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Scanning Kelvin Probe Blister test measurements of adhesive delamination – Bridging the gap between experiment and theory

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ABSTRACT

The delamination of an epoxy-adhesive film from a zinc coated steel substrate was studied by means of the electrochemical Height Regulated Scanning Kelvin Probe Blister Test (HR-SKP-BT[1]) under controlled atmospheric conditions, applied pressure and interfacial electrode potential. The experimental studies focused on the analysis of the critical environmental water activity that leads to a corrosive delamination process under applied mechanical load and the analysis of the corrosion and delamination mechanisms at the front of delamination. The influence of applied pressure and relative humidity on the increase in the maximum blister height and the delamination rate was measured under constant polarization of the defect. 90° peel-tests were performed in order to correlate the water activity with the resulting peel force. The corrosion products that formed across the delamination front were analyzed by Raman microscopy. Through these HR-SKP-BT studies, a critical value was found for relative humidity for the delamination process. A transition zone was detected in which electrochemical degradation precedes mechanical delamination. In addition to the experimental studies, the critical energy release rates of the blister were calculated in finite element (FE[2]) simulations so as to enable a better understanding of the delamination of adhesives on metal surfaces. The combined experimental and theoretical studies show that the delamination process is controlled by the interfacial electrochemical reactions at the delamination front and that a transition area of few hundred micrometers exists in which the adhesion strength is lowered by the cathodic oxygen reduction process to a value which can be overcome by the mechanical stress in this area.

1. Introduction

The durability of structural-adhesive-bonded engineering metals is mainly determined by the ingression of water, oxygen and corrosive ions into the polymer/metal interface [1]. Water ingression leads to wet de-adhesion and, in combination with corrosive ions, to a corrosive attack in the interface region. Early models of wet adhesion and de-adhesion were developed by Brockmann and others [2]. The access of water to the interface and interfacial hydrolytic reactions play a major role in both wet adhesion and corrosion processes [3]. However, the interplay between the chemical and corrosive delamination mechanisms of adhesives is still not fully understood. On the one hand, studies have not taken the mechanics of the composites into account and, on the other hand, the mechanical aspects of the delamination of composites and adhesive interfaces have been very much highlighted in recent years [4].

The electrochemical fundamentals of the corrosive delamination of organic coatings have been intensively studied over the last twenty years [5–13]. The corresponding mechanisms for adhesives on metals, however, have only recently attracted significant interest [14,15]. While oxygen is always dissolved in adhesives in sufficiently large concentrations to sustain a cathodic undermining process, the ingress of water depends on the changes in the water activity in the environment [14].

Based on the understanding acquired of the electrochemical delamination processes, the focus has recently been placed on the development of new surface technologies for metals prior to organic paint application [16,17]. Galvanized steel and aluminum alloys, however, are adhesively bonded in the automotive industry without any chemical treatment, such as conversion chemistry, prior to the application of the adhesive. Only recently, have advanced techniques been developed for aluminum alloys, such as local laser treatments [18]. Here, the durability of the joint relies on the prevention of water

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[1] HR-SKP-BT: Height Regulated Scanning Kelvin Probe Blister Test.
[2] FE: Finite Element.

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and ion ingression into the joint. This is often accomplished by protecting joint parts with ED[3]-paint in addition to the barrier properties of the adhesive itself [19–21].

The Height-Regulated Scanning Kelvin Probe Blister Test was developed by Grundmeier et al. especially for analyzing the corrosive delamination of adhesive films on metals [22,23]. This development is based on an analysis of interfacial electrode potentials using the Kelvin probe, as published by Stratmann et al. [14,15,22,24,25]. This electrochemical technique permits contact-free, nondestructive, spatially resolved analysis of the interfacial corrosion potential between polymer films and metals based on the evaluation of the contact potential between a vibrating scanning metallic needle and the polymer-covered metal electrode. The scanning Kelvin probe has thus become a well-known and established technique for implementing nondestructive and, of course, in situ electrochemical measurements with controlled atmospheric conditions during the corrosive degradation of bare and coated metal substrates. The introduction of height regulation, based on the dependence of the AC current between the needle and the substrate on the needle-substrate surface distance, allowed for additional height regulation. This approach permits an analysis of the interfacial electrode potentials and the simultaneous characterization of the shape of a polymeric blister on a corroding metal substrate.

Based on the combination of the Scanning Kelvin Probe Blister Test and in-situ FTIR-ATR[4], Grundmeier et al. analyzed the delamination processes of adhesives in the presence and absence of an applied mechanical load [14,22]. As for organic coatings, free-standing adhesive films showed a cathodic delamination process, which was, however, accelerated by a simultaneously applied mechanical load [18,26]; the authors were able to correlate the delamination kinetics with the water activity in the environment and the applied mechanical load [14,15]. However, the authors did not quantitatively analyze the resulting mechanical stress in the delamination zone.

The fracture energy was extracted from a pressurized blister test in 1983 by Hinkley, who performed an elastic analysis of a spherical cap. An analysis of the blister test, considering blister plasticity as well as the interaction of the blister and the substrate represented by a cohesive zone model, was suggested by Liecht et al. [27]. A closed form solution for the pressurized blister, describing the transition from the bending to the stretching limit case, was developed by Arjun and Wan and compared to earlier models and a numerical solution [28]. Xu et al. [29] proposed an analysis of the peninsula blister test with allowance for the effect of residual stresses. Both finite element analysis and closed form solutions were applied by Nie et al. [30] with blister tests that employed loading by a rigid central block. More recently, a plate model for pressurized blisters was proposed by Cao et al. [31], who also considered residual stresses. Furthermore, Cao et al. deviated from the simple clamped boundary conditions at the delamination front. They did not use a cohesive law like Liecht et al. but clamping with rotational compliance. A modified test using a constant amount of pressurized gas instead of a constant pressure reveals the advantage of stable crack growth and was covered by Boddeti et al. [32].

The FEA[5] of Nie et al. used an axisymmetric model consisting of quadrilateral elements. Only the part of the blister located over the defect was modeled, while clamped boundary conditions were applied at the outer edge of the defect area. The load was applied by prescribing the vertical displacement of the nodes in the region of the central block. The energy release rate was calculated by comparing the elastic energy to a model with a slightly increased defect radius. This tallied well with the closed form solution as long as the central deflection was no larger than the blister thickness. Furthermore, the phase angle (mode-mix) was calculated from the stresses at the crack tip.

[3] ED: electrophoretic deposition.
[4] FTIR-ATR: Fourier-Transform-Spectroscopy under attenuated total reflection.
[5] FEA: Finite Element Analysis.

The concept covered in the work presented here is a combination of FE simulation and the experimental study of blister formation under controlled corrosive conditions and mechanical load. This approach involves the analysis of the blister shape and the progress of the interfacial delamination.

2. Experimental

2.1. Materials and chemicals

2.1.1. Substrates

All the chemicals and solvents were of p.a. quality. Use was made of zinc substrates (type ZE, electrically galvanized) from Salzgitter, which were cleaned with organic solvents (THF[6], IPA[7], EtOH[8]), for 10 min each in an ultrasonic bath at RT. Iron sheets, covered with an approximately 7-µm thick electrogalvanized zinc layer, were obtained from Salzgitter AG, Salzgitter/ Germany. These plates were ultrasonically degreased with organic solvents, and then alkaline cleaned, before being subsequently rinsed with ultra-pure water and dried in a nitrogen stream. As the next step, a circular hole with a diameter of 1 mm was drilled in the rear side of the metal sample (4×4 cm) through to the adhesive layer. For removing the alloy residues, the use of concentrated and tempered (60 °C) HNO_3[9] was considered. Employing this procedure, an undamaged adhesive film was obtained above the hole. These samples were used for the HR-SKP-BT investigations.

2.1.2. Preparation of adhesive films

The substrates were coated with a model adhesive consisting of three components provided by Dow Chemical (Midland/ USA): Bisphenol-A-diglycidilether (DGEBA, DER 332) and diglycidyl ether of polypropylene glycol (DGEPG, DER 736), plus the amine component Jeffamine (D 230) from Huntsman Corporation (Woodloch Forest Drive/ USA). The polymer coating was hardened for 2 h at 130 °C. To form a uniform layer, two spacers (one layer of magic tape, two layers of Scotch tape) were placed at the end of the sample, and use was made of a polycarbonate block wrapped with aluminum foil with an applied pressure of 50 g/cm^2 (sandwich technique). The thickness of the adhesive film (120 ± 30 µm) was confirmed by an electric sliding caliper. The samples were exposed to humid air (> 90% r.h.) for 1 h at 40 °C before employing the HR-SKP-BT method in order to prevent any electrostatic charging of the polymer.

2.2. Analytical methods

2.2.1. Height regulated scanning Kelvin probe blister test

To investigate the epoxy amine/zinc oxide interface stability, the HR-SKP-BT measurements were carried out using a custom-made SKP, which is described in [22]. The vibrating needle of the scanning Kelvin probe was made of CrNi and had a diameter of 50 µm. Based on the simultaneous analysis of the Volta potential difference between the needle and the adhesive surface, and the current flow between the substrate and the needle which form a capacitor, both the interfacial electrode potential and the topography of the blister can be studied [22]. The height regulation is based on the value of the alternating current of the capacitor measured at low frequency while the potential measurements is based on the high frequency analysis of the zero crossing of the current [22].

The blister hole was filled with 0.5 Mol NaCl solution and the sheets were fixed on the sample carrier. The area around the defect was polarized to −1.2 V_{SHE} in a three-electrode arrangement (platinum counter electrode, an Ag/AgCl-reference electrode and a grounded

[6] THF: tetrahydrofuran.
[7] IPA: isopropyl alcohol.
[8] EtOH: ethanol.
[9] HNO_3: nitric acid.