A R T I C L E

Materials and Corrosion

Comparative study between natural and artificial weathering of acrylic-coated steel, aluminum, and galvanized steel

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Abstract
Since testing organic coatings under natural conditions is a time-consuming process, accelerated methods are needed to produce results in less time. A simulated environment cannot fully reproduce actual operating conditions, so it is important to investigate the correlation between accelerated and natural aging test results. In this article, the natural aging of painted steel, aluminum, and hot-dip galvanized steel is studied for 1 year under continental climate conditions. The environmental parameters responsible for the change of the protective system in a continental urban environment were monitored: time of wetness, ultraviolet radiation, and temperature. The extent of deterioration is compared with similar samples weathered by accelerated testing using electrochemical impedance spectroscopy, differential scanning calorimetry, and gloss measurements. Neutral salt spray chamber, prohesion test, immersion in a quiescent salt solution, and ultraviolet B-rays (UVB) exposure test are considered. The results of the accelerated cabinet tests are discussed, and the effect is evaluated for the various coated metals. This study highlights the major problems encountered in building a model to predict durability in such a critical area as the durability of organic coatings for metal structures.

K E Y W O R D S
atmospheric corrosion, materials testing, organic coatings

1 | INTRODUCTION

Organic coatings are the most common solution for corrosion protection of metal structures in many applications, from automotive to architecture. Industry, military, and standards bodies have begun to develop specific procedures for testing and monitoring the performance of organic coatings to assess the effect, in terms of an increase in service life, of a metal structure/component. Predicting service life is still an important open question today. Since degradation is the superposition of various mechanisms and effects, a wide range of tests must be considered. Water uptake, ion migration through the paint or at the metal interface, and wet/dry adhesion are the most important factors affecting paint degradation.[1] The most reliable and effective method to assess the service life of a coating is the exposure of the specific painted substrate to the natural environment of

interest. However, this approach is time-consuming as it takes too long for the paint to fail, particularly if performance coatings are concerned. Thus, it is not suitable for industrial product research and development stages.[2] For this reason, many static and/or cyclic accelerated weathering tests have been developed to speed up the degradation process. Accelerated aging cabinets aim to simulate in days or weeks the extent of damage that, in real conditions, could occur in months or years. To be consistent with the performance in service, the accelerated aging tests should promote the same failure mechanism as experienced in real service conditions.[3] The modeling of the degradation kinetics was addressed in the last decades from different perspectives according to experimentally measurable parameters. The use of such proposed models has remained limited to specific cases, and a predictive method of general validity has not been developed yet. However, many authors have been involved in tackling this issue. Bierwagen et al.[4–6] published several studies focused on modeling the physical phenomena involved in the degradation of painted metals. They pointed out the possibility of predicting the coating's protective lifetime by interpreting the results obtained through electrochemical impedance spectroscopy (EIS) regarding electrolyte diffusion in the coating and the resulting change in its dielectric properties.

Several authors have also based their service life prediction models on optical properties such as the loss of gloss during the exposure time.[7,8] Such models are claimed to be capable of predicting natural weathering failure by extrapolating accelerated test results, but the correlation between the accelerated procedures and the actual service life is often disregarded. The limit of generalizing the results depends on the variability of the outdoor exposure conditions and the impossibility of designing a laboratory methodology able to accelerate aging without affecting the degradation mechanisms occurring in service conditions. However, some efforts to provide a quantitative estimation of the severity of the laboratory test are present in the literature. Deflorian et al.[9] estimated an acceleration time factor of 13 given by the neutral salt spray test[10] with respect to outdoor weathering located in Daytona (USA). A study devoted to evaluating the different behaviors under different accelerated procedures to face the actual decay of natural weathering is essential to handle the large variety of standard tests available.

This work considers 1 year of natural exposure to the continental climate (Trento, Italy) of painted mild steel, aluminum, and hot-dip galvanized steel for these purposes. The outdoor durability of the investigated samples is accompanied by the results of accelerated

aging tests such as neutral salt spray chamber,[10] Prohesion test,[11] and quiescent saline solution immersion.[12] The selected weathering procedures consider several stress factors, such as the electrolyte permeation in the coating, the effect of the temperature on the paint's physical properties and the electrochemical processes' kinetics, and the presence of detrimental compounds such as chlorides or sulfates. Since natural weathering is strongly influenced by solar radiation, a laboratory ultraviolet B-rays (UVB) radiation test is also included in the investigation.[13–17] The aggressiveness, acceleration, and degradation morphology of the accelerated test investigated in this work are assessed by coupling the EIS results with the visual inspection of the aged samples. EIS is a nondestructive technique capable of evaluating the corrosion protection properties,[18–21] and it is recognized to provide insights into the water uptake[22] and the electrochemical activity of the metal/polymer interface.[23] In this work, the impedance modulus at low frequencies (noted $|Z|_{0.01Hz}$) is considered a simplified representative value of the overall protection properties of the organic coating. From the single spectra analysis, it is possible to extract more precise physical quantities by the equivalent electric circuit modeling. However, frequently the high variability in the results between the samples makes it difficult to have a comprehensive approach and to distinguish between all the circuit's elements. Therefore, a simplified procedure following a widely used approach based on the impedance modulus at low frequencies could be adopted.[4,24–27] This parameter is the combination of the resistive and capacitive contributions to the electrochemical impedance, which correspond to the coating, the faradic process, and the corrosion products. Following the approach based on $|Z|_{0.01Hz}$ monitoring during the aging time, the coating could be assumed as failed when such a value is comparable with the resistance of the uncoated metallic substrate.[4–6]

This article aims to compare the aging effect of various weathering procedures on three different acrylic-coated metallic substrates (aluminum, steel, and galvanized steel). The degradation extent of the coated substrates was monitored during 1 year of outdoor exposure in a continental environment. The protective performances during the natural exposure were compared with several accelerated tests usually employed in the literature: continuous immersion in saline solution, neutral salt spray test (NSST), Prohesion test, and UVB exposure. In particular, we evaluated the potential of the different accelerated tests to simulate exposure in the natural environment. The differences and similarities between accelerated and natural weathering were assessed considering diverse physiochemical properties

instead of focusing on one single experimental technique. Thus, the aim is to compare the diverse accelerated tests and evaluate to what extent they are a reliable acceleration of the natural outdoor aging of the different painted metals. In addition, we highlighted the pros and cons of diverse experimental techniques employed for paint degradation monitoring.

Along with EIS, other techniques were employed to investigate the weathering effect on the coatings and the metal/paint interface. Physical properties such as the glass transition temperature of the coating and the optical-related loss of gloss could contribute to depicting more comprehensively the decay in the barrier effect of the polymeric layer. Using different experimental techniques to evaluate the protective properties changes, the limits and the key points of each approach can be pointed out by discussing them in relation to the specific aggressive agents at stake. In addition, a visual inspection was carried out (the transparency of the acrylic-based varnish permits the observation of the metal surface) to investigate the corrosion morphology development and loss of adhesion. Despite the well-known issues arising when seeking for correlation between natural weathering and laboratory cabinet tests, the results collected in the present work contribute to the identification of the most suitable accelerated test to carry out to trigger the same failure mechanism as that occurring during outdoor exposure. In addition, the different aging kinetics of the accelerated weathering test compared with the outdoor scenario are discussed.

2 | MATERIALS AND METHODS/ EXPERIMENTAL

Three different metal substrates coated with the same commercial two-component polyamide-based clearcoat (supplied by Palini Vernici) were tested: aluminum (Q-Panel AQ 5005 H14), mild steel (Q-Panel R-36), and hot-dip galvanized steel with a 15 μm thick zinc coating (HDG, supplied by Liberty Steel Italy). For HDG sheets, energy dispersion X-ray spectroscopy (EDXS) revealed the content of a small amount of Al (0.26 wt.%) in the zinc layer, a typical composition of the HDG zinc layer applied in a continuous coil coating plant. The base metal for HDG is DX51D low carbon steel EN10346:2015 (C max. 0.18 wt.%; Mn max. 1.2 wt.%; Si max. 0.5 wt.%; P max. 0.12 wt.%; and Fe. bal.) A clearcoat was chosen due to the need to visually inspect the corrosion evolution at the metal–paint interface. The metallic substrates were degreased and pickled before applying the liquid varnish using an Elcometer 4340 motorized film applicator. After curing for 1 h at 60°C, a dry thickness of about 75 μm is

obtained. The organic layer is characterized by a glass transition temperature of 46°C. Ten samples of the different metallic substrates were exposed in an outdoor site located in Trento-Italy (46°4′1.13″ N, 11°9′18.11″ E), which is classified as "C2" (low aggressivity impact) in the corrosive classes following the ISO 12944-1 standard.[28] The most relevant meteorological data were collected during 1 year (starting from March 2021). EIS measurements were performed on each specimen once a month. In the meantime, identical samples (three coated panels for each type and test) were exposed to two cabinet tests such as NSST[10] and Prohesion test,[11] and immersed in a quiescent saline solution (0.5 M NaCl) at room temperature.[12] NSST is the most common continuous cabinet test: it involves using a 5 wt.% sodium chloride solution atomized to create a saltwater mist at 100% relative humidity and 35°C. The Prohesion test is a wet/dry cyclic test consisting of 1 h of exposure to a continuous indirect fog of a dilute solution (0.05 wt.% NaCl, 0.35 wt.% $(NH_4)_2SO_2$) followed by 1 h of drying at a chamber temperature of 35°C. It is recognized to reproduce a typical industrial environment. Furthermore, the coated panels were tested through ultraviolet lamp exposure in the UVB range.[29] The extent of degradation of the organic layer was assessed by differential scanning calorimetry (DSC) on a Mettler DSC 30 apparatus from 0°C to 200°C with a constant heating rate. The variation of the glass transition temperature and the loss of gloss at 60° during the laboratory aging and natural sunlight were investigated (utilizing a Glossmeter NL3A Co.Fo.Me.Gra).

EIS raw datasets were periodically collected using an Autolab PGSTAT302N potentiostat. The spectra were collected at room temperature in a 0.5 M NaCl aqueous solution (quasi-neutral pH 6.2), applying an amplitude of the signal of 15 mV in a frequency range varying from 100 kHz to 10 mHz. An electrochemical cell equipped with a platinum counter electrode and an Ag/AgCl/3.5 M KCl reference electrode is used, having a circular testing area of 25 cm^2.

The impedance modulus |Z| in the low frequencies range (10^{-2} Hz) was obtained from EIS raw data sets and referred to as $|Z|_{0.01 Hz}$ throughout the manuscript. The evolution with time of $|Z|_{0.01 Hz}$ for the samples exposed to the different environments was compared regarding the decrease in protection properties and the degradation morphology.

Paint adhesion strength to the metal substrate in dry conditions was assessed by the pull-off test[30] on the samples before and after the 1 year of natural aging. This standard technological procedure is necessary to verify the actual interface bonding condition regardless of the impedance response and visual appearance. Indeed, the

impedance modulus does not necessarily correspond to a good adhesion despite it being an index of the overall degradation of the system.[25] High $|Z|_{0.01Hz}$ may be measured for highly durable and thick coatings, while rust is already developed at the metal–paint interface and the residual adhesion is minimal.

3 | RESULTS

The meteorological data collected during 1 year of outdoor exposure are presented in Figure 1. Starting from March 1, 2021, the samples experienced about 2000 h of relative humidity (Figure 1a) over the threshold of 80% taken as the cumulative time of wetness (ToW) during 1 year.[9] The duration of the cabinet accelerated test was determined by the time to failure of the coating system, assessed both from visual inspection and EIS: 2000 h for NSST and immersion, and about 3000 h of Prohesion test. The ToW experienced during 1 year of natural exposure turns out to be comparable with the cumulative amount provided during the cabinet test

(notice that the prohesion test cycles between dry and wet stages). However, there is no intention to assume any correlation in weathering time between the cabinet test and/or the weathering in the continental environment since they involve the very different presence of aggressive species and aging factors. The observation of the degradation kinetics between different weathering tests could be interesting anyway since industries commonly adopt cabinet aging for general quality control purposes regardless of the final service environment.

Regarding outdoor exposure of paints, UV radiance is considered by far the most detrimental component of the entire solar spectrum. The infrared portion of the light plays a role in terms of the temperature increase of the panel, but it hardly modifies the acrylic layer chemically or morphologically due to the energetical content.[27] The two main components of the UV portion (UVA and UVB) of the ultraviolet spectrum are collected separately to discriminate the different contributions to the organic coatings' aging and set up the corresponding accelerated aging test (Figure 1c). Figure 1b shows the rear-panel temperature during the exposure time of the three
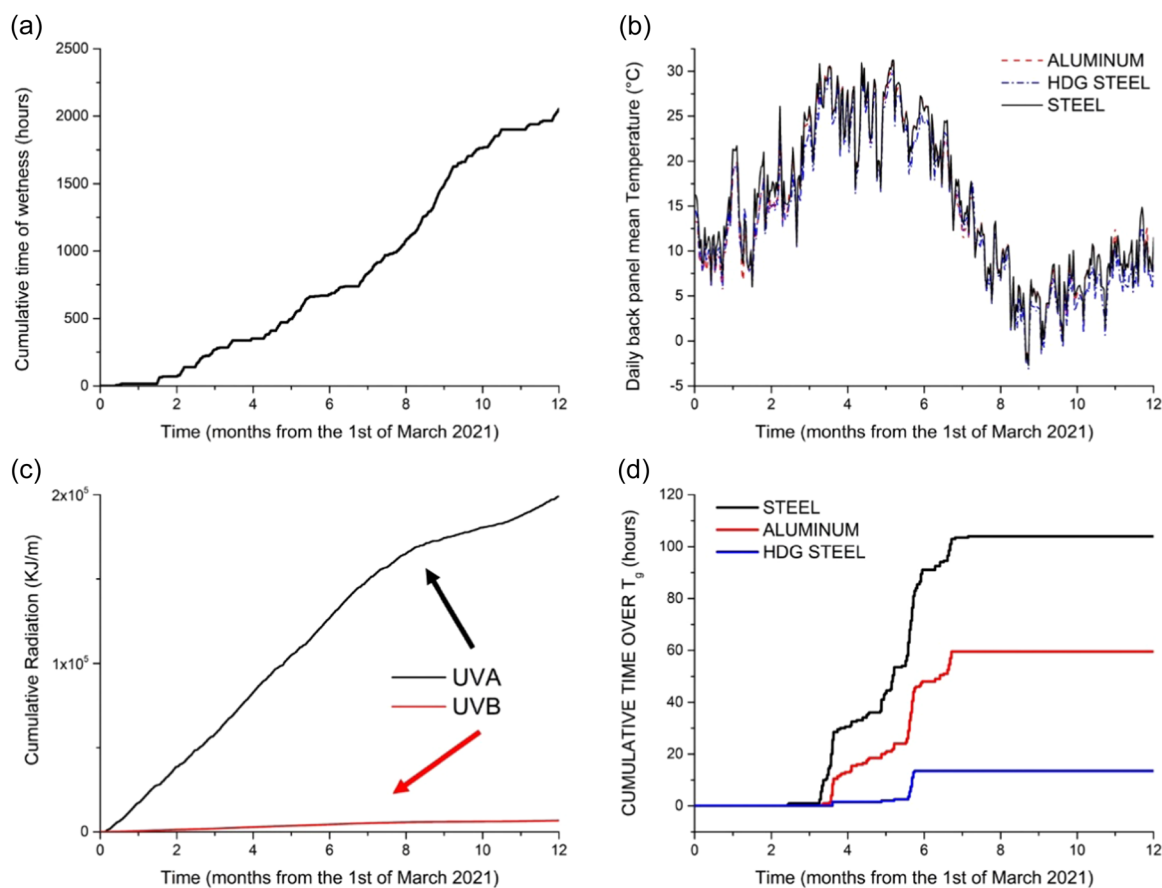

FIGURE 1 Meteorological data collected for 1 year from March 1, 2021 in Trento (Italy). [Color figure can be viewed at wileyonlinelibrary.com]

different coated substrates. It can be observed that the rear panel temperature differs from one substrate to another. Since the coating is a varnish, the base metal brightness influences the light absorbed. In Figure 1d, the cumulative time experienced by the rear-panel temperature over the threshold of paint glass transition temperature is reported. For the given pristine acrylic paint, the T_g is measured to be 46°C by differential scanning calorimetry. The investigated painted substrates show a significantly different behavior, particularly during summer (the solar radiation is less intense in the rest of the year, not to overcome the T_g value). The role of solar radiation and the associated overcuring effect on the polymeric matrix of the paint is investigated by differential scanning calorimetry. The comparison between the glass transition temperature of the coating before and after 1 year of natural weathering is presented in Figure 2. The results obtained are very similar, regardless of the substrate ($T_g = 50$–52°C). The T_g shows increases with respect to the initial value (unexposed, $T_g = 46$°C). This drop is noticeable, but no clear correlation between the rear-panel temperature and the effect on the glass transition temperature is observed. It could be possible that some differences between the various samples will be visible after longer weathering periods or this effect could be hidden by the overwhelming UV radiation. Figure 2 also compares the effects of natural sunlight exposure and accelerated UVB radiation tests. The coated samples were exposed under a constant power of 5 W/m^2 for 300 h in a QUV testing chamber. In such configurations, the total UVB radiation (J/m^2) received by the samples in the accelerated test is comparable with the cumulative amount collected during the year of natural exposure (Figure 1c). The
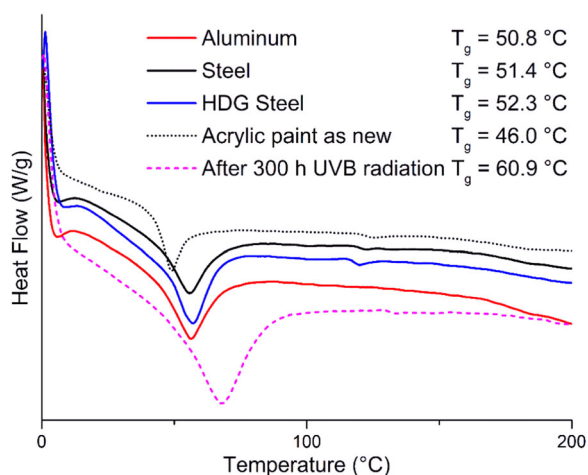
UVB intensity in the UV test chamber is remarkably increased concerning the average value provided by the natural sunlight. The results are similar regardless of the substrate (only one curve is reported as representative of all three coated substrates). In the end, a significant increase in the glass transition temperature to about 61°C is observed, markedly higher than the T_g measured after 1 year of natural aging. Those findings suggest that although the accelerated UV aging test provides an identical amount of specific power per unit of surface, it does not reproduce a degradation extent comparable to 1 year of outdoor weathering.

Figure 3 shows the outcomes based on gloss loss evaluated at 60° of incident light. A progressive decrease of gloss is observed for the samples exposed outdoors (sharp decrease in correspondence of the summertime). The most significant drops are experienced by coatings applied on steel and HDG steel substrates. It can be noted that the higher measured panel temperature corresponds to a deeper drop in gloss over time. Such a reasonable correlation is related to the larger portions of absorbed radiation in the case of darker samples which keep the coated panels at higher temperatures. Since the gloss is related to the surface roughness, its change is probably related to an increase in the surface profile unevenness.[31,32] Different mechanical internal stresses derived from temperature cycles experienced could lead to a slightly different magnitude of coating alteration appreciable by 60° glossmeter employment.[33–35]

In comparison, also the total gloss loss measured after the UVB accelerated test is reported in the graph as dashed horizontal lines. Note that the gloss loss after 300 h under UVB is lower compared with the effect of 1 year of natural exposure. This might suggest that gloss
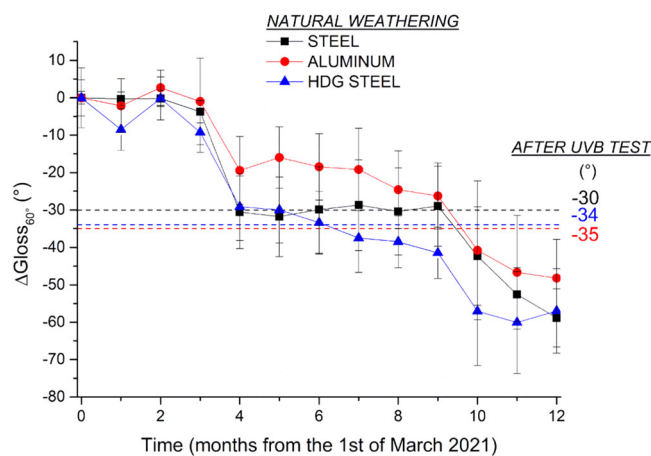

FIGURE 2 Comparison between DSC analysis of paints aged on different substrates before and after weathering. [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 3 Decrease in gloss at 60° during outdoor exposure and after 300 h of UVB test at 5 W/m^2 (dashed lines). [Color figure can be viewed at wileyonlinelibrary.com]

modification is influenced by additional factors such as water absorption, temperature cycling, or contaminants.[36] Accordingly, the correlation between the service life in outdoor exposure with the accelerated test cannot be based only on the durability against light radiation but should include a more comprehensive set of physiochemical stresses.

The EIS spectra were collected for each sample once a month during the outdoor exposure period of 1 year. Figure 4 shows an example of Bode plot evolution in weathering time for the three types of coated substrates. It can be noted that all the specimens experience a well-defined capacitive behavior before aging; after 6 months, the response is clearly changed to a resistive behavior in the low-medium frequencies range (10^{-2}–10^3 Hz), especially for coated steel and HDG steel. At the same time, the phase angle shifts from the almost pure capacitor value of $-90°$ to the rise of several time constants, testifying to the corrosion-increasing activity in the electrochemical system. On the other hand, the modulus value at 10^{-2} Hz ($|Z|_{0.01Hz}$) drops significantly in time for all the samples; its average over the 10 monitored specimens was reported with time for all the substates in Figure 5a. A decrease in $|Z|_{0.01Hz}$ with time is observed

for all the samples, regardless of the type of substrate. However, diverse degradation rates were observed. For steel and aluminum, a decay of one order of magnitude occurs. For the galvanized samples, the initial decrease in $|Z|_{0.01Hz}$ is recovered, likely due to the formation of zinc corrosion products that could act as a defect sealant in the early stages of degradation.[37] Painted aluminum shows better corrosion resistance regardless of the aging test performed, likely due to its passive behavior in a neutral environment, which is the case for all the exposure environments considered in this study. The annual visual inspection of the coated panels shows the absence of any corrosion products at the metal–paint interface despite the drop in the protective performance detected by EIS (Figure 5b–d).

In both the cabinet tests, despite the stable behavior of $|Z|_{0.01Hz}$ of the painted aluminum samples, both steel and HDG steel show a marked decrease in impedance modulus (Figures 6a and 7a) approaching the last 500 h of aging. This is a noticeable discrepancy compared with what is observed during natural exposure; the trend seen in the cabinet tests is characterized by a steep drop in $|Z|_{0.01Hz}$ while the effect of the outdoor aging is smoother. Examples of Bode plots evolution during cabinet tests is
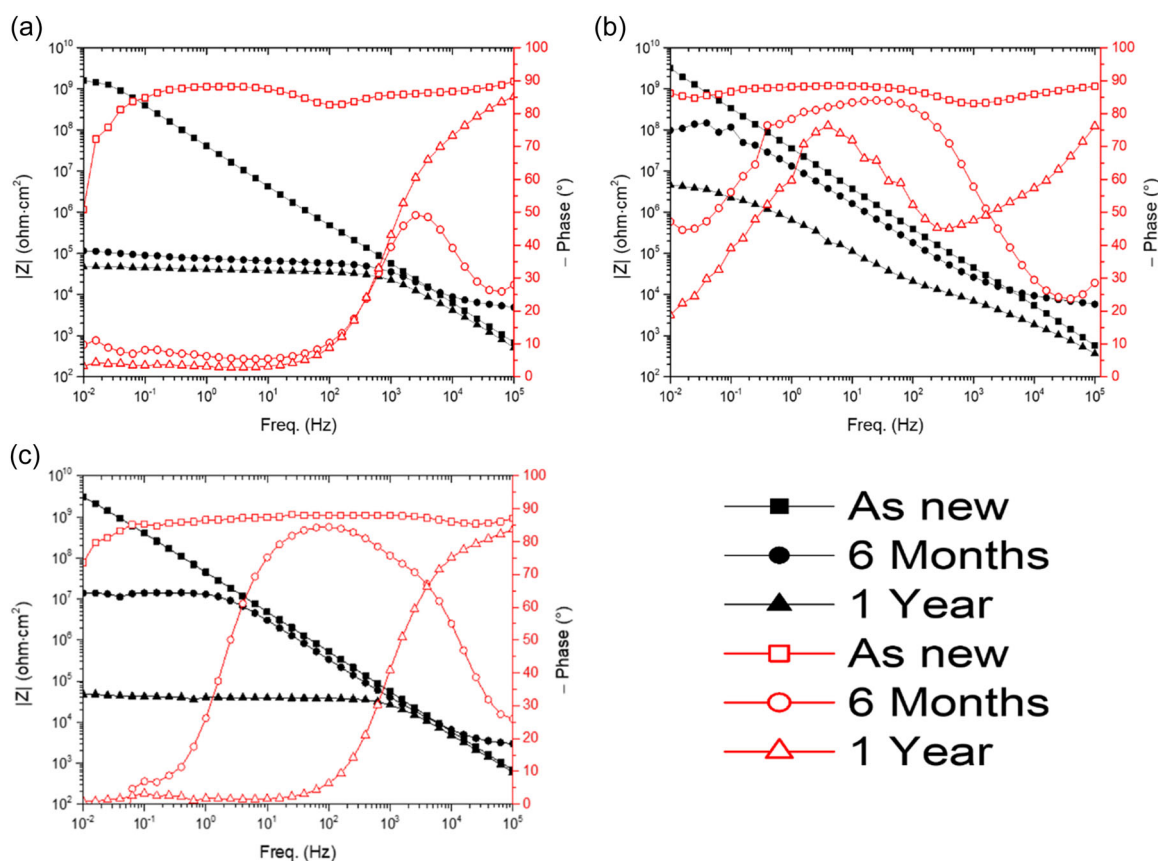

FIGURE 4 Example of electrochemical impedance spectroscopy (EIS) spectra evolution during natural weathering for three acrylic-coated samples: steel (a), aluminum (b), and hot dip galvanized (c). [Color figure can be viewed at wileyonlinelibrary.com]
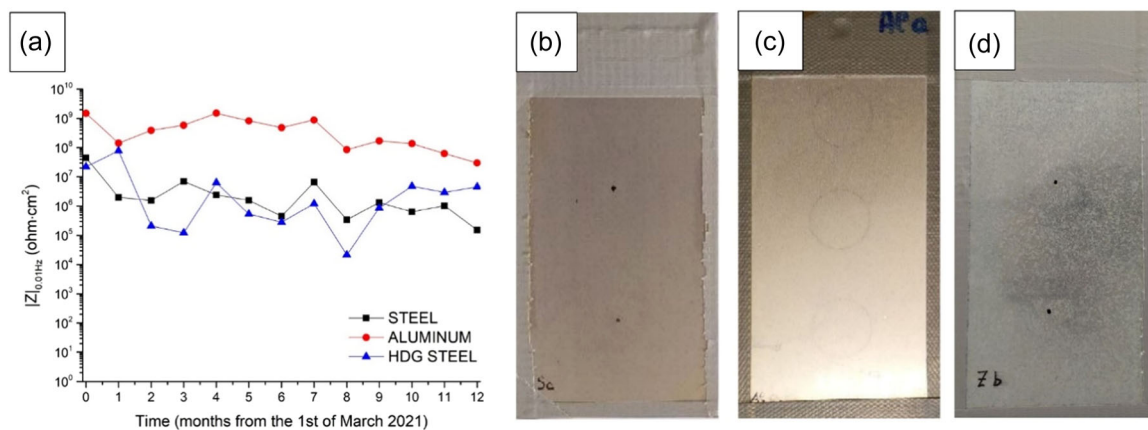
FIGURE 5 Normalized impedance modulus at low frequencies during 1 year of outdoor exposure (a) and visual appearance of the acrylic-coated samples after 1 year of natural weathering for steel (b), aluminum (c), and HDG steel (d). [Color figure can be viewed at wileyonlinelibrary.com]
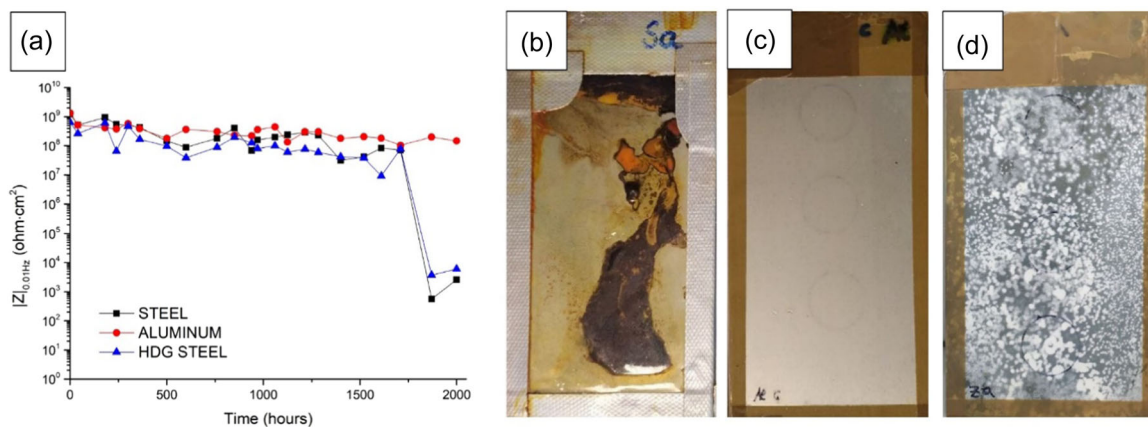

FIGURE 6 Normalized impedance modulus at low frequencies during 2000 h of neutral salt spray test (NSST) (a) and visual appearance of the acrylic-coated samples at the end of the aging test for steel (b), aluminum (c), and HDG steel (d). [Color figure can be viewed at wileyonlinelibrary.com]
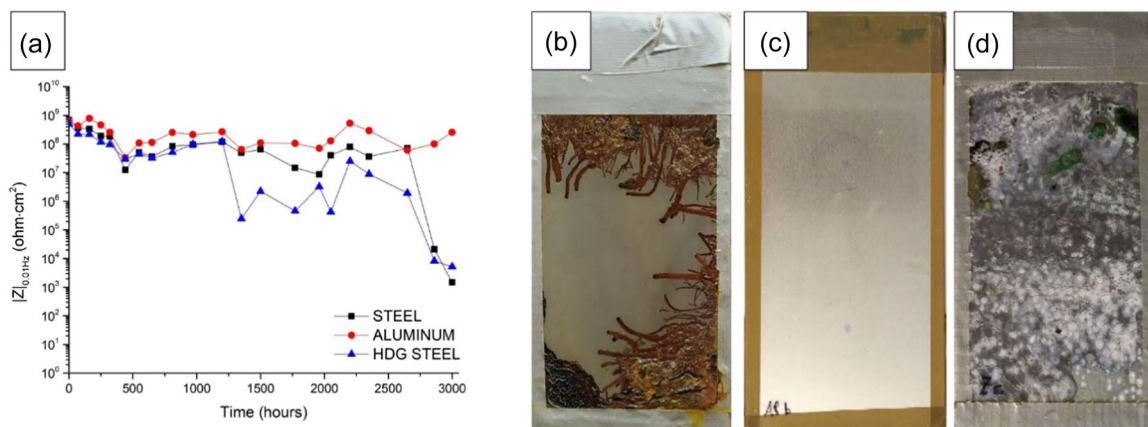

FIGURE 7 Normalized impedance modulus at low frequencies during 3000 h of prohesion test (a) and visual appearance of the acrylic-coated samples at the end of the aging test for steel (b), aluminum (c), and HDG steel (d). [Color figure can be viewed at wileyonlinelibrary.com]

included in the Supporting Information Section (Supporting Information: Figures S1 and S2). The sharp loss of protection observed by EIS could correspond to the formation of a macro defect in the coating due to the accumulation of corrosion products at the metal/polymer interface and their volumetric expansion. This hypothesis is supported by the abundant presence of corrosion products underneath the paint observed for the steel test and the HDG steel samples after about 2000 h of exposure both in the NSST (Figure 6b,d) and at the end of the Prohesion test chamber (Figure 7b,d). On the other hand, no corrosion products are visible in the naturally aged samples at this point, and no damage caused by the corrosion product formation is found. The presence of aggressive ions in the cabinet test atmosphere leads to more corrosion product formation at the metal–paint interface until the coating is damaged and the sheltering effect fails. Given the amphoteric behavior of aluminum,[38] the neutrality of the environments taken into account does not lead to the oxidized compounds over its surface, preventing the coating from a manifest detachment.

Immersion in the quiescent electrolyte (Figure 8) turns out not to significantly accelerate the degradation rate, at least based on the coating features detectable by EIS, since the average impedance moduli do not show any significant change during 2000 h. In this case, despite the presence of chlorides, and the constant contact with the electrolyte, the procedure seems not so detrimental compared with the cabinet test atmosphere. The coating system behavior is steadily capacitive during the testing period and it is barely noticed a change in the impedance spectra at the end of the test (Supporting Information: Figure S3).
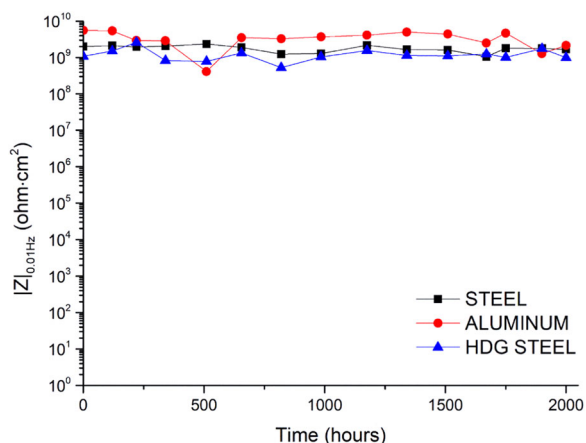
Beyond the EIS results, which could be a black box analysis,[39] a visual inspection of the corrosion morphology deposits shows a different damage mechanism between the different experiments.

From the simulation accuracy point of view, the observation does not provide encouraging information because different tests lead to various corrosion morphology and, therefore, different degradation mechanisms. The cabinet environment should not decouple some weathering stresses that are proven to act synergistically. Humidity, solar radiation, and temperature effects are shown to be strongly related. The procedures have to be cycled by mixing all these contributions to trigger the correct failure mechanism to be investigated. In the case of the Prohesion test, the cyclicity between dry and wet conditions turned out to be not a speed-up factor, but it results to be less aggressive than the NSST where the fog continuously stresses the coating system.

After 1 year of natural exposure, there are no signs of corrosion product at the interface. By visual inspection, coatings seem to be protective. However, evaluating the residual adhesion strength by the pull-off test, it was found that the paint is no longer well bonded to the substrate. In Figure 9, a substantial decrease in adhesion strength is shown by comparing the new samples with those aged outdoors for 1 year. The most severe effect is observed for the HDG steel substrate, for which the residual coating adhesion is near zero. Nevertheless, the corrosion is not yet flared up thanks to the barrier effect of the coating, but the system is very vulnerable, and if a defect in the organic layer forms, the low adhesion will rapidly trigger a significant corrosion expansion over the entire substrate. Dry adhesion performance was not
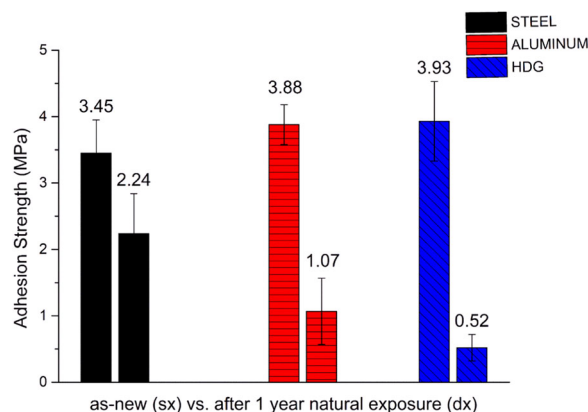

FIGURE 8 Normalized impedance modulus at low frequencies during 2000 h of quiescent immersion. [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 9 Comparison of dry adhesion assessed by pull-off test before (on the left) and after 1-year natural weathering (on the right) for three different metal substrate painted samples. [Color figure can be viewed at wileyonlinelibrary.com]

assessed on the samples in accelerated aging conditions due to the abundance of corrosion products deposited at the interface, damaging the substrate and the organic layer itself. In such conditions, the pull-off test cannot be performed, and the paint adhesion is considered null.

4 | DISCUSSION

The study considered five weathering tests (four accelerated aging tests and 1 year of outdoor exposure). The experiments revealed that none of the accelerated cabinet tests seemed suitable for correctly simulating natural exposure. After 1 year of natural aging, despite the unchanged visual appearance of the samples and no clear signs of corrosion, the evaluation of the residual adhesion revealed the complete failure of the metal/paint interface. This destructive test provided a straightforward indication of the damages caused by the atmospheric agents, significantly better than what gloss measurement and EIS (decrease in impedance modulus in the low-frequency range) did. Differently, cabinet tests promoted the formation of a high quantity of corrosion products at the interface in the case of steel and HDG steel. Concerning aluminum, no significant formation of corrosion products was observed along with relatively stable values of the impedance modulus during time (Figures 4 and 5). However, pull-off findings also revealed the failure of the metal/paint interface in this case. Accordingly, it seems that the nondestructive techniques employed to assess the degradation extent of the painted systems can lead to misleading conclusions.

The gloss measurements seem to be able to highlight changes in the appearance of the paint surface even for a relatively short exposure time (1 year) in a mild outdoor environment (C2). The interaction between the paint surface and the light affects the gloss value as it affects the surface roughness. The higher the roughness, the lower the gloss level is.[32] Roughness increase affects the esthetic appearance and the temperature rising during sunlight exposure, thus influencing the stability of the polymeric matrix.[32,36,40,41] Hence gloss detection seems to be a useful technique to check slight changes in the coating system and seems particularly suitable to assess the evolution of the surface morphology of paints quickly. However, a straightforward relationship between the gloss changes and the durability of the paint was not found.

As far as EIS is concerned, although this technique is often employed to monitor the degradation of organic coatings exposed in accelerated aging cabinets and outdoors, it has not been revealed to provide a reliable

description of the degradation extent occurring on the investigated samples. The paint's high dielectric and barrier properties might likely have shielded the breakdown of the polymer/metal interface[39] when the coated panels are exposed in the accelerated aging cabinets. In fact, we recorded relatively high electrochemical impedance values (Figures 6 and 7) even in the presence of a significant accumulation of corrosion products at the metal/polymer interface. Exposure to UVB lamps affected the polymeric matrix differently than the in-field exposure, even if the cumulative amount of UVB radiation in (J/m^2) was the same. The effect of the UVB exposure test on the thermal properties of the polymer was more pronounced than when the samples are exposed to natural radiation. However, it has to be underlined that in this case, the weathering mechanism (i.e., overcuring of the polymer, which increases T_g) induced by the laboratory scale test and outdoor exposure is the same.

It is very complex to characterize the protection performances of a coating system completely, and even more ambitious is to deal with the kinetics of degradation. The accelerated tests investigated in this study are suitable for comparing different samples in a relatively short time, but they fail to simulate a natural outdoor environment. The tests and analysis choice should be tailored to the service environment.

5 | CONCLUSIONS

The study considered five weathering tests (four accelerated aging tests and 1 year of outdoor exposure) performed on three different metal substrates (mild steel, aluminum, zinc). The simulation of the outdoor environment as the sum of different weathering stresses (ToW, UVB, etc.) leads to misleading results. Similarly, the findings of the present work highlight the limits of using a single parameter (EIS modulus, gloss, T_g, etc.) to monitor the degradation of the painted substrates. Cabinet tests lead to an abundant formation of corrosion products that do not occur in natural weathering, so they do not trigger the same mechanisms as natural agents. On the other hand, the UVB test stresses the system in the same way by paint overcuring, but the magnitude of changes in glass transition temperature is not matched, despite the higher intensity of radiation in the laboratory test, it turns out to be lower.

The adhesion test turned out to be the most reliable tool to assess the residual protection provided by the paint since it highlights the drop in such crucial properties even in the absence of corrosion products. Loss of gloss is sensitive to very slight chemical and

morphological changes in the polymeric layer, but any straightforward relationship was found with the metal–paint interface evolution. For this purpose, EIS could be exploited to better understand the electrochemical activity underpaint. However, in this case, the interfacial contributions were shielded by the high dielectric and barrier properties of the coating.

CONFLICT OF INTEREST STATEMENT
The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION
Additional supporting information can be found online in the Supporting Information section at the end of this article.