Electrochimica Acta 55 (2010) 6195–6203

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Investigation of the self-healing properties of shape memory polyurethane coatings with the 'odd random phase multisine' electrochemical impedance spectroscopy

Jean-Baptiste Jorcin[a,*,1], Gill Scheltjens[a,b], Yves Van Ingelgem[a,1], Els Tourwé[a,1], Guy Van Assche[b], Iris De Graeve[a], Bruno Van Mele[b], Herman Terryn[a], Annick Hubin[a,1]

[a] Research Group Electrochemical and Surface Engineering, Vrije Universiteit Brussel, Pleinlaan 2, B–1050 Brussels, Belgium
[b] Research Group Physical Chemistry and Polymer Science, Vrije Universiteit Brussel, Pleinlaan 2, B–1050 Brussels, Belgium

ARTICLE INFO

Article history:
Received 30 July 2009
Received in revised form 11 January 2010
Accepted 11 January 2010
Available online 18 January 2010

Keywords:
Self-healing
Organic coating
EIS
Odd random phase multisine
Electrical equivalent circuit

ABSTRACT

The aim of this work is to study the physical self-healing properties of shape memory polyurethanes (SMPUs) with cerium ions on top of a pure aluminum substrate. To achieve this, the 'odd random phase multisine' electrochemical impedance spectroscopy (EIS) is used. The additional information given by this technique (stochastic noise, non-linear and non-stationary behavior of the sample during the measurement) has been useful to verify the quality of the measurement. Moreover, combined with a fitting algorithm weighted by the stochastic noise, these elements of information proved powerful in rejecting, accepting or improving electrical equivalent circuit models used to fit the impedance spectra.

These SMPU consist of two parts: a soft matrix in caprolactone and a hard part in polyurethane. SMPU with 12, 30 and 41% of hard phase were investigated. The results showed that a physical self-healing can be observed for the coating with 12% of hard phase.

1. Introduction

Nowadays, organic coatings are widely used to prevent corrosion of metallic substrates. They provide a good protection due to their barrier properties and their ability to carry active pigments like corrosion inhibitors. Finally, they can be easily applied at a reasonable cost.

Nevertheless, the mechanical properties of these organic coating systems remain weak compared to the metallic substrate. Hence they can be deteriorated by mechanical impacts and lose their protective properties. To avoid this problem, researchers try to develop new organic coating systems with self-healing properties. Currently, there are two main possibilities to have a healing effect. The first one, more common, is the addition of a 'free-moving corrosion inhibitor' in the polymer matrix. If a scratch reaches the metal, diffusion of the inhibitor to the exposed metal is expected to result in metal passivation. The second one is to apply a polymer coating which is able to do a physical self-healing [1,2]. Obviously, a combination of the both effects would allow having a better protection against corrosion.

The aim of this work was to investigate the self-healing properties of shape memory polyurethane with an inorganic corrosion inhibitor on top of a pure aluminum substrate. In this context, odd random phase multisine electrochemical impedance spectroscopy (ORP-EIS) was used as a characterization tool. This technique allows not only measuring the electrochemical impedance, but provides also additional information, useful to assess the quality of the measurements and to perform the interpretation of the results. We recently developed this integrated methodology to measure, analyze and model electrochemical systems in a correct and reliable way. We published a number of papers on this methodology: the theoretical background can be found in [3,4] and the advantages of the methodology were demonstrated on an electrical circuit in [5].

2. Experimental

The organic material used in this study is a shape memory polyurethane (SMPU). SMPU is mostly used for bulk polymer applications, but in the present work SMPU is considered for potential coating application. These SMPU's are segmented block co-polymer constituted of soft poly (ε-caprolactone) (PCL) segments and hard polyurethane segments (PUs) (Fig. 1). Polymer syntheses were performed by the research group of Prof. Du Prez F. (Vakgroep Organische Chemie, Ghent University) [6] with three different amounts of hard segment: 12%, 30% and 41% (this percentage rep-

* Corresponding author.
E-mail addresses: jb.jorcin@gmail.com, jjorcin@vub.ac.be (J.-B. Jorcin).
[1] ISE member.

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doi:10.1016/j.electacta.2010.01.027

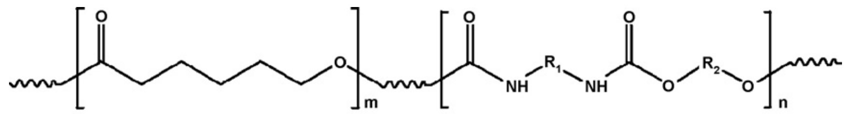

Fig. 1. Structure of the shape memory polyurethane (SMPU). Here, R_1 is a cyclohexamethylene group and R_2 a tetramethylene group, m and n correspond to the amount of each segment to have the good percentage of PU in the bulk polymer.

resents the number of PU segments in a polymeric chain with a known number of segments). Bulk polymers were dissolved in the dimethylsulfoxide (DMSO) at a temperature of 80 °C to create 5 wt% SMPU's solutions. Then, 0.5 wt% of cerium (III) nitrate (with respect to the SMPU mass) was added to the coating solution as corrosion inhibitor [7]. It is important to note that the melting point of the PCL is around 52 °C, while the one of the PU is close to 173 °C. Due to their functional groups, it is possible to create hydrogen bonds between the PU segments. If the coating is damaged, a physical self-healing is expected after an increase of the temperature between the melting point of the two compounds PCL and PU. Indeed, with the relaxation of the soft matrix, the polymer can fill the damaged area, the hard segments maintaining the mechanical properties.

The metallic substrate is a pure aluminum sheet (99.99%) with a thickness of 0.1 mm and an investigated area of 3.14 cm^2. The surface was activated by immersing the sample in an alkaline 25 wt% NaOH solution for 5 s. Afterwards the sample was rinsed with deionized water.

The samples were coated by bar coating at 80 °C. The distance between the bar and the substrate was 10 μm. The samples were cooled to room temperature before they were annealed for 24 h at 80 °C in a vacuum oven.

The medium was a 10^{-1} M Na_2SO_4 solution at room temperature to avoid pitting problems. As a first step, samples were immersed for 24 h in the electrolyte to reach the steady state. During this time, 8 impedance spectra were recorded. Then the samples were removed from the solution, scratched with a cutter up to the metal over a length of 1 cm in the middle of the investigated area. They were immediately put back in the electrolyte and a new set of 12 impedance spectra was recorded during 24 h, 4 of them were recorded in the first hour of immersion to follow a possible quick evolution of the nude metal in the scratch. Finally, the samples were taken out of the solution and put in a vacuum oven at 80 °C for 24 h to try to induce a physical healing. At the end, a third set of 8 measurements was performed on the heated samples during 24 h of immersion.

The measuring setup consisted of an EG&G Princeton Applied Research potentiostat (PAR model 2273) and National Instruments PCI-4452 DAQ-card with a build-in anti-aliasing filter. The applied multisine signal was digitally composed with Matlab software release 12.1 from the Mathworks Inc. Matlab 12.1 was also used for processing of the collected data and controlling the DAQ-card. The amplitude was set to 10 mV rms. Measurements were performed in the frequency range (0.1 Hz; 20 kHz). The excitation signal was an odd random phase multisine [8,9]. The high value of the lowest frequency measured (0.1 Hz) is due to very high amount of memory needed by the odd random phase signal and the physical limit of the computer used to perform the measurements. Each impedance diagram took 2 min with a lot of points (320 excited frequencies in this case). The collected information consisted of the amplitude and phase of the impedance, the stochastic noise, the non-linear contribution to the impedance spectra and/or the non-stationary behavior if present. Obviously, to be able to give an interpretation of the result, the EIS measurements must be linear and stationary.

The interpretation was based on an electrical equivalent circuit modeling approach. The cost function, which is a measure for the agreement between model and experiment, was minimized to obtain the best-fit values of the elements in the equivalent circuit model. A self-written procedure in Matlab, using a Gauss–Newton algorithm followed by a Levemberg–Marquard minimization scheme was used to that purpose [10–13]. It can cope with unity, amplitude, noise level or non-linearity weighting. By using the noise level or level of non-linear behavior as a weighting factor more weight is attached to high-quality data points (linear behavior or lowest noise level) and less weight to low-quality data points. Using this weighting, it is possible to determine the reliability of the parameters assessed from the fitting procedure, based on the experimental data.

3. Results and discussion

The impedance diagrams recorded for each sample (12%, 30% and 41% of hard segments) are plotted in Bode coordinates in Fig. 2. Spectra with a round symbol are performed after 24 h of immersion on an intact coating, those with a square are obtained after 24 h of immersion for the sample with a scratch, and spectra with a triangle are measured after 24 h of immersion after the heating process.

Samples with intact coating present two time constants, which is typical for a coated system. The high frequency region (HF) is more related to the coating properties, the low frequency part represents the Faradaic processes occurring at the bottom of the pore of the coating [14]. For the undamaged coating, two kinds of spectra can be observed. The SPMU with 12 and 30% of hard segment have a similar behavior. On the other hand, the spectrum obtained for the SMPU with 41% of hard segment is quite different, the modulus of the impedance is 10 times lower (10^5 Ω cm^2) than the other coatings (10^6 Ω cm^2), and the diagram is shifted in the low frequencies. Moreover, the visual aspect of the sample, white and hazy, is totally different from the other coatings with less hard segments, which are clear and transparent. At last, a deeper analysis of the multisine EIS results (Fig. 3) show the presence of non-linearity, in the low frequency part of the diagram, and they are present in all spectra recorded for this sample. This is concluded from the fact that the curves for the stochastic noise and the stochastic noise + non-linear contribution are not coinciding. The content of hard phase in this coating is too high, creating phase separation and poor barrier properties. Considering these results, only the self-healing properties of the SMPU 12 and 30% were investigated.

The diagrams measured on these samples (scratched SMPU 12 and 30%) are also plotted in Fig. 2. There is a significant difference in the spectra obtained on an intact coating and those obtained on the scratched one. A decrease of both modulus and phase can be noticed in the high frequency part of the diagram for damaged samples, this is the frequency range related to the properties of the organic coating. The low frequency range of the impedance diagrams is also affected by the presence of the defect. Indeed, it is obvious that the defect will influence the faradic process because the metal is not covered by the coating anymore.

The last two spectra plotted in Fig. 2, were measured after the heating process. Depending on the nature of the polymer (SMPU 12% or SMPU 30%), two types of results were obtained. In the case of the SMPU 30%, no significant modification can be observed on the damaged sample before and after the heating process. On the other hand, for SMPU 12%, the spectrum obtained after the heating