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Degradation of Organic Coatings Subjected to Alternating Mechanical Stress Impact*

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The paper presents results of the investigation on cyclic mechanical stress impact on two types of organic coating systems – epoxy and vinyl ones. They have been subjected to a series of bend/release cycles within elastic deformation region of metal substrate. The state of the coatings has been evaluated using electrochemical impedance spectroscopy. Behaviour of as-received coatings has been compared with the response of the samples pre-exposed in the conditions enhancing coating degradation.

Key words: organic coating, cyclic mechanical stress, bend/release cycles, electrochemical impedance spectroscopy

Stress is a factor responsible for coating failure. It can be imparted to a coating at a number of ways including chemical attack [1], degradation by UV [2], thermal expansion/contraction due to ambient temperature variations [3,4], volume contraction at cure [5–7]. The information on coating durability *versus* purely mechanical stress imposed at exploitation stage is scarce. Ueda *et al.* [8] have investigated the stress originating from forming of pre-painted metal substrates. The impact of permanent substrate deformation on the protective properties of coatings has been examined by Bastos and Simoes [9]. The effect of plastic deformation on metallic coatings has been described by Sacco *et al.* [10]. Baragetti *et al.* [11] published on the fatigue behaviour of thin-metal coated components.

The focus of this paper is cyclic mechanical stress – the kind of stress, which still remains a puzzle as far as organic coatings are concerned. Although many constructions and installations protected by coatings such as bridges, cargo cranes, car bodies and large volume storage tanks suffer from cyclic stress [12,13], literature lacks in the reports concerning the investigation of repetitive mechanical load impact on organic coatings.

From the theoretical point of view the coating response to any kind of stress including cyclic one relies on its ability handle the energy of impact [14]. Polymers are viscoelastic in their nature. It means they possess the properties of both viscous liq-

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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uids and elastic solids. The way they behave upon load is much affected by the temperature and the rate at which the experiment is carried out [5]. As the temperature drops or the frame of the experiment decreases polymers tend to be more like elastic solids. Similar effect is attained while polymeric materials are subjected to the processes of chemical degradation and physical aging. They become more stiff and solid-like being more prone to stress-induced degradation. It is connected with the way the impact energy is absorbed and relieved. Coating ability to return to its original shape once the stress is removed is a function of its elastic component. As long as the coating maintains the ability to absorb the energy of impact when stressed and release it as the load is removed it remains intact. Then the energy is gradually dissipated through internal molecular reorientation. Such ability ceases or rather becomes impaired as solid-like features prevail over liquid-like behaviour. In that case the molecular relaxation is not effective enough to relieve the stress imposed and coating failure occurs. Depending on what is the weakest interface of the coated system the failure mode can be adhesive or cohesive one.

For fatigue degradation the stress cycles are often sub-critical in their nature. It means the stress associated with each cycle is not significant enough to damage the coating at once. It is the number of cycles and their repetitiveness that makes the coating fail. Each successive load brings some stress, at least a fraction of which is retained by the coating. As a result the stress accumulates and when certain threshold value is exceeded it is released *via* formation of defects.

In this paper the authors evaluated cyclic mechanical stress impact on two types of coatings designated for protection of bridge structures – epoxy and vinyl ones. Behaviour of as-received coatings was compared with the same type of samples but pre-exposed in the conditions enhancing coating degradation (1 week exposure to 70°C and alternatively 1 week exposure to UV radiation).

EXPERIMENTAL

Coating/metal systems. Two types of coating/metal system were designated for the study: a) epoxy coating deposited on St3S steel substrate, b) vinyl coating on St3S steel substrate. Both coatings were applied in two layers using brush. The average thickness was equal to $111.6\pm 8.8\mu$m for epoxy system and $60.8\pm 7.4\,\mu$m for vinyl coating. The samples were seasoned for 1 week in the laboratory prior to the investigation.

Steel substrate was in the form of an isosceles triangle to provide uniform stress distribution all over the specimen surface [15]. The characteristic dimensions are provided in Fig. 1. The substrates were prepared by grinding with abrasive paper of the 180–1200 gradation and degreased with acetone.

One set of samples was tested against cyclic mechanical stress in as-received form. The second one was exposed to the conditions enhancing coating degradation – 1 week exposure to 70°C and alternatively 1 week exposure to UV radiation.

Fatigue test. All the specimens were subjected to bend/release cycles with the frequency $f = 0.07$ Hz simulating fatigue damage. The force applied was adjusted experimentally and provided maintenance of the substrate within elastic deformation region. The cycles were accomplished with a self-made fatigue test machine presented schematically in Fig. 2. The total number of bend/release cycles imposed was equal to 200000.

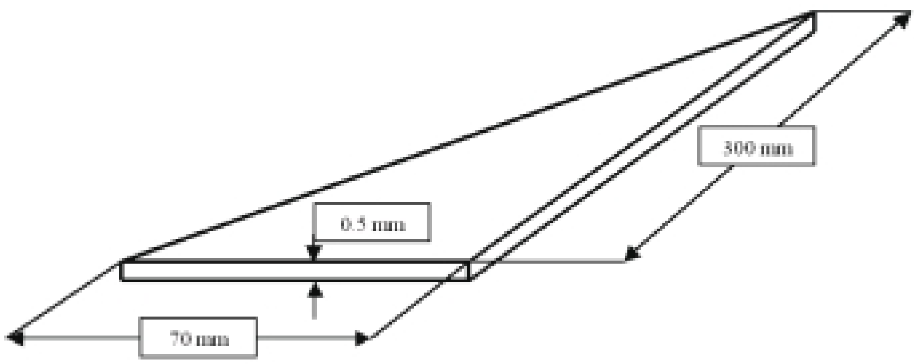


Figure 1. Characteristic dimensions of the test specimen.

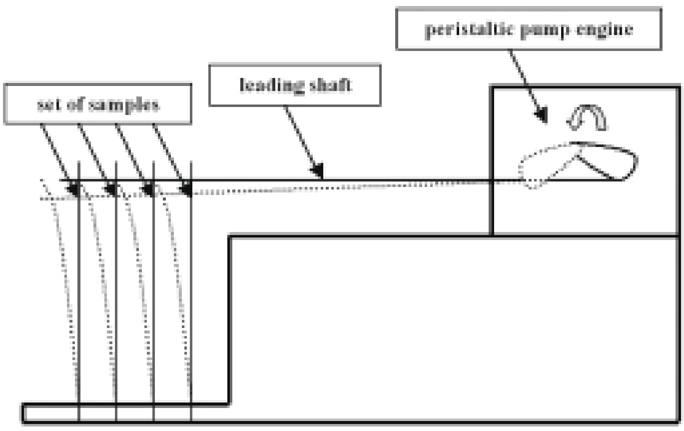


Figure 2. Self-made fatigue test machine utilized in the investigations.

Electrochemical impedance spectroscopy. The state of the coatings was evaluated using electrochemical impedance spectroscopy technique. Impedance spectra were registered regularly after fixed number of bend/release cycles using Schlumberger SI 1255 Frequency Response Analyser coupled to a high input impedance buffer ATLAS 9181. The spectra were registered in the frequency range 1 MHz – 1 mHz and the amplitude of perturbation signal was equal to 30 mV. The investigation was carried out upon immersion in 3% NaCl in a two-electrode system. Metal substrate was a working electrode and platinum mesh served as a counter electrode. The area exposed to examination was 10.2 cm^2. The impedance spectra registered were modeled with the equivalent circuit presented in Fig. 3. Fitting results for the proposed circuit are depicted in Fig. 4 for an exemplary spectrum – Vinyl 1 sample after 65 000 cycles. Electrical parameters of the coatings were acquired using Boukamp's software [16]. Their evolution with the number of mechanical load cycles imposed provided information on the changes taking place inside the coated systems.

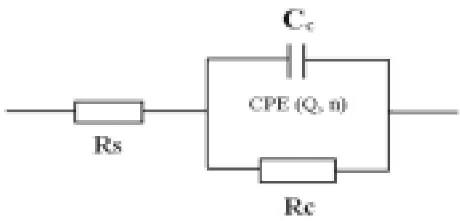


Figure 3. Equivalent circuit used to model the spectra registered.

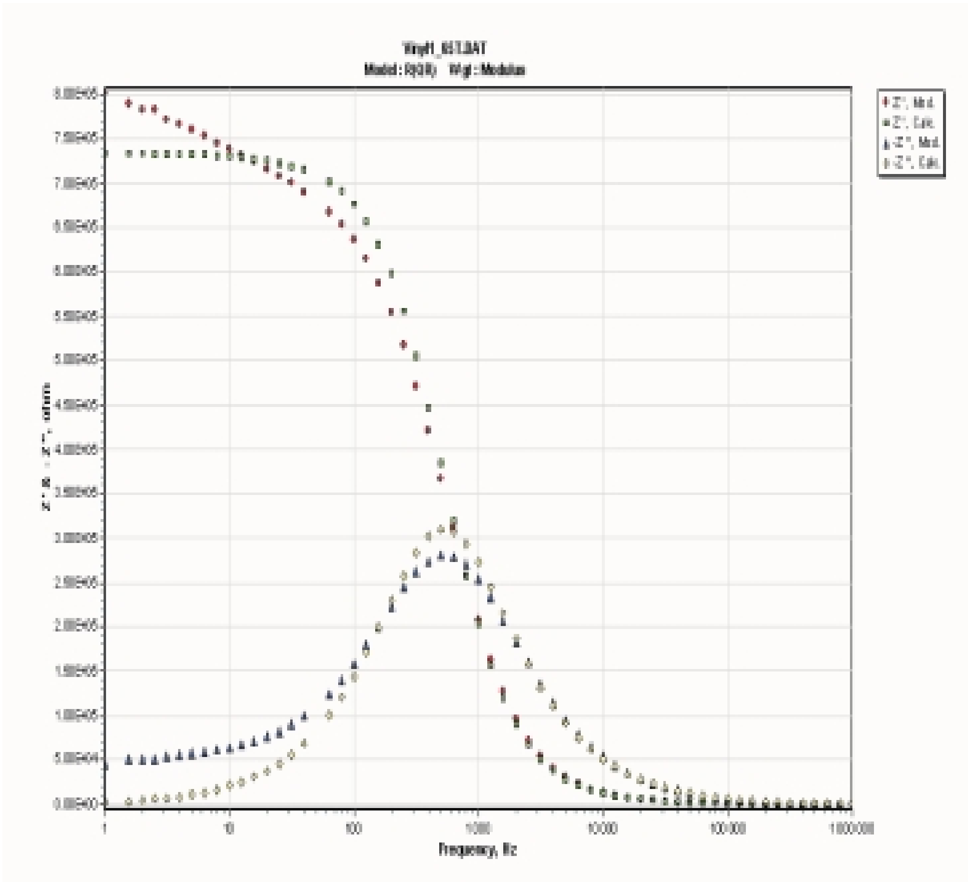
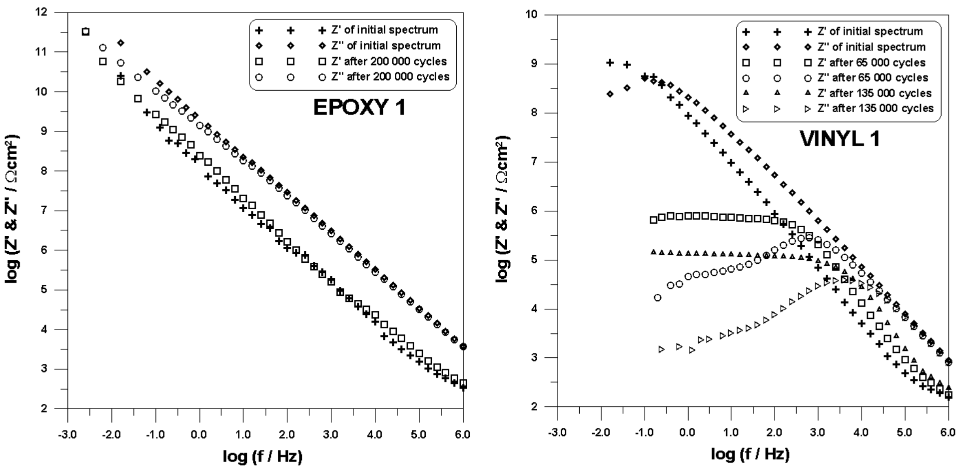


Figure 4. Fitting results for the proposed equivalent circuit for an exemplary spectrum – Vinyl 1 sample after 65000 cycles; χ^2 = 3.514E-3.

RESULTS AND DISCUSSION

Fig. 5 depicts the impedance spectra in Bode format for epoxy and vinyl samples subjected to 200000 bend/release cycles. These are the spectra for the specimens that were examined in as-received state.

A B



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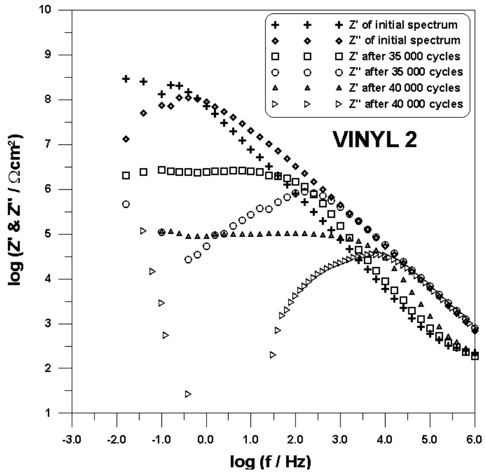
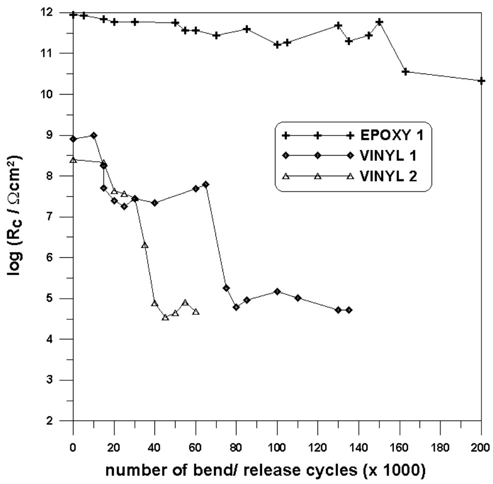


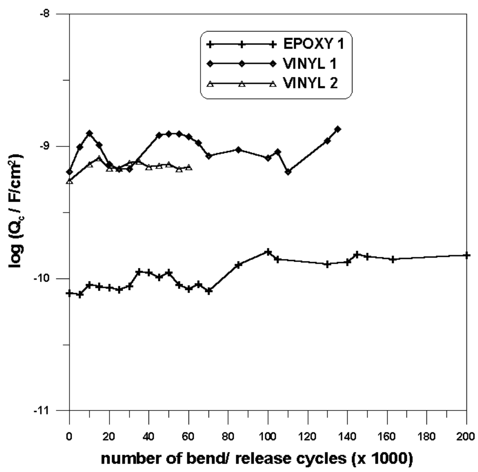
Figure 5. Bode plots for as-received coatings subjected to bend/release cycles: a) Epoxy 1 system, b) Vinyl 1 system, c) Vinyl 2 system.

It can be seen that epoxy coating withstood the test without any damage. The spectra registered at the beginning and after 200000 cycles are very much alike. Coating pore resistance (see Fig. 6) remains at the level of 10^{12}–10^{11} Ω cm^2 indicating strong dielectric and barrier properties of the coating. Different behaviour is observed for both vinyl samples. They exhibit gradual degradation with the number of bend cycles imposed. Coating pore resistance of Vinyl 1 decreased from 10^9 to 10^5 Ω cm^2 after 135000 cycles. In practice the system failed after 65000 cycles as then its resistance achieved 10^6 Ω cm^2, the value which is believed to be a boundary distinguishing between good and damaged coating. The second vinyl sample (Vinyl 2) underwent degradation even earlier. Its resistance dropped well below 10^6 Ω cm^2 already after 40000 cycles.

A



B



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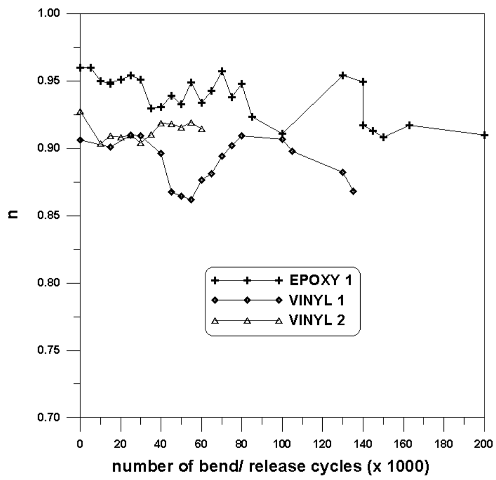


Figure 6. Evolution of electrical parameters: a) coating pore resistance, b) Q parameter of CPE element related to coating capacitance, c) n parameter of CPE related to coating capacitance, for as-received coatings subjected to bend/release cycles.

Tracing the evolution of coating electrical parameters one can notice that mechanical cycles had the most significant impact on the pore resistance. It is the most evident in the case of vinyl samples, which exhibit progressive R_c decrease with the number of cycles imposed. Remaining parameters, namely Q_c, n of the CPE modeling coating capacitance, change in relatively small extend. They follow typical trend accompanying coating degradation but the range of their changes is not as significant as the one registered for R_c.

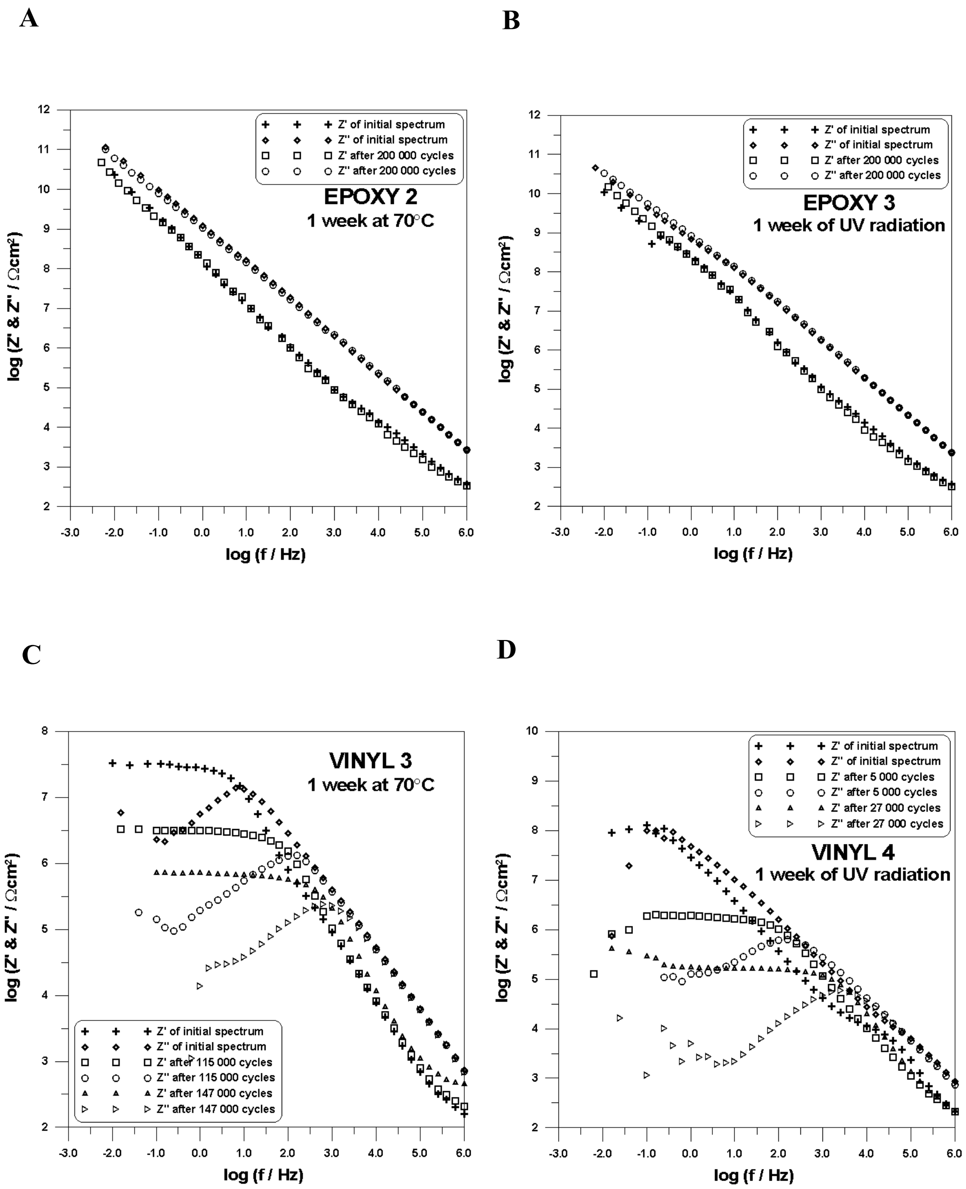


Figure 7. Bode plots for pre-exposed coatings subjected to bend/release cycles: a) Epoxy 2 system exposed to 70°C for one week, b) Epoxy 3 system exposed to UV radiation for one week, c) Vinyl 3 system exposed to 70°C for one week, d) Vinyl 4 system exposed to UV radiation for 1 week.

The Q_c parameter can be regarded as an indicator of the amount of water absorbed by the coating. So slight increase in Q_c with the number of cycles applied observed for all the samples can be attributed to limited immersion time prior to the measurements. While mechanically cycled the specimens were kept in an ambient atmosphere. After fixed number of cycles they were conditioned for 24 hours in 3% NaCl solution before the measurements. The electrolyte absorption process could probably require more time so the increase in capacitance was not as high as one might have expected.

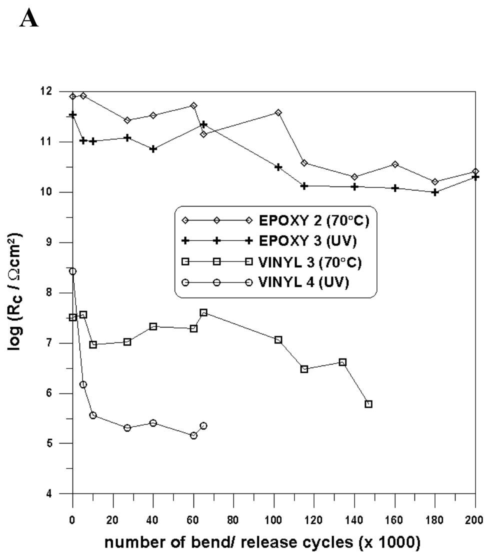
N parameter although generally decreasing with the number of bend/release cycles imposed exhibits some fluctuations. They are probably due to some motions of polymer segments upon cycling contributing to temporal, reversible increase in coating structure homogeneity.

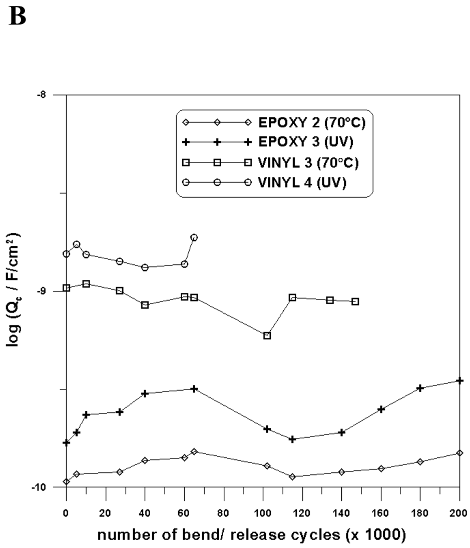
The impedance spectra depicted in Fig. 7 have been registered for the samples pre-exposed in the conditions promoting coating degradation. Epoxy 3 and Vinyl 4 have been subjected to UV radiation for 1 week. Epoxy 2 and Vinyl 3 are the specimens that suffered from 70℃ for the same period of time. An intention was to identify how the coatings behave under combined influence of alternating mechanical stress and the factors believed to cause coating degradation. Elevated temperature is said to accelerate aging of organic coatings [17], while UV radiation has been selected as one of the factors associated with coating damage during outdoor service.

Looking at the spectra and changes of coating electrical parameters shown in Figs. 7 and 8 respectively it can be inferred that epoxy coatings occurred to be resistant to 200000 bend/release cycles even though pre-exposed to high temperature and UV radiation. They maintain excellent barrier properties just like the sample not subjected to any additional degradation factors (comp. Figs. 5 and 6). Ultraviolet radiation turned out to be more harmful for vinyl coating. It imposed more negative impact on vinyl system than 70℃ temperature. The irradiated sample lost its protective properties after 5000 cycles. High-temperature exposed one failed after 147000 cycles. That system exhibited similar durability to its as-received counterpart. Unexpectedly, epoxy coatings, which are said to be the most susceptible to UV radiation, performed much better than vinyl ones. The reason lies probably in difference in coatings' thickness and limited pre-exposure time. One-week exposure was not long enough to injure the epoxy coating. In such case the crucial factor seems to be lower thickness of vinyl system deciding about its accelerated damage.

Similarly to the as-received coatings, alternating load cycles resulted in the most significant changes in pore resistance. The other two electrical parameters (Q_c, n) were affected in smaller degree due to the reasons described earlier.

Summarizing tested epoxy coatings exhibited higher resistance to cyclic mechanical stress as compared to vinyl ones. Regardless the presence of pre-exposure conditions epoxies maintained the ability of effective impact energy absorption/emission. Throughout the test their molecular rearrangement forced by the mechanical load, prevented the material from fatigue damage. On the contrary vinyl coatings lost their ability of prompt molecular reorientation. As the number of cycles increased a gradual deterioration of coatings' dielectric properties was observed. One week of UV radiation imposed more negative impact on vinyl coatings than one-week exposure to the elevated temperature. It seems to be justified to state that results obtained were also influenced by coatings thickness. More resistant to the conditions imposed were the samples of higher thickness namely epoxy ones.





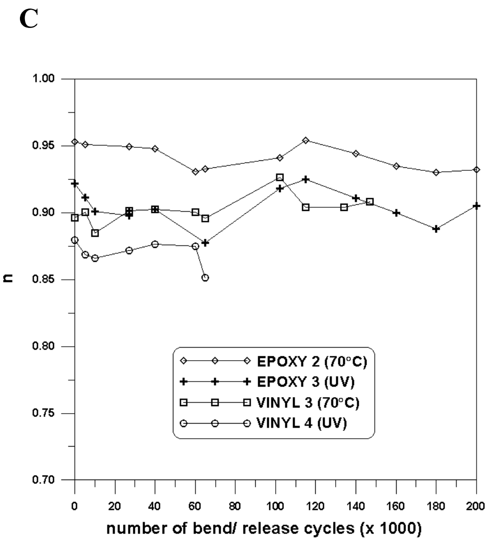


Figure 8. Evolution of electrical parameters: a) coating pore resistance, b) Q parameter of CPE element related to coating capacitance, c) n parameter of CPE related to coating capacitance, for pre-exposed coatings subjected to bend/release cycles.

CONCLUSIONS

The investigation of alternating mechanical stress impact on two types of organic coating systems yield the following conclusions:

1. After 200000 bend/release cycles epoxy coatings occurred to be more resistant to cyclic stress than vinyl coatings. While epoxy systems remained intact, vinyl systems were no longer a barrier for corrosive agents. The reason was probably higher thickness of epoxy films.

2. One week pre-exposure to UV radiation aimed at accelerated damage of the samples prior to mechanical cycling affected vinyl system only. Epoxy coating exhibited no signs of degradation.
3. In the case of vinyl coating UV radiation exerted more negative impact than the pre-exposure to elevated temperature (70°C). Irradiated specimen failed after 5000 cycles, while durability of the heated sample was comparable with the as-received one's.
4. Cyclic mechanical stress is a factor contributing to coating degradation and thus deserves more attention.

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