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A combined mechanical, microscopic and local electrochemical evaluation of self-healing properties of shape-memory polyurethane coatings

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ABSTRACT

In the present paper, a shape-memory polyurethane (SMPU) film consisting of a two-segmented block co-polymer is presented as a novel organic coating for the protection of metals against corrosion. When the coating is damaged, a physical self-healing and consequent recovery of the barrier properties are induced after an increase of the temperature. Indeed, thermal treatment leads to the relaxation of the soft matrix in the polymer and subsequent coverage of the damaged area. The scanning vibrating electrode technique (SVET) is employed to visualize local variations of the electrochemical activity in the damaged area of the SMPU coating, proving that the physical-repairing of the film during the thermal treatment leads to a recovery of the protective properties of the coated system. By using laser scanning confocal microscopy (LSCM), observation of the coating defect before and after the thermal healing allowed to establish the efficiency of the polymer to cover the coating defect qualitatively. Complementary experiments using dynamic mechanical analysis (DMA) allowed to study the mechanical properties of the co-polymer under a gradient of temperature and to prove its stability during the healing treatment.

1. Introduction

One of the most common and generally established methods in the protection of metals is the application of polymeric coatings as a physical barrier between the metallic material and the corrosive environment. Nevertheless, coatings are susceptible to degradation processes and can be deteriorated by mechanical impacts during manufacturing, transport and service life which may induce a significant loss of their protective properties. In recent years, the effort to develop new organic coatings has focused on the design of self-repairing material systems. These systems having intrinsic healing properties allowing the repair of damaged areas. Healing mechanisms can be induced by a release of corrosion inhibitors which will hinder the corrosion reactions taking place on the metal surface [1,2]. Or, it can be a non-active healing in which the integrity and barrier protection of the film are (partially) recovered as microencapsulated systems containing healing agent [3–5] or thermally remendable polymers based on Diels–Alder mechanism [6–9]. A novel non-autonomous healing approach is the application of shape-memory (SM) polymers as protective coatings on metals [10–12]. SM polymers are dual-phase materials belonging to the group of polymers with intrinsic mobile capacity. These polymers have the capability of changing their shape upon exposure to an external stimulus such as heat or light [13]. SM materials are an emerging class of polymers with applications in very diverse areas such as smart fabric, heat-shrinkable tools for electronic devices, films for packaging or intelligent medical devices [14–17]. In this work, a shape-memory polyurethane (SMPU) film is used as a polymeric coating for the protection of aluminium alloys. Shape-memory polyurethanes can be processed like typical engineering polymers by conventional techniques like injection, molding, extrusion, coating and casting techniques which make them suitable for corrosion coating application [13]. In general SM materials are elastic polymer networks that are equipped with suitable stimuli-sensitive switches. The polymer network consists of molecular switches and netpoints. The SMPU polymer applied in this work is constituted of two segregated domains presenting a physical cross-linking network. The mechanism of the thermally induced shape-memory effect on linear block co-polymers is based on the thermal transition of the domains which in our case is the melting temperature of the segments [13]. Domains related to the highest thermal transition temperature (T_{perm}) act as netpoints (a hard segment) providing the mechanical strength of the material. On the other hand, chain segments with the lowest thermal transition (T_{trans}) act as molecular switches (a switching segment). If the working temperature is higher than T_{trans}, the switching domains

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are flexible, resulting in an entropic elastic behaviour of the polymer network above T_{trans}. Then, if the coating is damaged, a physical healing is expected after an increase of the temperature due to the relaxation of the "soft" domain (switching segment) which will fill the coating defect.

The final aim of the application of SM films as corrosion protective coatings is not only a physical recovery of the film by the thermal treatment. This process must be accompanied with a significant recovery of the barrier properties of the coating restoring an effective protection of the metal. At this point, the use of adequate electrochemical techniques plays an important role in the study of self-healing processes and their effect on the protective properties of the coating. Electrochemical impedance spectroscopy (EIS) is the most general method used to study changes taking place in the coating and at the coating–metal interface during corrosion events [18,19]. Although EIS provides important and fundamental electrochemical information about the barrier properties of the coatings, the spatial resolution is limited considering that healing processes and electrochemical activity in coating defects may take place at the (sub-)micrometer range. For this reason, local electrochemical techniques are emerging as complementary techniques in the field of self-healing materials. In general, these local techniques, consisting of a probe (microelectrode) scanned near to the surface provide valuable in situ information about the electrochemical activity on the studied system with high spatial resolution. In recent times, Scanning Kelvin Probe (SKP), scanning electrochemical microscopy (SECM), local-impedance spectroscopy (LEIS) and scanning vibrating electrochemical technique (SVET) have proven to be very powerful local techniques in the study of a wide variety of corroding and corrosion protective systems [20–31]. More recently, SVET has been used in the investigation of healing mechanisms by the action of corrosion inhibitors in several works [29,32–34]. However, in very few investigations local electrochemical methods have been employed for the study of non-autonomous healing processes. SVET and more recently SECM results have been published from our group in the rapidly emerging research field of self-healing coatings [5,12].

SVET is a technique which provides valuable in situ information on the behavior of the corroding system at a microscopic level and with high spatial resolution. This technique is based on the detection of electric fields generated in a solution due to a homogeneous distribution of electric charges such as ions [28]. A gradient of concentration caused by a source of ions at the metal surface results in a corresponding variation of potential in the solution. Ionic flows can arise from corrosion processes on a metal. The oxidation reactions occurring at anodic sites on a metal surface in contact with an electrolyte cause electrons to flow through the metal substrate to adjacent cathodic areas. This flow of electrons through the metal is supported by a flow of ionic current in the electrolyte, which in turn causes potential gradients to exist in the solution close to sites of localized corrosion. The measured potential variation, ΔV, can be related with the ionic currents by use of the equation [35]:

$$I = \frac{E}{\rho} = \frac{1}{\rho}\frac{\Delta V}{\Delta r} \quad (1)$$

where E is the electric field measured between two points of the solution, ρ is the resistivity of the solution, and Δr is the distance between the two extremes of the vibration amplitude of the microelectrode. The resulting signal, which is in effect a measure of the DC potential gradients in solution, can be converted to current density by a simple calibration procedure [36,37].

In the present paper, the healing capability and efficiency of a SMPU film as a self-healing coating for the protection of metals against corrosion are studied by a variety of complementary mechanical, microscopic and local electrochemical evaluation techniques. The SMPU polymer used in this work consisted of a two-segmented block co-polymer, polyurethane (PU) and poly (ε-caprolactone) (PCL) which have very different melting temperatures: 173 °C and 52 °C respectively. If the coating is damaged, a physical self-healing is expected after an increase of the temperature between the melting point of the domains which has been observed in previous works [11,12]. Indeed, with the relaxation of the soft matrix, the polymer is found to be capable to fill the damaged area while the hard segments maintain the mechanical properties. SVET is employed to visualize local variations of the electrochemical activity in the damaged area of the SMPU coating at high spatial resolution and to prove that the thermal healing process leads to a recovery of the protective properties of the coated system in the initially damaged area. By using laser scanning confocal microscopy (LSCM), a morphological observation of the damaged area in coated-samples before and after the thermal healing allows to establish the efficiency of the polymer to fill the defective area. Finally, dynamic mechanical analysis (DMA) is used to study the mechanical properties of the co-polymer under a gradient of temperature and to prove its stability during the healing treatment.

2. Experimental

2.1. SMPU coating preparation

The shape-memory polyurethane (SMPU) used in this work consisted of a two-segmented block co-polymer. It is constituted of poly-(ε-caprolactone) (PCL) as the soft domains and polyurethane segments (PUs) as the hard domains. The synthesis of the SMPU polymer containing 8 wt% of hard segment and coating application were performed as described in Refs. [11,38]. Bulk polymers were dissolved in the dimethylsulfoxide (DMSO) at a temperature of 80 °C to create 12.5 wt% solutions of SMPU. The metallic substrate was AA2024-T3 aluminium alloy sheets with a thickness of ~0.4 mm. The surface was activated prior to coating by immersing the sample in an alkaline 25 g/l NaOH solution for 5 s. Afterwards the samples were rinsed with de-ionized water. The samples were coated by bar coating at 80 °C. The distance between the bar and the substrate was 40 μm which leads to a dry-thickness of the film of ~5 μm which was measured using an Eddy current instrument. The samples were cooled to room temperature before they were annealed for 24 h at 80 °C in a vacuum oven. Subsequently, the samples were scratched with a razor blade. Thermal treatment consisted of heating the samples in an oven at 40 °C or 80 °C during 24 h.

2.2. Dynamic mechanical analysis (DMA) measurements

DMA measurements were carried out in tensile mode on a TA Instruments DMA Q800. An oscillation amplitude of 20 μm was applied to the sample, at a frequency of 1 Hz and with a force track of 125%. The temperature was increased in an oven at a rate of 2.5 °C/min from 25 °C to 100 °C under nitrogen gas shielding.

2.3. Laser scanning confocal microscopy (LSCM)

LSCM represents a complementary technique for obtaining 3D morphological information of topographically varying surfaces. A series of regularly spaced (at a minimum of 40 nm), shallow optical sections are created by displacement of the sample-table. The resulting series of optical sections are then post-processed to create a 3D representation of the surface with high lateral resolution. 3D images of a damaged area of the coating were performed by using a laser scanning confocal microscope Leica TCS NT which achieves an x-/y-resolution of 0.18 μm and a corresponding z-resolution better than 0.35 μm at λ = 488 nm. Images of the scratch in SMPU-coating