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Evaluating the performance of organic coatings under mechanical stress using electrochemical impedance spectroscopy

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Abstract Stress in coatings originating from a mechanical load imposed during exploitation is a relatively unexplored field of investigation. Paradoxically, a number of constructions and installations seem to operate under such conditions. The purpose of this work was to investigate the impact of a cyclic mechanical load exerted on coating/metal systems. It was the authors' aim to verify whether repeated mechanical stress constitutes a significant factor contributing to coating degradation. Epoxy coated St3SA1 steel samples were subjected to 21,000 uniaxial strain/release cycles. The maximum force applied assured maintenance within the elastic deformation region of the metal substrate. The state of the protective film was monitored using electrochemical impedance spectroscopy. The coating response to the mechanical load occurred in a three-stage process. The system subjected to the strain/release cycles revealed signs of degradation earlier compared to a non-strained, reference sample.

Keywords Electrochemical impedance spectroscopy · Mechanical load · Organic coating · Strain/release cycle

Introduction

Stress constitutes one of the factors contributing to degradation of construction materials, limiting their lifetime and being of extreme importance in terms of

safety aspects. Although attempts are undertaken towards stress minimization, it will always be associated with engineering practice. Coating/metal systems are not an exception here. Each of their components, metal substrate and polymer material, is characterized by different resistance against the stress applied.

Polymers behave as both a viscous liquid and a spring-like elastomer. Mechanical properties exhibited by polymer materials are due to such viscoelastic dualism. It is evident [1, 2] that as they are subjected to short-term loads with low deflection and small loads at room temperature, polymers act usually as springs, returning to their previous shape after the load is released. Long-term heavy loads or elevated temperatures make polymers behave in a viscous way. They will deform and flow similarly to viscous liquids, although still solid.

From the energetic point of view, an ability of polymer materials to withstand stress relies on impact energy handling phenomena. Owing to their viscoelastic nature, polymers can take various structural conformations. In an equilibrium state the conformation oscillates around the most energetically convenient one corresponding to the maximum entropy. The stress imposed induces a change in the chain conformation. A time at which a new, temporal conformation is attained and a time after which the previous conformation is restored depend on the coating's ability to absorb and dissipate the energy of impact. For free polymer films, such a property is determined via the dynamic mechanical analysis (DMA) approach [2]. A commonly utilized measure of the relation between the energy dissipated and absorbed in cyclic deformation is the phase angle.

The properties described above depend not only on the kind of polymer but also on the material history. Impact energy handling becomes handicapped when the polymer suffers from the processes of chemical degradation and physical ageing. Then new equilibria are established at the expense of defect formation.

In literature sources, among the number of factors having a negative impact on the coated systems [3, 4, 5], stress has been also recognized. There exist papers

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Dedicated to the memory of Harry B. Mark, Jr. (February 28, 1934–March 3rd, 2003)

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devoted to degradation induced by thermal cycles and thermal shocks [6, 7]. Internal stresses triggered by a difference in thermal expansion coefficients between the polymer layer and the metal substrate are believed to be a driving force for destruction. Some authors [8, 9, 10] report on the influence of intrinsic stresses related to volume contraction during curing process on the quality of coating. Attention has been also paid to the stress arising on forming pre-painted steel substrates [11]. However, information about the relation between the coating durability and the stress of purely mechanical origin, applied during the exploitation stage, is relatively scarce. Bastos and Simoes investigated the influence of permanent, uniaxial substrate deformation on the protective properties of coatings [12]. The effect of plastic deformation on metallic coatings has been described by Sacco and co-workers [13].

In reality, these are not the only constant stresses that coatings must withstand in the end-use environment. A number of installations like bridges, overpasses, cargo cranes, or the bottoms of storage tanks are subjected to cyclic mechanical load. From the experience of the authors of this paper it can be suspected that even small amplitude vibrations may have an impact on protective films. It was often the case during some field investigations that a paint system applied on the constructions submitted to repeating loads revealed signs of a degradation earlier than the same type of coating system but deposited on load-free objects. That is why the purpose of this paper is to present the results of investigation on cyclic mechanical stress impact on protective coatings. The aim was to approach the problem qualitatively and to verify whether this factor is really of substantial importance with respect to the durability of coating/metal systems.

Experimental

Coating/metal systems

The specimens under investigation consisted of an Epidian 5 epoxy coating deposited on St3SA1 steel. The coating was composed of resin and hardener only. No additives in the form of fillers, plasticizers or pigments were introduced, as the purpose of the investigation was to induce degradation of the coating in a relatively short time. The aim was not to test a particular paint for its durability but to explore the behaviour of a coated system under the impact of a cyclic mechanical load. A coating layer of average thickness 182 μm was applied on a steel panel with the use of a brush. The steel substrate was of 30 cm by 5 cm dimension; its thickness was equal to 1 mm.

Strain/release cycles

The samples investigated were subjected to a series of uniaxial strain/release cycles. The load extremes were 9 kN and 0 kN, respectively. This assured restriction to the region of elastic deformation of the steel substrate, as in a majority of service conditions the constructions are meant to operate within the range of reversible deformation, well below the yield point. The elongation at maximum load was equal to 1% of the initial specimen

length. One complete strain/release cycle lasted for 3 s and the force applied was changed in a linear manner. A total number of 21,000 mechanical loads was imposed over the samples tested. The strain/release cycles were accomplished with a FPZ 100/1 tensile testing machine.

Impedance measurements

The state of the coating/metal systems was monitored using the electrochemical impedance spectroscopy technique. A Schlumberger SI 1255 FRA coupled to a high-input impedance buffer (Atlas 9181) was employed in the measurements. Impedance spectra were registered in the released position after a fixed number of load cycles applied. The measurements were carried out in a two-electrode system under immersion in 3% NaCl solution at corrosion potential. The steel substrate constituted a working electrode and platinum mesh served as a counter electrode. The area of the specimen exposed to investigation was equal to 10.2 cm^2 .

Impedance spectra were determined within a 1 MHz–1 mHz frequency range. The amplitude of the perturbation signal was 60 mV. The impedance spectra registered were modelled with the parallel RC equivalent circuit, presented in Fig. 1. The electrical parameters of the coatings were acquired using Boukamp's software [14]. Their evolution with the number of mechanical load cycles imposed provided information on the changes taking place inside the coated systems. The results were compared with the ones obtained for the reference samples subjected only to immersion in 3% NaCl solution for an analogous period of time. A schematic representation of a ready-to-test sample is presented in Fig. 2.

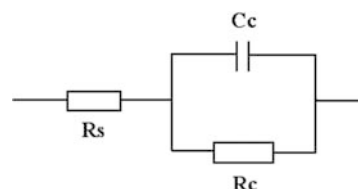


Fig. 1 Equivalent circuit used to model the spectra registered: R_s , solution resistance; R_c , coating resistance; C_c , coating capacitance

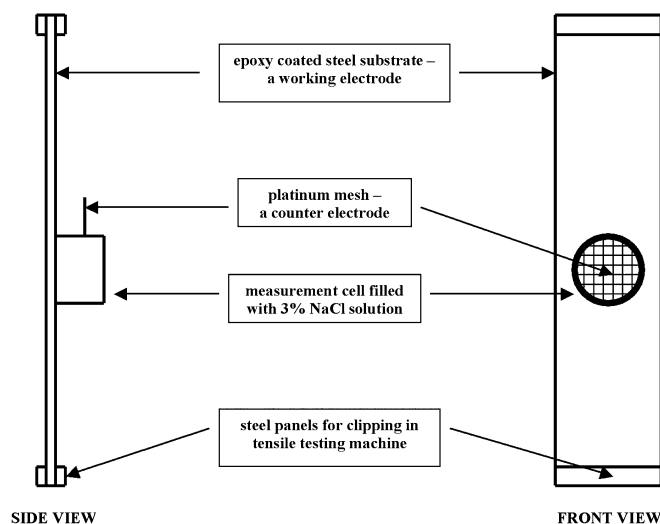


Fig. 2 Scheme of a ready-to-test specimen

Results and discussion

According to the results obtained, coating behaviour upon mechanical load cycling can be segmented into three stages: an improvement stage, a relaxation stage and a deterioration stage.

Figure 3 shows the impedance spectra for a selected specimen registered up to the 10,400th strain/release cycle. Gradual improvement in the dielectric properties of the coating is evident. An increase in the diameter of the high-frequency semicircle indicates a rise of the protective film resistance. Such results seem to be surprising. At present there is no unequivocal explanation for this phenomenon. What may be considered as a reason for this kind of behaviour is a decrease in the

residual stress inside the coating. The load cycles might have contributed to releasing some of the stress accumulated within the polymer and originating from volume contraction at cure. It might also be the case that polymer chains stretched by the load applied closed some of the diffusion paths within the coating that are responsible for corrosive agent transport through the polymer material. As a closer look is taken at a comparison showing the evolution of the coating resistance for the strained and reference samples, depicted in Fig. 4, one can notice that both of them experience an increase in pore resistance. However, a steeper characteristic was obtained for the mechanically loaded sample. Another suggestion is an additional curing process that might have taken place within the polymer. Stretching could have contributed to an increase in the

Fig. 3 Strained sample. Impedance spectra registered up to the 10,400th cycle; Nyquist projection

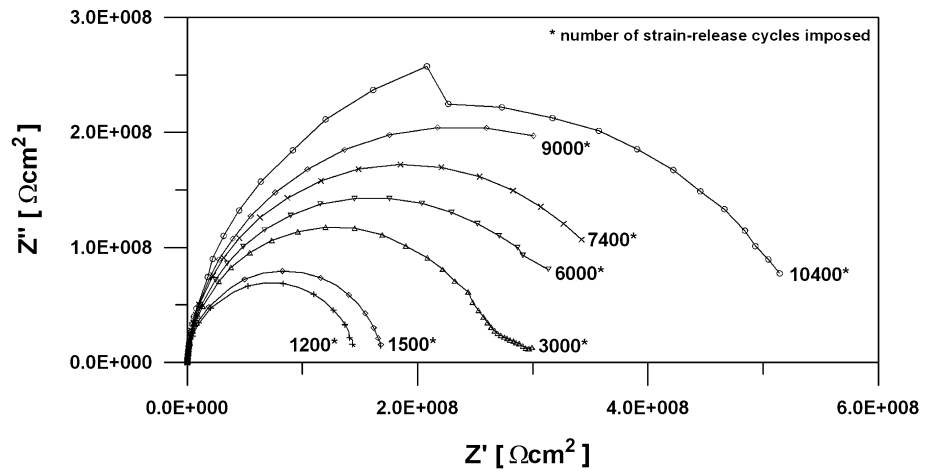
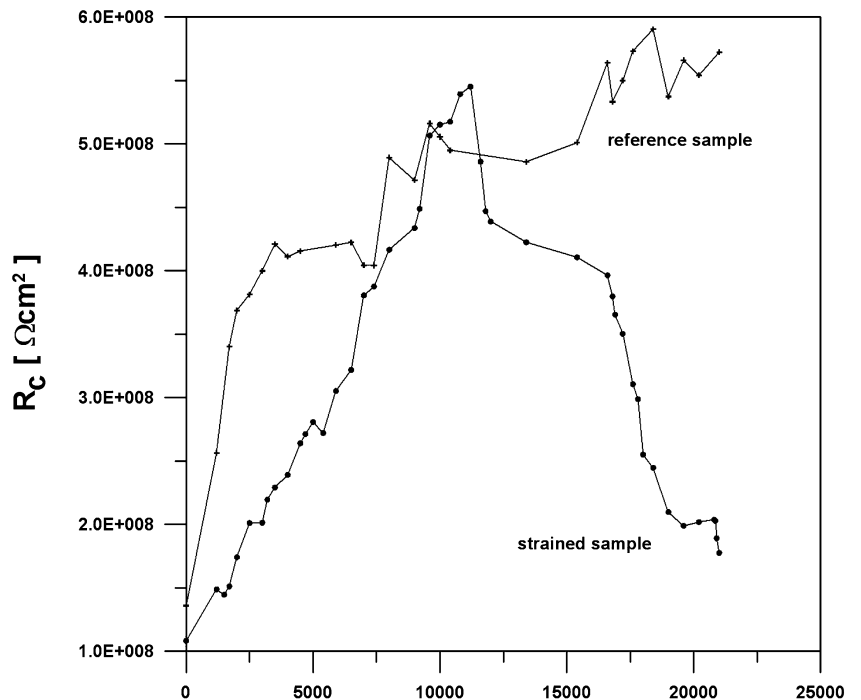


Fig. 4 Evolution of coating resistance during the investigation. Cyclically strained sample versus reference sample



area of contact between the resin and hardener and in this way improved the coating properties. Thus a discussion on an interpretation of the behaviour discovered is open and an explanation of the phenomenon observed seems to be not yet complete.

The second stage of the coating response to a cyclic mechanical load is characterized by relaxation processes that can be easily distinguished between the 10,400th and the 16,600th cycles. Exemplary impedance spectra registered at different times following 13,400 strain/release cycles are depicted in Fig. 5. They illustrate how the coating recovers from temporal damage induced by the load. Progressive improvement of the coating dielectric properties with time can be noticed. The material is flexible enough to release absorbed energy from the impact, although the process is clearly delayed in time and not as rapid as in the improvement stage. An ability for prompt molecular rearrangement allows the polymer to pass through a set of instantaneous equilibria until the final, stable conformation is attained.

Fig. 5 Strained sample. An example of the relaxation phenomenon registered after 13,400 cycles; Nyquist projection

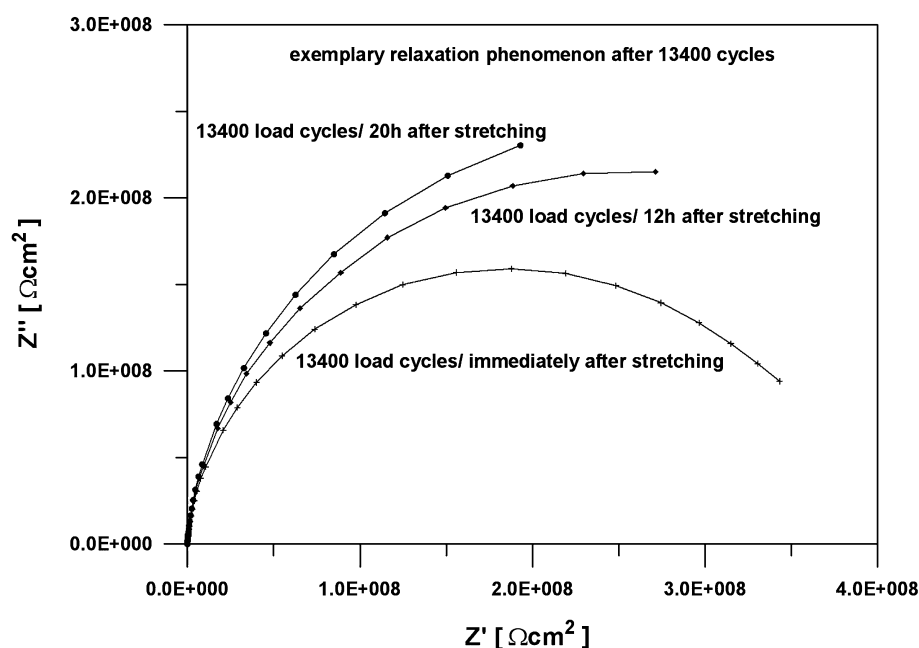
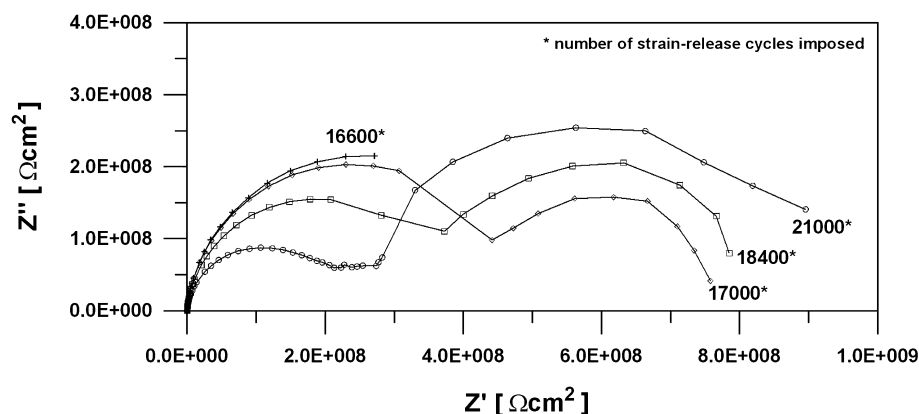
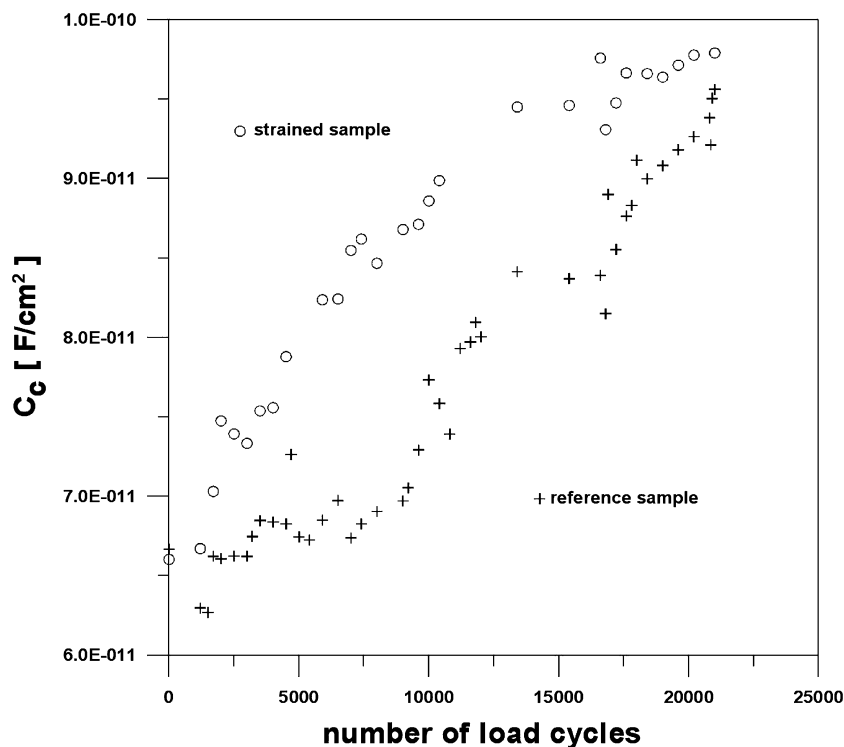


Fig. 6 Strained sample. Impedance spectra determined between the 16,600th and the 21,000th cycles; Nyquist projection



In the third stage of coating behaviour, the film exhibits a continuous decrease in dielectric properties. Each subsequent series of strain/release cycles is accompanied by a drop of the coating resistance. The ability to dissipate the energy associated with mechanical load has been impaired. The relaxation phenomenon was not observed any more. The evolution of the coating resistance shown in Fig. 4 indicates the fatigue effect of load cycles imposed on the coating/metal system. The stress experienced by the coating could not be handled without permanent damage of the protective film. It started to be relieved via formation of defects within the protective film, thus making it permeable to corrosive agents. This fact is confirmed by the appearance of the second, low-frequency time constant in the spectra registered between the 16,600th and 21,000th cycles (Fig. 6). There is evidence of the onset and progress of an electrochemical process at the coating/metal substrate interface, which is a result of the failure in the barrier properties of the coating.

Fig. 7 Evolution of coating capacitance during the investigation. Cyclically strained sample versus the reference sample



Concerning the coating capacitance, both strained and reference samples experienced an increase in C_c values during the time of investigation, as a result of electrolyte incorporation into the coating structure. However, the increase of the capacitance is more pronounced in the case of the strained system (Fig. 7). This points to accelerated degradation of the coating subjected to mechanical load impact.

Summarizing, the coating under investigation did not stand the test of 21,000 strain/release cycles. A comparison with the reference specimen, which maintained protective properties throughout the entire experiment, proves that cyclic mechanical load must be regarded as a factor contributing to coating degradation. Owing to this fact, an emphasis should be put on further, detailed studies of the problem.

Conclusions

Coating behaviour upon mechanical load cycling occurs in a three-stage process, consisting of an improvement of dielectric properties, relaxation phenomena and a deterioration stage. It can be concluded that such a coating response to the load applied stems from the evolving ability of impact energy handling during the exposure. After 16,600 strain/release cycles, unlike in the initial phase of the investigation, the polymer film was unable to entirely re-emit the energy absorbed during loading. Thus, each next set of cycles led to coating degradation, manifested by a gradual decrease in dielectric properties. At that time, an onset of a corrosion process at the

interface was also detected. On the other hand, a reference sample still constituted an effective barrier for corrosive agents.

The investigation presented brings about some novelty to coating science, as it has been the first attempt to evaluate the performance of organic coatings under cyclic load conditions. Although some of its aspects still remain unclear, small amplitude, reversible, uniaxial deformations turned out to be a key factor influencing coating durability. The results obtained are an incentive for further research in this field. Exploration of the problem is of significant practical importance due to the fact that a number of constructions operate under cyclic mechanical load. Accelerated laboratory tests incorporating the impact of cyclic stress on coating durability will certainly be more reliable and valuable in terms of comparison and selection of coating materials.

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