 1, 2 and 4 ageing cycles and after 14 days of immersion in the saline solution. The same results are given for the samples C after 7 days of immersion (Fig. 8b). When the number of ageing cycles increases, a resistive behaviour appears at low frequencies and the impedance modulus at lowest frequencies decreases. Fig. 9 illustrates the evolution as a function of immersion

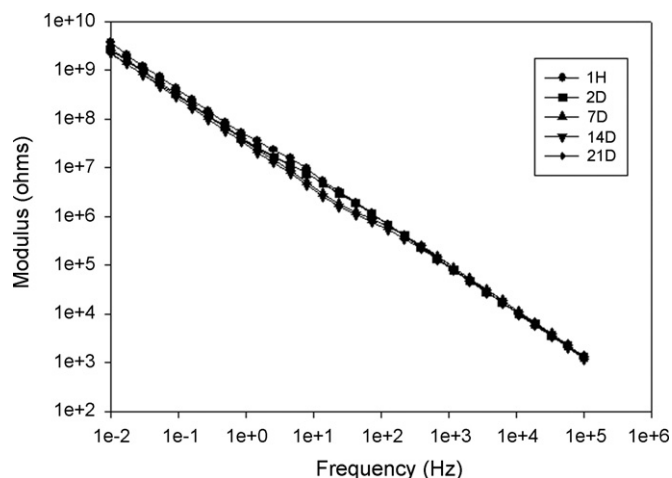


Fig. 7. Evolution as a function of the immersion time in 0.5 M NaCl solution of the impedance modulus vs. frequency (Bode-modulus plots) of coated samples A not aged.

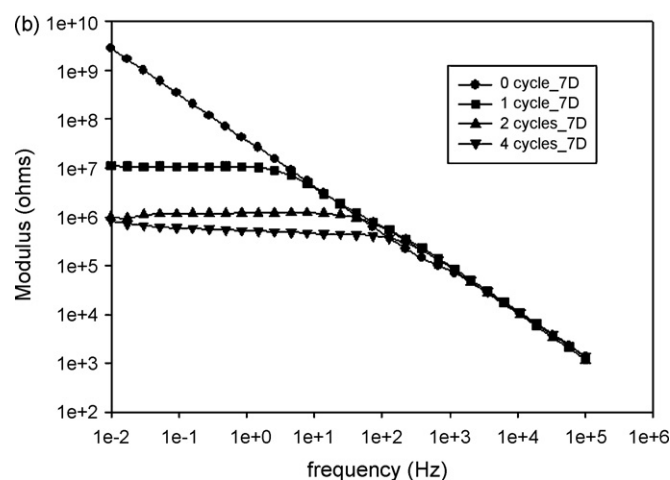
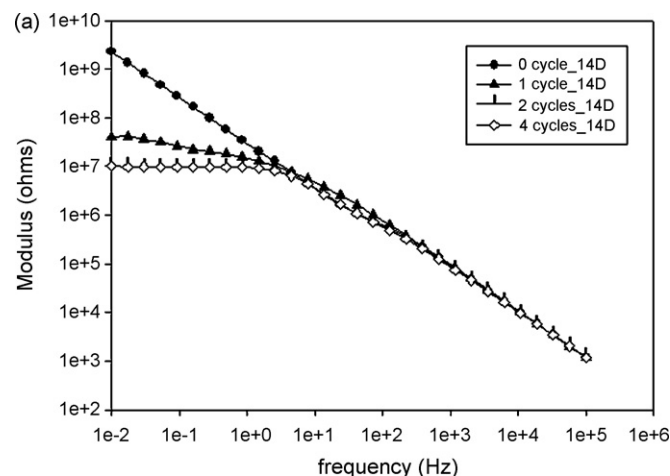


Fig. 8. (a) Evolution as a function of the immersion time in 0.5 M NaCl solution of the impedance modulus vs. frequency (Bode-modulus plots) of coated samples A submitted to 0, 1, 2 and 4 hydrothermal ageing cycles. (b) Evolution as a function of the immersion time in 0.5 M NaCl solution of the impedance modulus vs. frequency (Bode-modulus plots) of coated samples C submitted to 0, 1, 2 and 4 hydrothermal ageing cycles.

time of the low frequency modulus for both systems. The main loss of barrier properties is observed after 14 and 7 days for the aged samples A and C respectively. Intrinsically, the barrier properties of system C are lower than for system A. A good correlation between the increase of the stress in the coating and the loss of barrier properties can be established as shown in Fig. 10. The impedance values are measured after 14 days of immersion in the saline solution for system A and 7 days for system C. The differently induced stresses seem to be one of the factors responsible for the loss of barrier properties. An increase of stress decreases the barrier properties of the coating system.

The water uptake can be determined from the coating capacitance measurements following the Brasher and Kingsbury relation. The capacitance of the dry film was determined from the impedance measurement obtained for samples not submitted to hydrothermal ageing test and measured after 1 h of immersion. The water uptake for systems A and C as a function of immersion time in the saline solution is given in Fig. 11.

For each coating system (aged or not aged), the coating capacitance increases with immersion time in the saline solution due to an increase of the water uptake. The water uptake induces an increase of the dielectric constant of the layer. For a same

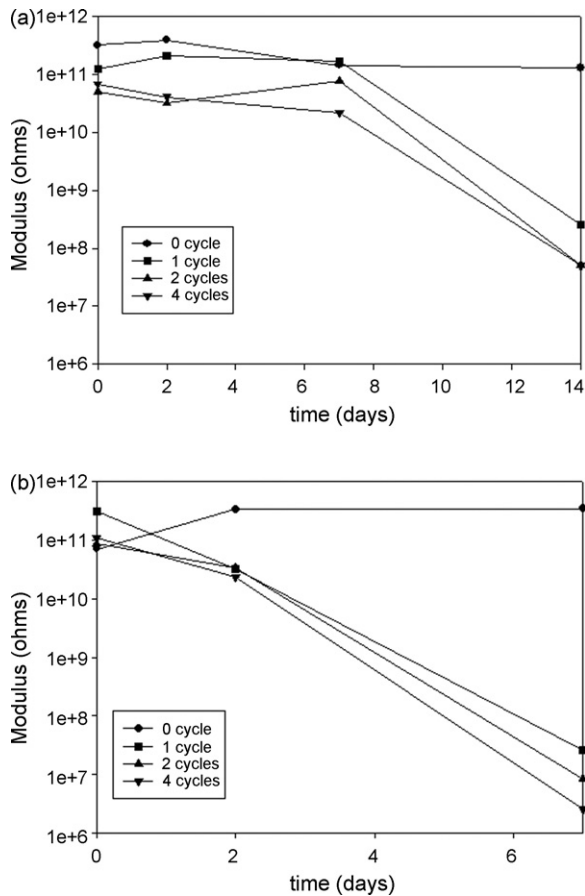


Fig. 9. (a) Low frequency impedance modulus as a function of immersion time in 0.5 M NaCl for the system A and for several thermal cycles. (b) Low frequency impedance modulus as a function of immersion time in 0.5 M NaCl for the system C and for several thermal cycles.

immersion time in the electrolyte solution, the water uptake increases with the number of hygrothermal ageing tests. For a same number of ageing cycles and the same immersion time in the electrolyte, the water uptake is always higher for coating C than for coating A. These results are in good agreement with stress measurements obtained during a humidity cycle on the A and C systems.

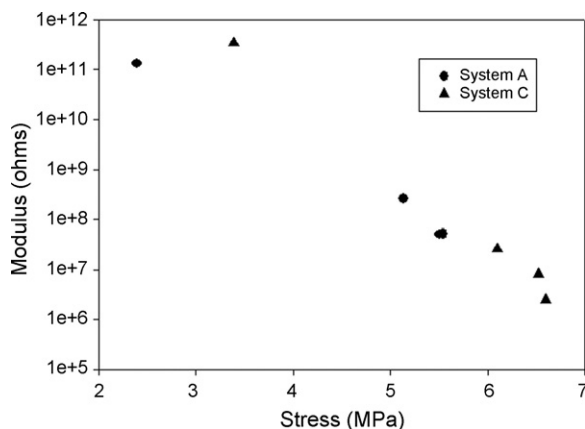


Fig. 10. The low frequency impedance modulus as a function of the stress (23 °C, 50% RH) for the system A (14 days of immersion in 0.5 M NaCl) and system C (7 days of immersion in 0.5 M NaCl).

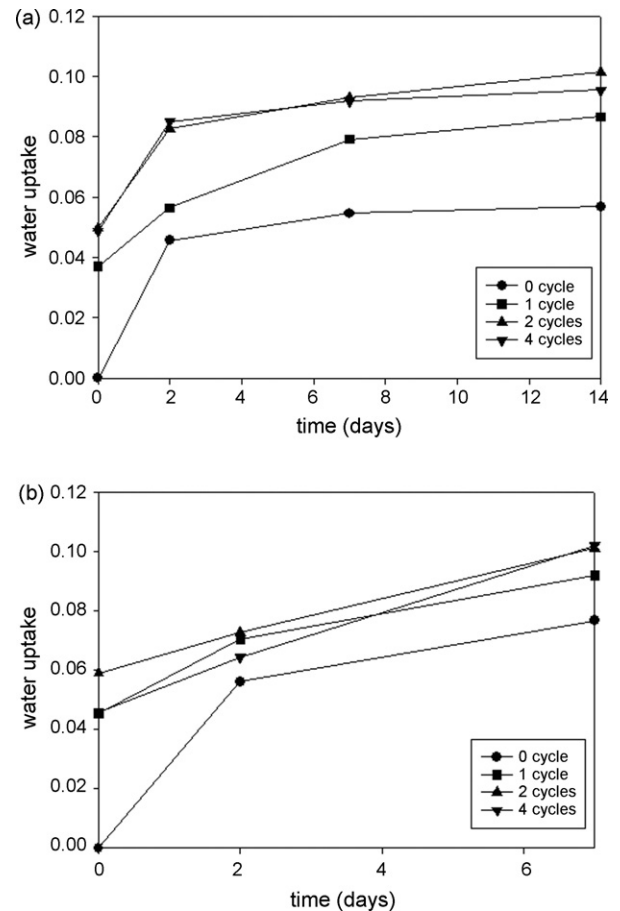


Fig. 11. (a) Water uptake of system A as a function of immersion times in 0.5 M NaCl solution for several thermal ageing tests. (b) Water uptake of system C as a function of immersion times in 0.5 M NaCl solution for several thermal ageing tests.

4. Conclusion

In this work, the combination of electrochemical impedance spectroscopy and stress (cantilever method) measurements are used to demonstrate the correlation between the loss of barrier properties of electrocoating systems and the increase of the stress induced by thermal ageing cycles. Two systems were studied: the system A known as giving a better corrosion protection than the system C.

The main causes of stress development in organic coatings are the film formation, the variations in temperature and in relative humidity and finally the ageing of the samples which modifies physical and chemical properties of the coatings. These different induced stresses were studied. System C has a T_g value slightly higher than system A. After electrodeposition, system C is always more stressed in the same operating conditions and more sensitive to changes in relative humidity. After several thermal ageing cycles (20 h at 55 °C and 84% RH and 4 h at 23 °C and 40% RH), a particularly high stress increase between 0 and 1 cycle can be observed. This induced stress leads to a higher humidity sensitivity and to an irreversible behaviour.

The use of electrochemical impedance spectroscopy reveals that this increase of the induced stress and the sensitivity of stress to humidity can be correlated with a decrease of the pore resistance and consequently of the barrier properties and with a higher water uptake of the layer during an immersion test.

Acknowledgements

This work was supported by the European Union (European Regional Development Funds) and le Ministère de la Région Wallonne. The authors like to thank PPG (France) for supplying the cataphoretic coating bath.

References

- [1] G.P. Bierwagen, L. He, J. Li, L. Ellington, D.E. Tallman, *Prog. Org. Coat.* 39 (2000) 67.
- [2] G. Bierwagen, D. Tallman, J. Li, L. He, C. Jeffcoate, *Prog. Org. Coat.* 46 (2003) 148.
- [3] L. Valentinelli, J. Vogelsang, H. Ochs, L. Fedrizzi, *Prog. Org. Coat.* 45 (2002) 405.
- [4] L. Fedrizzi, A. Bergo, F. Deflorian, L. Valentinelli, *Prog. Org. Coat.* 48 (2003) 271.
- [5] L. Fedrizzi, A. Bergo, M. Fanicchia, *Electrochim. Acta* 51 (2006) 1864.
- [6] H. Ochs, J. Vogelsang, *Electrochim. Acta* 49 (2004) 2973.
- [7] D.Y. Perera, P. Schutyser, *Proceedings of the 22th FATIPEC Congress, Budapest, Hungary, 1994*, p. 1.
- [8] D.Y. Perera, *Prog. Org. Coat.* 28 (1996) 21.
- [9] D.Y. Perera, *Prog. Org. Coat.* 44 (2002) 55.
- [10] D.Y. Perera, *Prog. Org. Coat.* 50 (2004) 247.
- [11] A.-P. Romano, M.-G. Olivier, C. Vandermiers, M. Poelman, *Prog. Org. Coat.* 57 (2006) 400.
- [12] G. Bierwagen, *Prog. Org. Coat.* 28 (1996) 43.
- [13] M. Destreri, J. Vogelsang, L. Fedrizzi, F. Deflorian, *Prog. Org. Coat.* 37 (1999) 69.
- [14] D.M. Brasher, A.H. Kingsbury, *J. Appl. Chem.* 4 (1954) 62.
- [15] D.Y. Perera, in: J.V. Koleske (Ed.), *Paint & Coatings Testing Manual, Gardener Sward Handbook, 14th ed.*, ASTM, 1995, MNL17.