

Influence of the curing temperature of a cataphoretic coating on the development of filiform corrosion of aluminium

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Abstract

Aluminium alloys are known to be particularly sensitive to filiform corrosion. The initiation of this particular type of corrosion is related to different parameters such as the presence of defects, the permeability of the coating to water and oxygen, the adherence of the paint system and the presence of salts.

In this work, the filiform corrosion resistance of Al 6016 substrates coated with a cataphoretic paint was studied. The curing of the coating was performed at different temperatures (185, 175, 165, 155 and 135 °C) in order to modify its mechanical properties and its permeability to oxygen.

The paint properties were studied by different techniques allowing the estimation of the degradation of the metal–primer system and giving some information about intrinsic paint properties.

The corrosion protection of the coating was evaluated by a normalized filiform corrosion test and by electrochemical impedance spectroscopy on scratched samples. The glass transition value and the internal stresses of the cataphoretic coatings obtained for different curing temperatures were determined by a stressmeter equipment.

This study enabled us to underline the influence of the curing temperature on the intrinsic properties of the coatings such as the glass transition temperature, the internal stresses, the adherence, the permeability and the corrosion protection properties.

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1. Introduction

Nowadays, to diminish the weight of car bodies, light metals such as aluminium alloys are more and more used in the automotive industry. The primer used for corrosion protection is in most cases an electrodeposited organic coating. Aluminium alloys are known to be particularly sensitive to filiform corrosion. This type is mainly a cosmetic attack because in most cases it does not weaken or destroy the metallic structure and concerns only surface appearance. Filiform corrosion is a specific delamination which occurs under atmospheric conditions with relative humidity between approximately 50 and 90%. This type of corrosion is produced between the coating and the substrate by the formation of filaments. The filaments generally follow irregularities on the surface (either rolling or grinding marks)

or defects in the organic coating. This specific type of delamination is driven by a differential aeration cell. In most cases, it is related to anodic undermining [1]. Galvanic corrosion develops between the head front of the filament (anode) and the tail (cathode) [2]. At the anode, the most important reaction is the oxidation of the aluminium while at the cathode, the reduction of O₂ in OH⁻ ions occurs, contributing to the delamination of the coating and the formation of corrosion products (Al(OH)₃). This corrosion is controlled by many parameters such as the metallic substrate, the surface preparation, the presence of defects, the permeability of the coating to water and oxygen, the adherence of paint system and the presence of salts.

Numerous papers refer to the efficiency of electrochemical impedance spectroscopy (EIS) as a tool for the evaluation of adherence properties of organic coatings [3,4]. Moreover, a work published by Fedrizzi et al. [5,6] shows that the sensitivity to filiform corrosion can also be revealed by EIS. This method is based on the electrical equivalent model proposed by Kendig. The circuit, shown in Fig. 1, consists of two time constants. The

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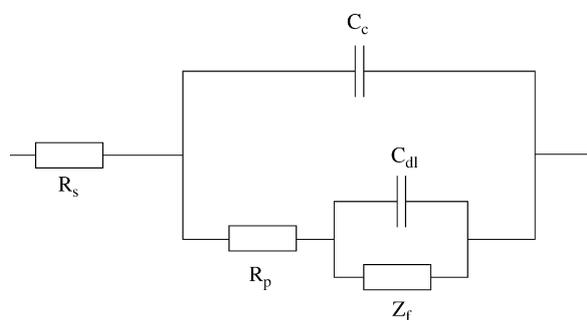


Fig. 1. Electrical equivalent circuit where R_s is the bulk electrolyte resistance, C_c the coating capacitance, R_p the pore resistance of the coating, C_{dl} the double layer capacitance and Z_f an element representing the faradic impedance.

first time constant observed at high frequency is related to the coating properties.

In the case of a very low coating capacitance (10^{-10} F/cm²) and a large defect as a scratch sample, this time constant is generally shifted towards higher frequencies than those reached with usual procedures.

The second time constant, at low frequency, takes into account the corrosion reaction of the substrate. This time constant is characterized by the double layer capacitance C_{dl} and an element Z_f which contains the charge transfer resistance R_{ct} and electrical elements taking into account the low frequency behaviour which appears when complex aluminium dissolution takes place [7]. C_{dl} and R_{ct} are two parameters which can be used to specify the sensitivity of the system to delamination or filiform corrosion. Indeed, the wet or active metallic area is proportional to the electrical parameters related to this time constant. From the C_{dl} value, it is possible to obtain information on the wet area (A_w) following the equation:

$$\frac{C_{dl}}{C_{dlo}} = A_w$$

where C_{dlo} is the double layer capacitance of the bare metal.

Such an equivalent circuit is valid for the study of scratched organic coatings given that the resistance under the film is sufficiently low.

Beyond the opportunity to get quantitative information about filiform corrosion, this technique also allows a rapid acquisition of data compared to the classical evaluation of this type of corrosion.

The durability of the organic coatings and thus, the development of filiform corrosion, also depend on the coating internal stress. The three main causes of stress development in an organic coating are: the film formation, the variations in temperature and in relative humidity (RH) [8–11]. The stresses arising are known as internal (S^F), thermal (S^T), and hygroscopic (S^H), respectively. The thermal and hygroscopic stresses are often referred as hygrothermal stresses. The total stress is defined by:

$$S_{tot} = S^F \pm S^T \pm S^H \quad (1)$$

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:

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

where S is the stress (N/m²), ε the strain, ν the Poisson's ratio, E is the elastic modulus (N/m²).

When coated substrates are exposed to variations in temperature, dimensional changes are induced. If the thermal expansion coefficients of the coating (α_F^T) and the substrate (α_S^T) are different, which is usually the case, a thermal stress (S^T) will develop in the coating.

Since the thermal strain, E^T is given by:

$$E^T = (\alpha_F^T - \alpha_S^T)\Delta T \quad (3)$$

The combination of Eqs. (2) and (3) gives:

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

The stress measurement can be used to evaluate important characteristics of a coating, such as the glass transition (T_g) and the critical pigment volume concentration (CPVC).

The aim of this work is to determine the influence of the curing temperature on the intrinsic properties of the coating such as the glass transition, the development of stress during a thermal cycle, the adherence and the permeability and to link these properties to the filiform corrosion sensitivity of the studied substrate/coating system.

2. Experimental

2.1. Materials

Filiform corrosion and electrochemical impedance spectroscopy tests were carried out on the 6016 aluminium alloy. The composition of this alloy is summarized in Table 1. The test panels (100 mm × 50 mm × 1 mm) were degreased with acetone and etched for 10 min in a commercial acid bath (Henkel Ridoline® 124N + Novox Activator® 12B) at 25 °C. The samples were then rinsed with deionised water. The aluminium plates were immediately covered with a commercial anticorrosive and toxic pigment free (without lead) cathodic epoxy electrocoating (PPG industries, France). The applied voltage was determined in order to obtain a film thickness of 20 μm. The bath temperature was 30 °C. The samples were coated for 3 min, rinsed and cured in an oven for 25 min. The curing temperatures were 135, 155, 165, 175 and 185 °C.

Table 1
Chemical composition (weight%) of the AA 6016 aluminium alloy

	Weight (%)
Al	97.900
Si	1.184
Mg	0.318
Fe	0.300
Mn	0.126
Cu	0.118
...	0.054

For the stress measurements, the electrocoatings were applied on a calibrated substrate in carbon steel ($282 \text{ mm} \times 12.6 \text{ mm} \times 0.1 \text{ mm}$) degreased with acetone. To obtain a coating thickness of $15 \text{ }\mu\text{m}$, the applied voltage was 100 V and the bath temperature $30 \text{ }^\circ\text{C}$. The samples were coated for $2 \text{ min } 30 \text{ s}$, rinsed and cured at 185 , 175 , 165 , 155 and $135 \text{ }^\circ\text{C}$.

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

2.2. Filiform corrosion standard test

For the classical filiform corrosion test the panels were submitted to the ISO/DIS 4623 standard. A scratch of 40 mm length and 1 mm width was produced in longitudinal and traverse directions. Filiform corrosion was inoculated by exposure to HCl vapours for 1 h and the samples were then placed in a humidity chamber with $82 \pm 3\%$ relative humidity and $40 \pm 2 \text{ }^\circ\text{C}$. Visual observation was carried out after 1 , 3 , 7 and 21 days of exposure and the extent of filiform corrosion was quantitatively assessed by measuring the lengths and the number of filaments using a LEICA MZ12 image analyser.

2.3. EIS

2.3.1. Electrochemical measurements

EIS measurements were carried out on scratched coated samples following the procedure developed in preceding papers [12,13]. The coated samples used for this test were scratched with a cutter reaching the metallic substrate. The linear defect produced was $2 \pm 0.02 \text{ cm}$ long and $40 \text{ }\mu\text{m}$ width with an area of about 0.8 mm^2 . The scratches were performed in orthogonal direction with respect to the rolling marks.

The procedure used to initiate and propagate filiform corrosion was the same as adopted in the ISO/DIS 4623 standard but with a shorter exposure time (maximum 96 h) to humidity. The samples were analysed by EIS at room temperature in $0.1 \text{ M Na}_2\text{SO}_4$ acidified at pH 1 by adding sulphuric acid. Each measurement was repeated three times, each time using a different sample.

A conventional three-electrode cell was used for the electrochemical tests. The working electrode was the investigated sample; the exposed area was 4.5 cm^2 . The counter electrode was a platinum plate and all potentials were measured with respect to an Ag/AgCl reference electrode.

The impedance measurements were carried out over frequencies ranging from 100 kHz to 10 mHz using a 5 mV amplitude signal voltage in a Faraday cage in order to minimize external interference on the system. The impedance spectra were acquired using a frequency response detector EG&G 283 potentiostat. Both devices were computer controlled using Powersuite[®] software. The impedance data were analysed by using ZsimpWin[®] software.

2.3.2. Equivalent circuit interpretation

The equivalent circuit model used to interpret the EIS data of coatings with an artificial defect is given in Fig. 2. This circuit consists in the uncompensated electrolyte solution resis-

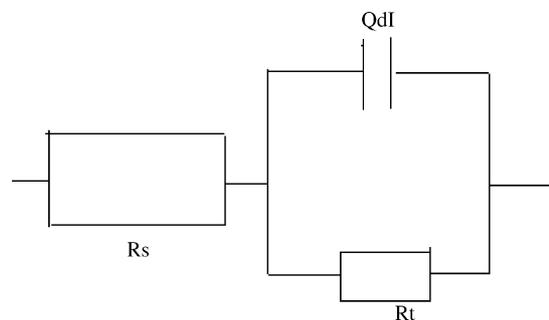


Fig. 2. Electrical equivalent circuit used to interpret the EIS data when the reactions are controlled by charge transfer.

tance between the reference and the working electrode R_s , the non-ideal double layer capacitance Q_{dl} (all the capacitances are mathematically modelled using a constant phase element) and the charge transfer resistance at the metal/electrolyte interface R_{ct} .

Q_{dl} and R_{ct} are parameters related to the delamination of the coating. Q_{dl} is proportional to the wet area or active metallic area and thus increases with filiform corrosion and disbonding of the coating. However, the accumulation of corrosion products at the interface reduces the active area resulting in the underestimation of the delaminated area. Q_{dl} and R_{ct} can only be determined when only one time constant is clearly observed in the impedance spectra. This condition can be obtained if the dissolution of corrosion products is complete. The dissolution of the corrosion products formed during exposure to humidity is possible by using an acidified electrolyte solution (Na_2SO_4). Different immersion times in the electrolyte were explored. The immersion has to be long enough to dissolve the corrosion products formed in the humidity chamber. However, too high immersion times may be accompanied by the growth of new corrosion products due to the reaction of the metal with the testing electrolyte [14].

2.4. Stress measurement

2.4.1. Method

The method used to measure the stress is based on the works by Perera and Schutyser [8–11]. He proposed to use the cantilever or beam method. It appears to be the most widely used and is suitable for determining the stress in an organic coating. 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.

A commercial equipment, the CoRI-Stressmeter can be 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 $-40 \text{ }^\circ\text{C}$ to about $200 \text{ }^\circ\text{C}$ under a variety of RH. In this work, the evolution of the stress as a function of temperature was used to determine the values of the glass transition for the different curing temperatures. For each curing temperature, the measurements were repeated three times. The stress evolution of an uncoated substrate, used as ref-

Table 2
Results of the filiform corrosion test (ISO/DIS 4623 standard)

Curing temperature (°C)	After 1 day	After 3 days	After 7 days	After 21 days
185	No degradation	Initiation of filaments	Many narrow filaments length: 1.5 mm	Many narrow filaments length: 2–3 mm
175	No degradation	Initiation of filaments	Many narrow filaments length: 1 mm	Many narrow filaments length: 2 mm
165	No degradation	Initiation of filaments	Many narrow filaments length: 1 mm	Many wide filaments length: 2–3 mm
155	No degradation	Many narrow filaments length: 1 mm	Many narrow filaments length: 2 mm	Many filaments length: 4–5 mm + disbonding over 2 mm
135	No degradation	Disbonding over 1 mm	Disbonding over 2 mm	Disbonding over 4 mm

erence, is always subtracted from data obtained with a coated one. The sample was placed in the stressmeter and submitted to the following thermal cycle: from 40 to 130 °C with a slope of 60 °C/h.

3. Results

3.1. Standard test

The ISO/DIS 4623 normalized test was performed for 21 days. The samples underwent visual and optical examinations after exposure times of 1, 3, 7, 21 days, respectively. The results obtained up to 21 days are summarized in Table 2.

After 1 day, for the five curing temperatures, the coating was intact without any visible degradation. After 3 days, for a curing temperature superior to 160 °C, some filament initiations were observed around the defect. For a curing temperature lower than 160 °C, the degradation of the substrate was more important. Indeed at 155 °C, narrow filaments were formed and at 135 °C, a delamination phenomenon was observed. For this curing temperature, the extent of disbonding increases up to 4 mm with exposure time in the climatic chamber. After 7 days, except for a coating cured at 135 °C which shows strong delamination, many narrow filaments were observed. The shortest ones were observed at 165 and 175 °C and the longest ones at 155 °C. After 21 days, the five systems are degraded. The degradation increases when the curing temperature decreases. At the lowest curing temperature (inferior to 165 °C), delamination was generally observed at the end of the normalised test. At 165 °C, the filiform corrosion is the main mechanism of degradation. However, the filaments are wider than at 175 and 185 °C. At 185 °C, the filaments are very narrow but a little longer than at 175 °C. These observations show the influence of the curing temperature on the permeability of the coating to oxygen. At 155 °C, the permeability to oxygen is probably high explaining that disbonding appears as well as filiform corrosion. Further the different filament morphologies observed for the higher curing temperatures (175 and 185 °C) could be related to a weaker permeability of the coating to oxygen allowing the development of a differential aeration cell. For a curing temperature of 135 °C the strong delamination observed can be related to a poor adherence of the coating to the substrate and to an incomplete coating cross-linkage.

Following this test, for this electrocoating applied on the 6016 aluminium alloy, the best performance was obtained with the

curing temperature of 175 °C for which the smallest filaments were observed (Fig. 3).

3.2. EIS detection of filiform corrosion

EIS measurements were used to estimate the active metallic area from the double layer capacitance values determination. Impedance data in Bode phase representation obtained for each different curing temperature are given in Fig. 4 after 4 h immersion in a sodium sulphate solution at pH 1 and for different exposure times to humidity.

For curing at 185, 175 and 165 °C, only one time constant is observed in the Bode phase representation for different exposure times to humidity. The single time constant may be assigned to the corrosion reaction of the exposed metal without accumulation of corrosion products. For curing at 155 °C, after 2 h in the humidity chamber, only one time constant is also observed. However, for longer exposures, a second time constant appears, probably related to the presence of corrosion products which could not be dissolved by the electrolyte. In this case, an exposure time in the electrolyte solution of 4 h is not sufficient to dissolve all the corrosion products.

At 135 °C, two times constants are clearly observed. The impedance diagrams are very complex due to a bad quality of the coating inherent to an incomplete reticulation and thus, at this curing temperature a physical interpretation is therefore difficult to establish.

The achievement of a single constant allows us to obtain Q_{dl} by fitting the experimental curves with the simplified electrical equivalent model (Fig. 2). The Q_{dl} values are shown in Fig. 5 as a function of exposure time to humidity.

For all the curing temperatures, an increase of Q_{dl} is observed as a function of exposure time to humidity. The highest values of Q_{dl} up to 24 h exposure are observed for samples coated at 155 °C. For exposure times longer than 24 h, it is not possible to determine Q_{dl} with the simplified electrical equivalent model. The lowest values of Q_{dl} and thus for the delaminated area are obtained with the curing temperature of 175 °C. Consequently, the quantitative data obtained with impedance measurement carried out at pH 1 follow the same sequence as that observed with the normalized filiform corrosion test.

The best sensitivity of this method is given by the results obtained after 24 h in the climatic chamber. In that case, all corrosion products are dissolved by the electrolytic solution whatever the curing temperature. After this period of exposure,

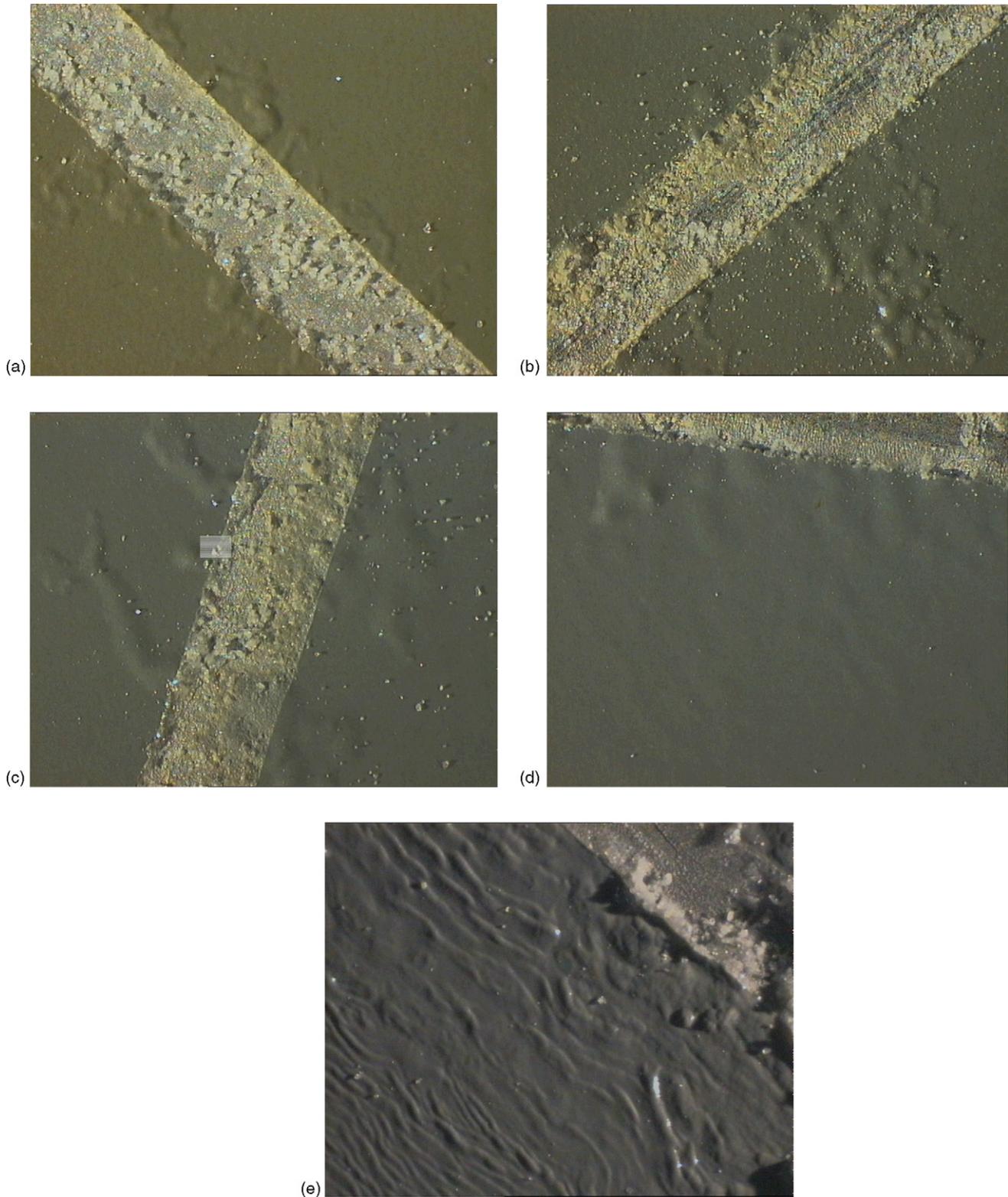


Fig. 3. Optical microscopic photographs of electrocoated aluminium 6016 samples which were subjected to a normalized filiform corrosion test, after 21 days of exposure to the humidity chamber and for different curing temperatures: 185 °C (a), 175 °C (b), 165 °C (c), 155 °C (d), 135 °C (e).

the increase of Q_{dl} observed for a curing temperature of 155 °C is high compared to the other curing temperatures, especially 175 °C. This rapid increase could account for a lower adherence of the coating to the substrate.

3.3. Stress measurement

Measurements of the stress evolution as a function of temperature were used to determine the glass transition temperatures.

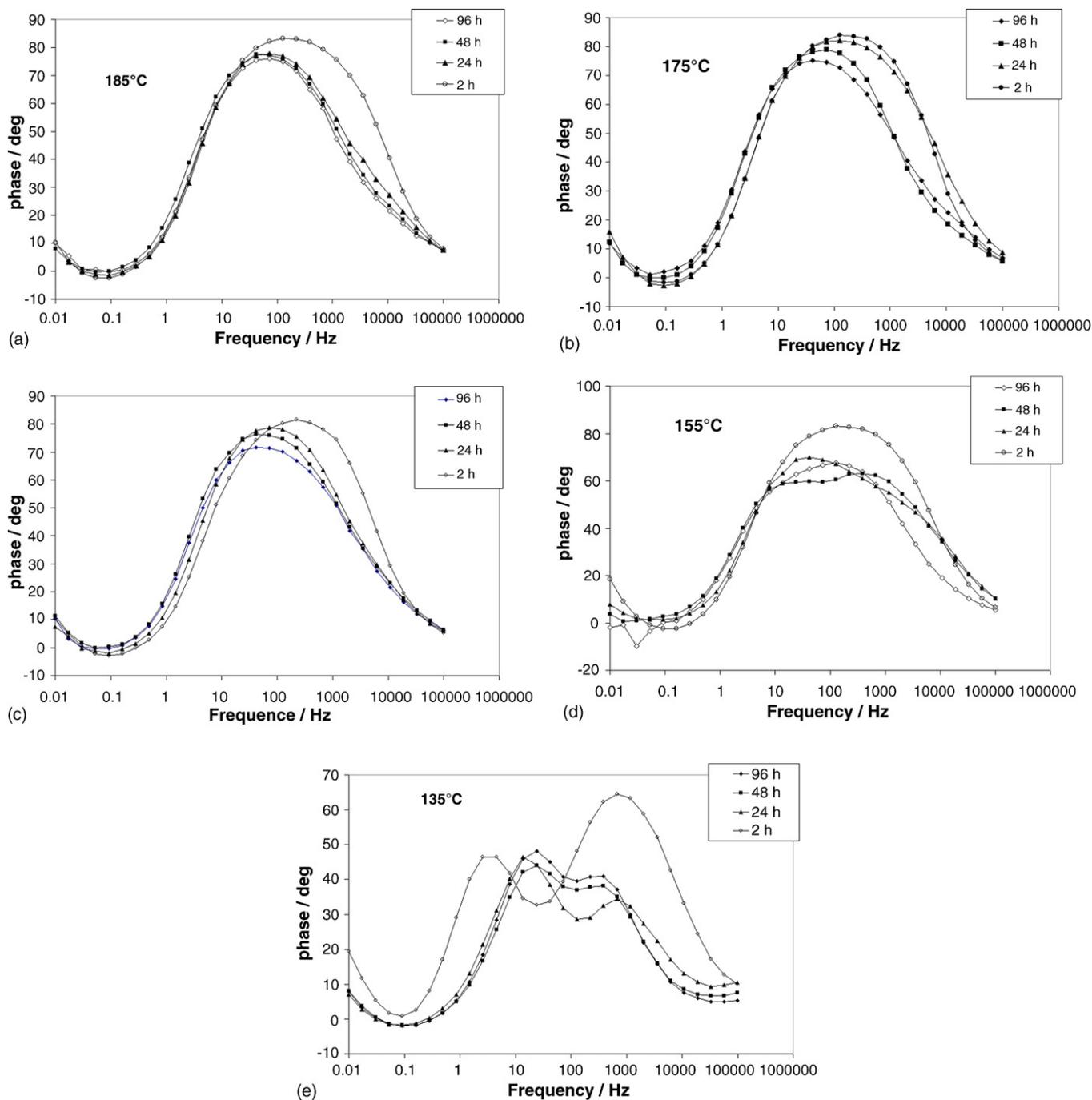


Fig. 4. EIS data in the Bode phase representation for different exposure times to humidity of scratched samples: curing temperatures of (a) 185 °C, (b) 175 °C, (c) 165 °C, (d) 155 °C, (e) 135 °C.

The coated substrates were submitted to a thermal cycle from 40 to 130 °C with a slope of 60 °C/h.

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

$$S = \frac{4d' E_s t^3}{3l^2 c(t+c)(1-\nu_s)} + \frac{4d' E_c (t+c)}{l^2 (1-\nu_c)} \quad (5)$$

where S is the stress (N/m²), d' the deflection in the middle of 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, t the thickness of the substrate (m), c the thickness of the coating (m), l is the distance between the two knives edges (m).

Eq. (5) assumes a good adhesion between the coating and the substrate, isotropic elastic properties of the coating and the substrate, the elastic limit of the substrate is not exceeded, and the stress is constant throughout the coating thickness.

The second term in Eq. (5), which contains a number of coating properties difficult to determine, can be neglected if like in that case $E_s \gg E_c$ and $t \gg c$.

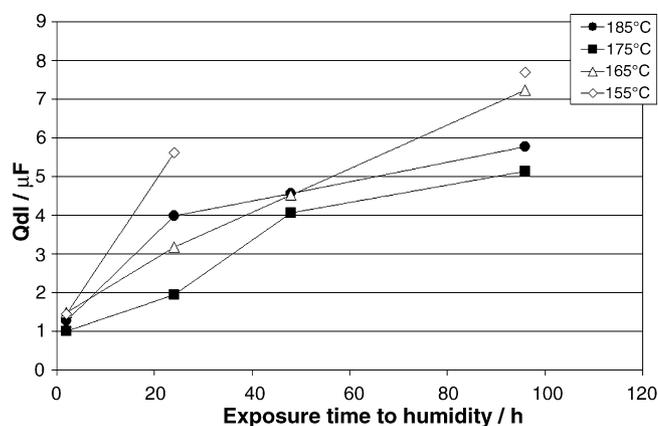


Fig. 5. Q_{dl} values as a function of the exposure time to humidity for different curing temperatures. Experimental conditions: 4 h of immersion in a sodium sulphate electrolyte solution at pH 1.

Fig. 6 giving $S=f(T)$, shows that the curing temperature affects the stress development of this coating.

In this test, each sample was submitted to the same hygroscopic and thermal conditions: relative humidity was very low and constant during the same thermal cycle. Only the conditions of film formation were modified by changing the curing temperature.

The glass transition can be determined from the interpretation of the $S=f(T)$ curves since that 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 extrapolated from the linear parts at low and high temperatures of the $S=f(T)$ curves.

At 185, 175 and 165 °C, the values of the glass transition are very close (Table 3). The lowest T_g value are obtained for the 155 °C cured samples. At 135 °C, the determination of T_g is not possible since the initial stress is close to zero from 40 to 130 °C.

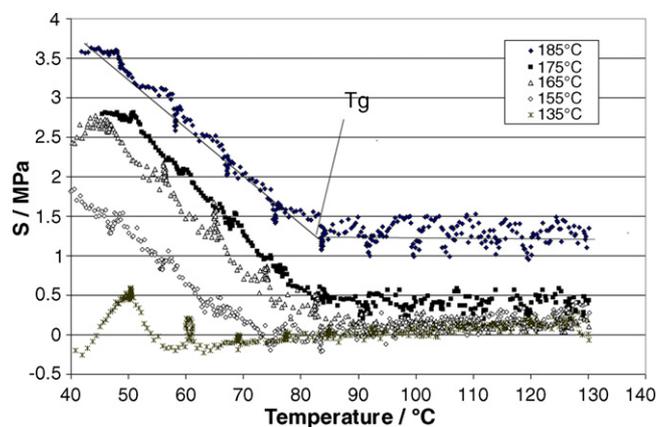


Fig. 6. Stress (MPa) dependence on temperature (°C) for the coatings cured at 185, 175, 165, 155 and 135 °C. Experimental conditions: thermal cycle from 40 to 130 °C with a slope of 60 °C/h.

Table 3

Glass transition values for different curing temperatures with a slope of thermal cycle 60 °C/h

Curing temperature (°C)	T_g (°C)
185	80.9
175	81.2
165	80.2
155	75.2

At 40 °C, which is also the temperature of the normalized filiform corrosion test, the influence of the curing temperature on thermal stress of the coating can be clearly observed. Indeed, below T_g , the thermal stress increases with the curing temperature and in agreement with the preceding results could be linked with the decrease of permeability of the organic coatings to oxygen and water and probably with an increase of the cross-linking ratio.

At curing temperatures superior to 160 °C, the thermal stress is higher and the main degradation observed on aluminium substrate is filiform corrosion. In that case, a higher stress probably corresponds to an increase of the cross-linking ratio which seems a parameter in favour of the adherence to the substrate and leading to a lower permeability of the studied system. At 185 °C, the highest internal stress and the longest filaments were observed. At 185 °C, the highest internal stress and subsequent lower permeability to O_2 could explain the higher oxygen gradient and thus the longest filaments.

At 155 °C, the thermal stress is much lower and the main degradation mechanism observed is the delamination due probably to a poor adherence of the coating to the substrate.

For $T > T_g$, a residual stress is observed for coatings cured at $T > 165$ °C. This residual stress could be related to the high cross-linkage density probably obtained for high curing temperature.

4. Conclusions

The sensitivity to filiform corrosion of a 6016 aluminium substrate covered by a cathodic electrocoating (cured at different temperatures) was studied by different methods: the ISO/DIS 4625 standard and electrochemical impedance spectroscopy.

The intrinsic properties of the coating obtained for the five curing temperatures were studied by using a stressmeter (CoRI-Stressmeter). This technique allowed us to follow the evolution of the stress at low/high temperatures and to determine the values of the glass transition temperature.

The filiform corrosion tests provide information about the adherence and the permeability of the coating to oxygen. The stress measurement technique was used to characterize the coating itself. The T_g value does not seem to be the only determining physical parameter. The best compromise between permeability and adherence seems to correspond to an optimisation of stress below T_g . For this system, this optimum is obtained at a curing temperature of 175 °C. If the stress is lower, the permeability to oxygen increases, the adherence decreases and delamination is observed. If the stress is higher, the adherence is good, the permeability to oxygen decreases and the system will be subjected to filiform corrosion rather than to delamination.

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