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ORIGINAL PAPER

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Impedance-based sensing of the interlayer adhesion loss in organic coating systems

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Abstract The detrimental effects of environmental conditions on the protective organic systems on the metals are well known. Variable parameters like temperature, humidity and UV radiation influence the protective properties of coatings on metals. Adhesion of coatings to the substrate and the interlayer adhesion between separate coating layers are main parameters describing the protective properties of coating systems. Traditional methods of evaluation are destructive and do not allow the monitoring of such influences. By using conductive electrodes between the layers of protective coating system and electrochemical impedance spectroscopy (EIS) method, it is possible to detect the changes caused by adhesive debonding and accumulation of water at the interface. Large changes in the impedance values were observed when humidity and temperature conditions were changed. A new approach to continuous monitoring and quantification of adhesion changes at real conditions using EIS was proposed. Examples of monitoring data during laboratory temperature cycling and during real outdoor exposure were shown.

Keywords Corrosion protection · Organic coatings · Adhesion · EIS

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Introduction

Generally, corrosion-related damages are recorded late, mostly when they become obvious. This usually leads to expensive replacements or unexpected failures. Early detection of material degradation enables easier repair with lower costs. Especially, monitoring of protection degree in remote or inaccessible regions of engineering structures represents a desirable challenge. Use of sensors can allow monitoring of critical parameters of coating system in situ [1, 2]. By combining data from sensor with laboratory evaluations of the protective system, a criteria can be established for the performance in service. High-performance coating systems are not immune to the effects of environment. They can adsorb moisture and deteriorate with UV exposure and climatic changes [3]. This can cause degradation of polymer. Typically, modern coating systems are multi-layer and especially interfaces between coating layers are susceptible to adhesion loss.

In the present work the sensor has been evaluated for integrity of interlayer adhesion in laboratory and outdoor conditions.

Experimental

A high-performance coating systems used in automotive applications were studied. The automotive waterborne polyurethane base- and clearcoat on steel panels at the thickness of 25 and 30 μm, respectively, were tested. Two <10 μm thick, 3 mm wide and 8-cm-long stripes of the conductive ink (Orgacon, E1-P1030, Agfa-Gevaert, Belgium) were applied on the primer layer 1 cm apart from each other and then overcoated with a topcoat and used as sensor electrodes in impedance measurements, Fig. 1.

The impedance measurement was made in two electrode arrangement, using a frequency response analyzer Solartron 1255 connected to High Impedance Interface

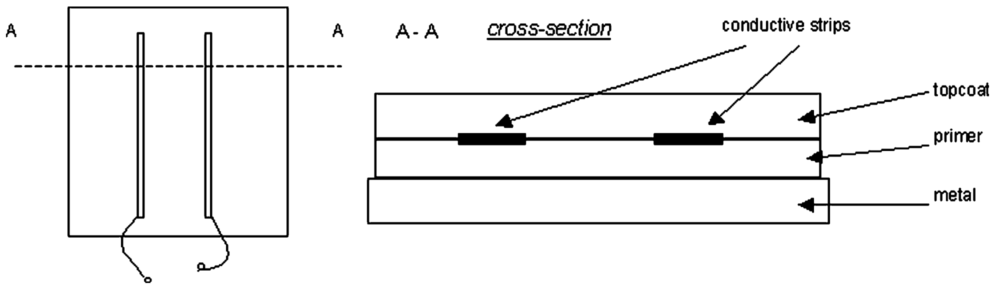

Fig. 1 Schematic presentation of electrode arrangement for interlayer impedance measurements

Atlas 9181. The impedance measurements were carried out on 10 points/decade over a frequency range from 1 MHz to 0.1 Hz and 5 points/decade over the range from 0.1 Hz to 0.001 Hz with 10–60 mV signal amplitude peak.

Coated panels were exposed to an atmospheric environment in marine-urban (Gdansk) climate and in laboratory conditions using special arrangement (Fig. 2). Electrochemical impedance spectroscopy (EIS) measurements were carried out on samples exposed to a defined relative humidity (rh), adjusted by using saturated salt solutions such as potassium carbonate (43% rh), potassium chloride (84% rh) and potassium sulphate (97% rh) [4–6]. Impedance spectra were recorded in stationary conditions, usually 4–5 h after exposure to parameter change. The stationarity was controlled by the comparison of impedance spectra measured before proper measurement. Presented impedance spectra were measured after ca. half an hour after spectrum stabilization. For the temperature variations of the sample, a programmed PID heating device was used. The glass transition temperature (T_g) of tested coating system was about 94–98°C determined by DMTA measurements using Perkin-Elmer DMA-7e apparatus. This means that all impedance measurements were conducted at the temperatures below T_g.

Results and discussion

Generally, impedance spectra measured between embedded electrodes depend on temperature and humidity conditions of the exposure environment. Figure 3 shows exemplary impedance spectra recorded in laboratory at the temperature of 40°C (Fig. 3a) and 60°C (Fig. 3b), and at the relative humidity of 43, 84 and 97% measured in stationary conditions. This behaviour can be associated with the water ingress into the coating and especially into the interlayer region as well as a build-up of the water conductive paths between electrodes along the interlayer region. This is confirmed by the comparison of impedance spectra measured between steel substrate, embedded electrodes and additional electrode applied on the clearcoat surface [7]. The ionic mobility in an interlayer region depends on the attractive forces between the layers. In a

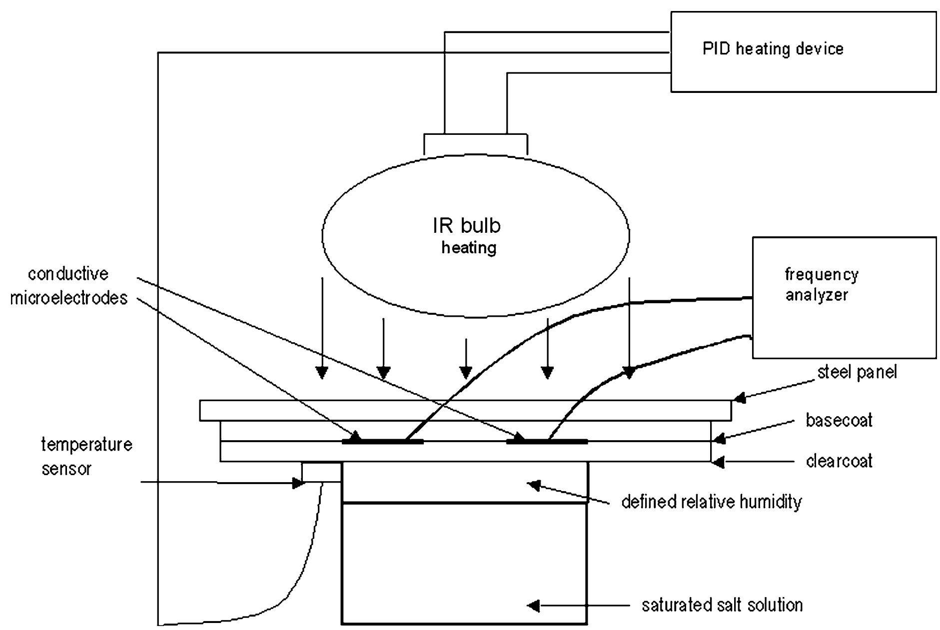

Fig. 2 Diagram of an experimental set-up to determine an impedance with humidity and temperature

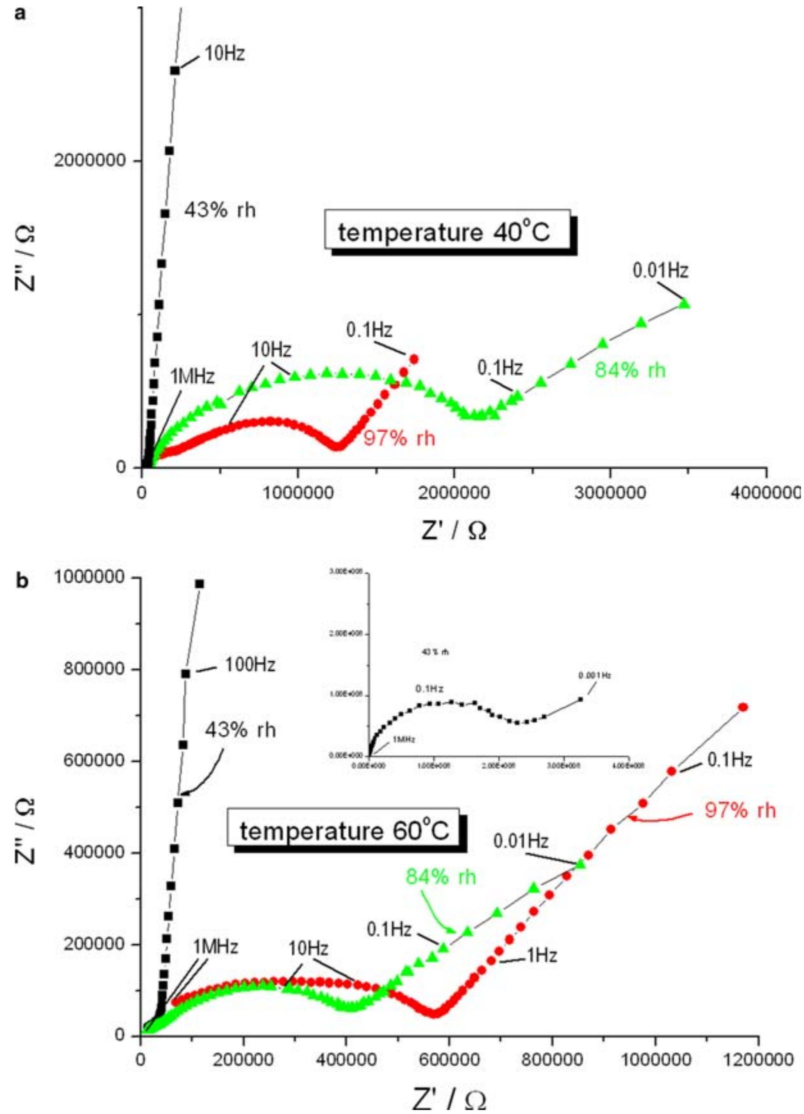

Fig. 3 Impedance spectra for the interlayer region at the temperature of 40°C **a** and 60°C **b** and at different relative humidity measured in stationary conditions (4–5 h after exposure parameter change)

strong field of the high attractive forces between the layers (good adhesion), the ionic mobility will be smaller as in a weak field of the attractive forces (poor adhesion). In order to obtain the temperature dependence of the impedance, the measurements were made at the temperature of 30, 35, 40, 45, 50, 55 and 60°C by rh of 43, 84 and 97%. The semicircle diameters are plotted in Fig. 4 as a function of $1/T$, where T is an absolute temperature (Arrhenius plot). The slopes of the plots relate to the activation energy of the ionic mobility. Therefore, the activation energy can be taken as a criterion for the quantification of an interlayer adhesion. In order to demonstrate that this criterion is valid, a comparison between obtained results and results of traditional destructive adhesion measurement suitable to measure interlayer adhesion named ‘‘blister test’’ was made [7]. A good correlation was found between impedance and blister test data [7].

By using a new developed technique, it is possible to continuously monitor the influence of variable environmental parameters on the adhesion strength during, e.g., atmospheric exposure. The absence of water at the interlayer region would assure that no bond degradation occurs from environmental attack. Figure 5 shows the changes of a real part of the impedance at the frequency of 10 kHz during a sinusoidal temperature cycling between 32 and 77°C by rh of 43%. From this plot, the interdependence between the measured real part of the impedance and the temperature of the surrounding environment is evident.

In Fig. 6a the Arrhenius plots for the separate temperature cycles are given. To make the procedure as simple as possible, the data refer to a maximum and a minimum temperature of 77 and 32°C, respectively, and to one frequency. Following the changes of $\Delta R_{10\ kHz}$ in the course of cycling, the easy quantification and monitoring of the interlayer adhesion of coatings is possible (Fig. 6b).

The same procedure was applied to the sample exposed in atmospheric conditions employing natural

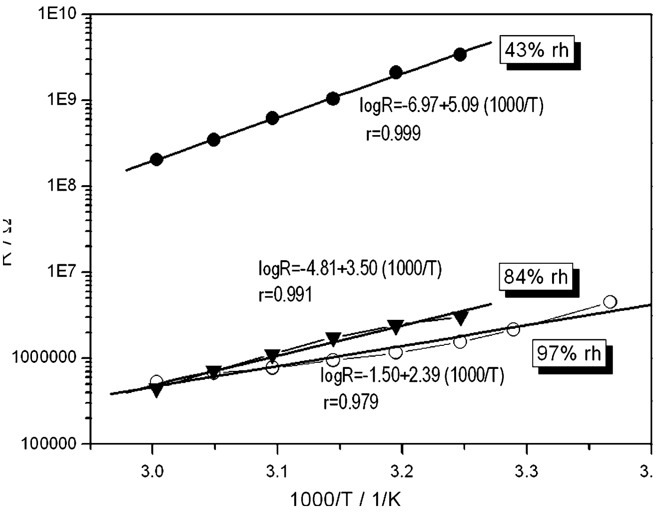

Fig. 4 Log R versus $1000/T$ for various air rh, where R stands for a semicircle diameter, T temperature in Kelvin scale

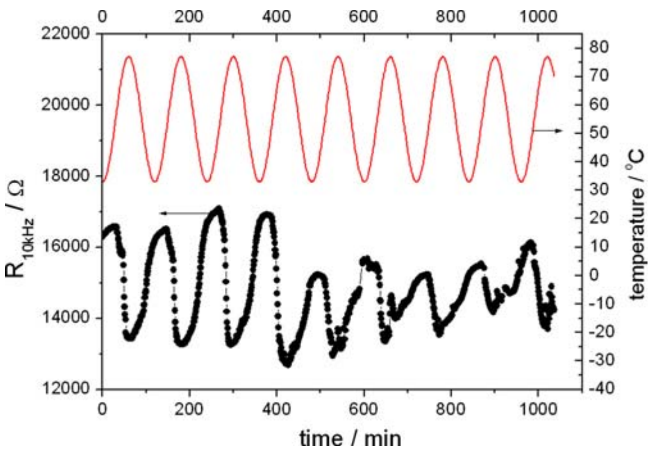

Fig. 5 Real part of the impedance at 10 kHz $R_{10\ \mathrm{kHz}}$ depending on the temperature cycling for the basecoat/clearcoat system

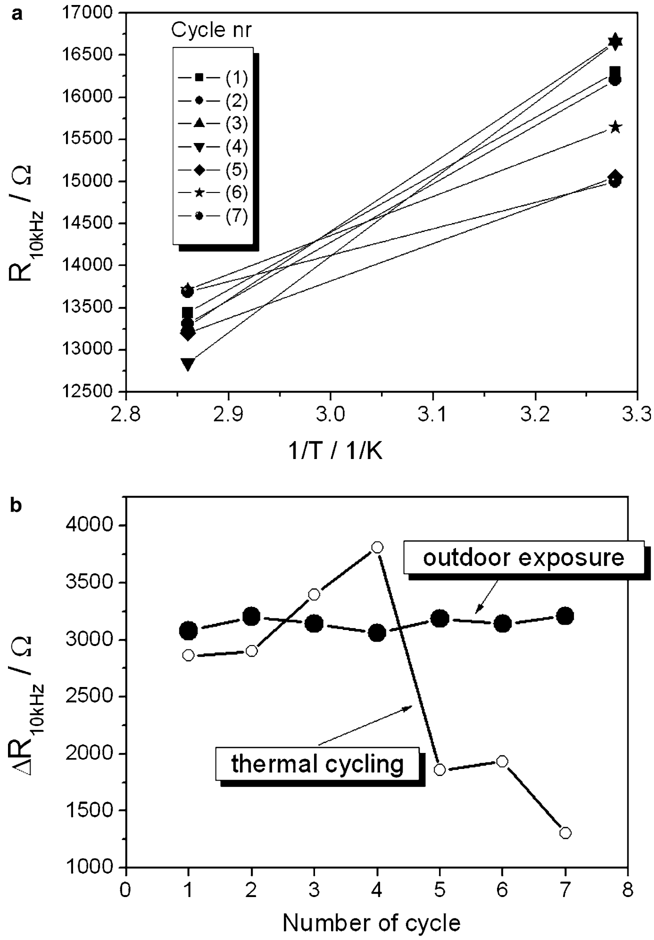

Fig. 6 Real part of the impedance at 10 kHz $R_{10\ \mathrm{kHz}}$ as a function of $1/T$, where T is temperature in Kelvin, for a number of consecutive temperature cycles between 77 and 32°C **a** and the relevant $\Delta R_{10\ \mathrm{kHz}}$ data (*b*). Additional results for outdoor exposure are also presented in **b**

temperature variations during night and day periods. Figure 7 shows temperature and relative humidity of the atmospheric environment and sunlight variations (days and nights) during exposure. The extrapolated to the same temperature range $\Delta\ R_{10\ \mathrm{kHz}}$ values in this case were added to the Fig. 6b for comparison with laboratory results. This figure shows that the influence of thermal cycling between 32 and 77°C was more destructive to interlayer adhesion compared to the 7 days of outdoor exposure. It seems that because adhesion loss is the main endangering agent for coating destruction, testing of the delamination resistance using proposed approach should provide valuable data for the evaluation of coating systems.

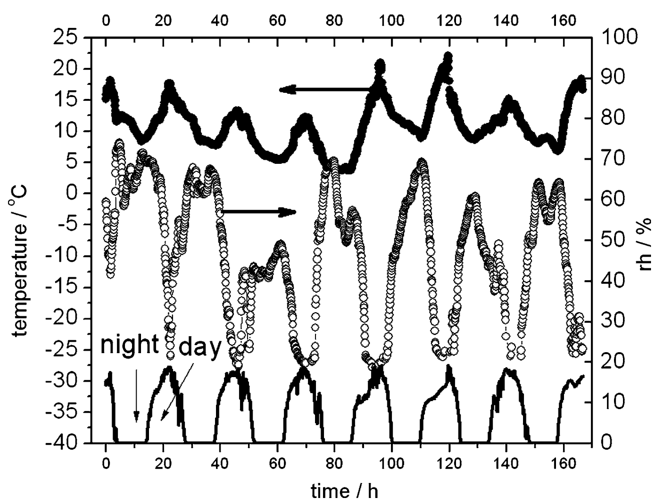

Fig. 7 Temperature, relative humidity (*rh*) and light (night and day periods) variations during outdoor exposure

Conclusions

The application of the impedance spectroscopy was tested for the quantitative evaluation and monitoring of the interlayer adhesion in automotive coating system. A new concept of impedance measurements with conductive microelectrodes placed in the interlayer region was presented.

Using the microelectrodes, the transport and accumulation of water and ions in the interlayer region can be evaluated. From the Arrhenius plots of the interlayer resistance R, the slope of $R(1/T)$ can be determined. It is therefore possible to continuously record the interlayer adhesion during the exposure time at various changing conditions such as temperature and humidity. For this purpose, it is enough to conduct one frequency measurement for a given temperature which has to be also monitored.

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