



Studying interfacial bonding at buried polymer–zinc interfaces



P. Taheri^{a,b}, H. Terry^{a,c}, J.M.C. Mol^{b,*}

^a Materials innovation institute (M2i), Elektronicaweg 25, 2628 XG Delft, The Netherlands

^b Delft University of Technology, Department of Materials Science and Engineering, Mekelweg 2, 2628 CD Delft, The Netherlands

^c Vrije Universiteit Brussel, Department of Electrochemical and Surface Engineering, Pleinlaan 2, B-1050 Brussels, Belgium

ARTICLE INFO

Article history:

Received 28 January 2015

Received in revised form 14 March 2015

Accepted 20 March 2015

Available online 28 April 2015

Keywords:

Metal oxide

Polymer coatings

Interfaces

Adhesion

Delamination

Model compounds

ABSTRACT

This manuscript is a critical appraisal of our recent studies on the possible parameters influencing the interfacial bonding properties between carboxylic polymers and Zn surfaces as well as approaches to effectively understand interfacial phenomena. It has been shown that different surface pretreatments result in a set of ranging chemical compositions, morphologies, roughnesses and semiconductor properties, while each parameter in turn influences the interfacial properties. Moreover, polymer functional groups available for interfacial interactions effectively influence the interfacial phenomena. To overcome the limited analytical depths of the available spectroscopic techniques to study underneath thick polymer coatings, i.e. buried interfaces, several approaches are examined in this study. Polymer and metal interfaces are modeled by adsorption of the representative functional molecules forming thin semi-monolayers on the metal surface. Towards understanding the real polymer and metal interactions, polymer coatings were mechanically removed from the metal surface and residue layers were shown to exhibit the metal and polymer interface. Moreover, interfaces were analyzed by means of Kretschmann geometry in which a thin metallic substrate was deposited on an internal reflection element. In this case, an electric field passes the metallic substrate and reaches the metal and polymer interfaces. Both formation and degradation of the interfacial bonding in dry and wet conditions were analyzed respectively. The later case was integrated with electrochemical impedance spectroscopy to obtain a thorough understanding of the ongoing polymer degradation and interfacial electrochemical interactions.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Corrosion protective polymer coatings should retard water, oxygen and ionic diffusion to provide enduring protection of the metal substrate. Nevertheless, due to the existence of micro- and macroscopic pathways in polymer structures, ions can reach the metal surface. In that case, the corrosive medium accumulates at the metal–polymer interface leading to initiation of cathodic and anodic reactions, typically oxygen reduction and metal oxidation reactions [1]. Anodic undermining or cathodic delamination may lead to interfacial bonding deterioration. Because of the bonding degradation, the polymer at the defect edges starts to delaminate from the metal surface accelerating the diffusion of ions and water molecules at and towards the interface.

The interfacial bonding degradation and delamination rates depend on several aspects depending on the metal surface and

polymer properties. Hereto, interfaces are evaluated from several disciplinary fields, e.g. metal surface and polymer physics and chemistry, etc. Since adhesion is provided by physicochemical interaction between the metal surface and polymer [2], the polymer density at the interface and the interfacial bonding mechanism are important factors determining the adhesion level and interfacial durability.

This manuscript reviews different aspects of the metal–polymer interfaces and integrity assessment methods. In this case, the interfacial bonding properties are correlated to polymer and metal surface properties while a wide range of spectroscopic and electrochemical methods and approaches are described to obtain a comprehensive understanding of the interfacial properties. Fig. 1 schematically illustrates the research approach. First, model compounds are applied on the differently pretreated metal surfaces and the formed interfacial bonding properties are evaluated. Furthermore, the interfacial bonding mechanisms due to the residue polymer coatings are characterized as well. Finally, the interfacial bonding formation and degradation of the carboxylic polymers are assessed by means of spectroscopic and electrochemical methods.

* Corresponding author.

E-mail address: J.M.C.Mol@tudelft.nl (J.M.C. Mol).

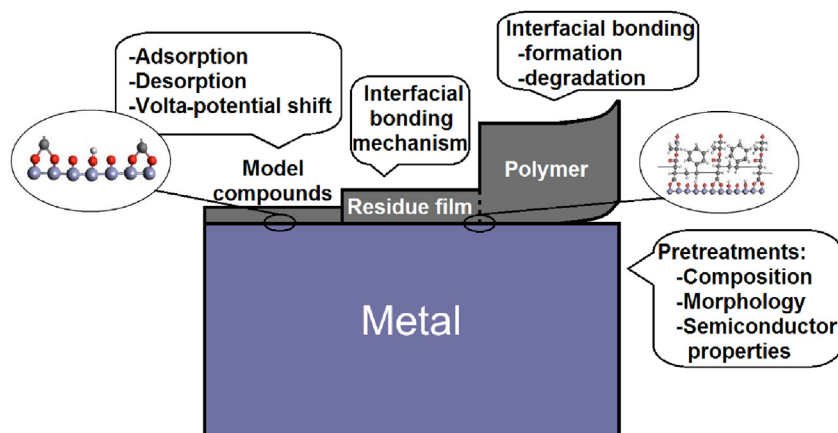


Fig. 1. Schematic sketch of the research approach.

2. Research assumptions

To evaluate the fundamentals of interfacial bonding properties between the metal surface and polymer coatings a thorough control of the experimental parameters is essential to scrutinize the underlying mechanistic principles. However, metal surfaces, e.g. galvanized steel surfaces are composed of various elements such as Zn, Fe, Al, Mg, etc., according to the steel grade, bath composition and the subsequent heat treatments [3,4]. This prohibits a mechanistic interfacial study and increases the system complexity. Consequently, pure Zn sheets (99.95%) supplied by Goodfellow are selected in this study as a model galvanized steel substrate to develop the fundamental knowledge and understand the interfacial mechanisms. This provides a solid basis for further researches based on applied approaches.

Moreover, various industrial pretreatments and cleaning procedures are widely applied on metal substrates to improve the polymer adhesion [5]. The solutions used for the treatments are composed of different organic and inorganic components changing the surface properties, the extent of which is hardly controllable. Consequently, in this study a set of different aqueous solutions ranging from acid to alkaline were prepared to provide different well-defined surface compositions.

On the other hand, polymer coatings are mainly composed of various components such as solvents, adhesives, pigments, etc. [6,7]. Each of these additives may influence the metal-polymer interfacial bonding properties. Adhesives are the functional groups determining the interfacial bonding characterizations [8–10]. Carboxylic functional groups such as polyesters are often used in industrial polymer coatings because of their desirable structural and interfacial performances [11,12]. Consequently, they have been used in this study to scrutinize their role in adhesion mechanisms and performance.

3. Interfacial variables

3.1. Surface oxide properties

The surface oxide property is a key factor governing the metal surface-polymer interface and consequently the system integrity [13,14]. In this case, a proper surface pretreatment is expected to permanently change the oxide surface chemistry as well as morphology and/or roughness. A change of surface chemistry is expected to adjust the surface electronic and semiconductor properties as a result of variation of doping concentration type and/or

density as well as charge carriers [15–17]. In this study, model pretreatments are defined to thoroughly control surface properties.

3.1.1. Surface oxide composition

According to the Pourbaix diagram [18] exposing Zn to solutions at different pHs and applied external potentials results in obtaining a range of surface compositions. In this study, pretreatments are outlined accordingly to obtain different surface compositions. Table 1 shows the experimental parameters defined for the surface pretreatments and the measured hydroxyl fractions by means of X-ray photoelectron spectroscopy (XPS).

Different pretreatments result in various hydroxyl fractions obtained on the untreated (25%) and differently treated zinc samples (Table 1), while the hydroxyl fraction increases gradually from sample 1 to 5. The reason behind formation of different oxide/hydroxide fractions on zinc samples lies on formation and growth mechanisms. Dirkse [19] showed that the oxide/hydroxide formation on zinc substrate proceeds by formation of $\text{ZnO}/\text{Zn}(\text{OH})_2$ and subsequently dissolving the formed compounds to $\text{Zn}(\text{OH})_3^-/\text{Zn}(\text{OH})_4^{2-}$ in the electrolyte. Since the dissolving step proceeds by charge transfer reaction, the process proceeds when the system reaches a thermodynamic equilibrium state, the level of which is strongly correlated to the electrolyte composition and temperature.

The low portion of hydroxyl fraction formed on sample 1 can be explained by the low pH (5.4) of 0.05 M HCl solution used for the treatment. In this case, according to the Pourbaix diagram, the treatment resulted in dissolution of a considerable fraction of surface hydroxyls and formation of metal oxides. On the other hand, the high portion of hydroxyl fraction formed on sample 3 and 5 can be ascribed to the alkaline solutions used for the treatments resulting in oxide dissolution in favor of hydroxyl formation towards reaching an equilibrium state. The high hydroxyl fraction formed on sample 5 is achieved by the application of an external potential as well as the buffering effect of boron components in the solution used.

It can be seen that the hydroxyl fraction detected on the sample treated in water at 25 °C is considerably higher than that of the sample treated in water at 65 °C. It is noticeable that the temperature plays a substantial role in the oxide/hydroxyl formation on zinc surfaces. Formation of hydroxyl on the zinc surface is under a mixed control of diffusion/activation and an increase in the temperature appears to prolong the hydroxyl formation time [20]. Kotnik [21] and Gilbert [22] reported that zinc hydroxyl is usually produced in cold water (0–30 °C) whereas in hot water (30–90 °C) the surface product is mainly zinc oxide. On the other hand, when the sample treated in hot water is exposed to the ambient air, water molecules

Download English Version:

<https://daneshyari.com/en/article/692240>

Download Persian Version:

<https://daneshyari.com/article/692240>

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