



ELSEVIER

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

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

Ageing mechanisms of polyurethane adhesive/steel interfaces

J. Weiss^a, M. Voigt^a, C. Kunze^a, J.E. Huacuja Sánchez^b, W. Possart^b, G. Grundmeier^{a,*}^a University of Paderborn, Technical and Macromolecular Chemistry, Warburgerstr. 100, D-33102, Germany^b Saarland University, Chair for Adhesion and Interphases in Polymers, Campus C 6.3-6, D-66123 Saarbrücken, Germany

ARTICLE INFO

Article history:

Accepted 25 June 2016

Available online 29 June 2016

Keywords:

Polyurethane
Adhesive
Steel
Corrosion
Interface

ABSTRACT

For the achievement of a complete understanding of the ageing and corrosion of adhesively bonded steel substrates, both the ageing of a polyurethane reference adhesive and the simultaneous corrosion of a mild steel substrate were studied by combined spectroscopic, electrochemical and microscopic techniques. A corundum-blasted mild steel was used as metal substrate in combination with a cross-linked reference polyurethane adhesive free from additional additives or fillers. The ageing was performed under full immersion in a chloride-free aerated electrolyte at elevated temperature. A strong influence of the water saturated polymer phase on the change in the interfacial oxide film structure of the metal substrate was observed. The thickening and hydroxylation of the metal oxide film during the corrosive delamination of the polyurethane film indicated that the de-bonding mechanism of the polyurethane adhesive is mainly based on interfacial water enrichment and a thereby induced growth of the interfacial oxide. The measured electrochemical properties of this oxide indicate that it is highly conductive and allows for oxygen reduction as the counter reaction to metal oxidation.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The corrosive degradation of adhesively bonded steel joints is of significant importance for many technical applications. In most cases such adhesively joined structures are exposed to corrosive environments and the functionality of the component relies on the durability of the joint over long times of exposure. However, it has been observed that the bonded joint experiences a decrease in shear strength after industrial ageing tests or in the field [1–5]. As the durability of such a joint is based on the ageing of the steel/adhesive composite system, the overall observation of loss in performance is not sufficient to clarify the underlying critical mechanisms of degradation.

The fundamental mechanisms of corrosive delamination of organic coatings and adhesives so far have been mainly studied in their initial states neglecting the ageing process of the polymer phase itself [6,7]. Mainly, free standing adhesive films, not adhesive joints, were studied to predict critical mechanisms of corrosive delamination [8–11]. Wapner and Posner combined spectroscopic, microscopic and electrochemical techniques such as the Scanning Kelvin Probe to reveal the corrosive delamination process of epoxy adhesive films on steel and galvanised steel [12,13]. They could show that the cathodic oxygen reduction reaction

dominates the delamination for epoxy adhesive coated mild steel substrates [13]. Wapner et al. could moreover reveal by means of FTIR-spectroscopy the kinetics of water transport into these adhesive joints. Their studies showed the crucial role of interfacial water activity in combination with corrosive anions which attack the ultra-thin surface oxides of the metal alloys [12]. However in such studies, the state of ageing of the adhesive/metal interface prior to the analysis of the corrosive de-adhesion process was neglected. Moreover, the analytical approaches which considered free-standing adhesive films, led to an acceleration of the access of water and oxygen through the open surface of the adhesive film.

Meiser et al. considered mainly the chemical ageing of several epoxy networks both at the free contact to the environment (moist air or water at different temperatures) and at the buried contact between the adhesive and metals (Al, Cu, Au) [14]. The authors showed that the chemical degradation of the epoxy network responds to the ageing temperature. For given temperature, it follows similar basic steps of oxidation in both regions but the kinetics and the hierarchy of these reactions are different in both regions. Water significantly accelerates these oxidations, especially for moderate ageing temperatures. Copper migrates deeply into the epoxy and forms amine complexes [15]. Moreover, the ageing regimes change the network morphology and the mechanical properties to some extent, in addition to the plasticisation and the shift of the glass transition due to the diffusive uptake of water [16].

* Corresponding author.

E-mail address: g.grundmeier@tc.uni-paderborn.de (G. Grundmeier).

Due to the wide range of chemical and structural variations that can be achieved with polyurethanes, their ageing behaviour cannot be discussed in general terms. Concerning the poly(ether urethanes) utilised in this work, the literature attests very good stability to such polymers, at least under mild conditions in the dark. For example, thermoplastic poly(ether urethane) improved compatibility between hard and soft segments during aging at temperatures from 40–70 °C for up to 300 days but degradation did not occur [17]. Another technical poly(ether urethane) for bio-applications resisted chemically to water at 95 °C and dry air at 90 °C for up to 56 days [18]. In crosslinked systems the stability against chemical degradation is similar. Hints of hydrolytic aging are observed in a poly(ether urethane) coating after 100 days of ageing in salt water above a threshold temperature of 70 °C [19]. Lower temperatures do not start a chemical degradation in this material even if this is aged up to 18 months. A crosslinked poly(ether urethane) used as a shape memory polymer does not show any chemical degradation of the urethane bond while being stored at 60 °C during 180 days [20]. Ageing of polyurethane adhesives is rarely studied. The few reported results indicate a good stability of the urethane groups, as shown in [21] for medical poly(ether urethane) adhesive in distilled water or physiological solution at 20 °C and 100 °C, respectively. In summary, the ageing behaviour of poly(ether urethane) deserves further attention. Particularly, this holds for the situation in a polyurethane adhesive joint.

Based on these findings the study reported here is focused on the interplay between the water up-take and ageing of a polyurethane adhesive and the interfacial chemistry and electrochemistry of the mild steel substrate in an adhesive joint. Reference materials were employed in this study to reduce the complexity compared to technical adhesives while keeping the principal materials properties as close as possible to the application.

2. Materials and methods

2.1. Materials and chemicals

Sheets (2 × 20 × 130 mm³) of S235 mild steel alloy were utilised as adherend. Just prior to bonding, the sheets were solvent cleaned in an ultrasonic bath with a sequence of solvents (tetrahydrofuran (purity > 99.5%), 2-propanol (97%), ethanol (99%)) for 10 min each step.

Then, they were grit blasted (white corundum from EW Würth, Bad Friedrichshall, Germany, grain size 125–180 μm, blasting with dried air at 6 bar, angle 90°) at room temperature (RT). Loose corundum particles and dust was removed by acetone washing in an ultrasonic bath. The elemental composition of the corundum particles is shown in Fig. 1.

Besides Al₂O₃ and the usual carbonaceous surface contamination, the corundum particles contain some sodium and calcium

most probably as carbonates as sodium and calcium ions are not stable under atmospheric conditions.

Except the area for adhesive bonding (100 × 20 mm²), all faces and edges of the steel sheets (130 × 20 mm², 2 mm thick) were protected with a 3-layer anti-corrosion coating (Sika Zink R, EG 5 and EG1, Zurich, Switzerland). Finally, for reproducible cleanliness, the bonding area was gently blasted with pressurised dried air.

The reactive PU adhesive is formulated from three technical monomers (Bayer Material Science, Leverkusen, Germany): The diisocyanate Desmodur VP.PU1806 consisting of the isomers 2,4'-methylene diphenyl diisocyanate (2,4'-MDI, 53.7 mass%), 4,4'-MDI (46.2 mass%) and 2,2'-MDI (0.1 mass%), the polyether diol Desmophen 3600Z, and the polyether triol Baygal K55 as the crosslinker. For their chemical formulae, see Fig. 2.

The triol and diol monomers were mixed (OH group ratio OH_{triol}:OH_{diol} = 90:10 mol-%). The MDI isomer mixture was added slowly up to the stoichiometric ratio of hydroxyl and isocyanate groups. All components were handled and stirred at RT in dried air (dew point below –50 °C). For removal of dissolved gas, the monomer mixture was evacuated at 0.01 mbar for 15 min.

Curing of bulk samples at RT (ca. 23 °C) for 7 days plus 7 days at 60 °C in dried air results in a fully cured polyurethane network (the caloric glass transition extends from ca. –18 °C to +59 °C with T_g = 27.3 °C).

2.2. Preparation of adhesive joints

Right after the final step of steel surface treatment, adhesive joints (bonding area 20 × 100 mm²) were prepared at RT by filling the space between two steel sheets with the liquid reactive adhesive (average thickness of 500, 300 and 100 μm) by a syringe. Bonding was carried out immediately after the adhesive was mixed (cf. previous section) and in the same dried atmosphere. The bond line thickness was set by two polytetrafluoroethylene separators which were placed between the two steel substrates but outside the bond line. The adherends were fastened upright in a metal jig keeping the bond line at the desired thickness. Except for the upper slit, all sides of the bond line were sealed by adhesive tape in order to avoid liquid reactive spill out. The joints were then cured in the same two-step regime as bulk samples for full crosslinking and stable mechanical properties.

2.3. Ageing regime

The fully cured samples (bulk and adhesive joints) were immersed in bi-distilled water at 60 °C as sketched in Fig. 3. They were taken from the bath for analysis at different times from 7 to 180 days. The water was not exchanged during the course of ageing.

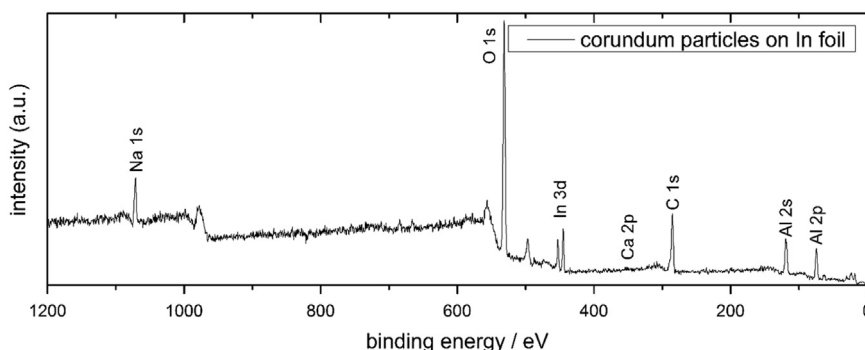


Fig. 1. XPS survey spectrum of corundum on an indium foil.

Download English Version:

<https://daneshyari.com/en/article/776042>

Download Persian Version:

<https://daneshyari.com/article/776042>

[Daneshyari.com](https://daneshyari.com)