On the Importance of the Chemical Interface between Organic Coatings and Metals

Herman Terryn¹,², Tom Hauffman¹, Sven Pletincx¹, Abrahami Shoshan², Laura-Lynn², Arjan Mol²

¹ Vrije Universiteit Brussel, Department of Electrochemical and Surface Engineering, Pleinlaan 2, B-1050 Brussels, Belgium.

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

hterryn@vub.ac.be
Introduction

Aspects determining the protection efficiency:

- coating chemistry: constitution, composition...
- Interface: oxide surface and bulk properties
  - acid-base properties
  - hydroxyl fraction
  - surface energy
  - surface contamination
  - stability
  - IEP
- composition
- structure
- stability
- electronic properties

Delamination: local electrochemical activity

General idea is not to work on real systems but on model systems where we control everything from metal composition, oxide film, interface and polymer coating
Influence of the interface on delamination

Delamination controlled by cation migration along the oxide/coating interface

Delamination study of epoxy coating from carbon steel

![Scanning Kelvin Probe (SKP)]

- Delamination is under control of ion mobility at the interface.
- Zirconia treatment effectively decrease the delamination of epoxy coated carbon steel samples.

\[ i = 1, \ ii = 7, \ iii = 18, \ iv = 25, \ v = 35, \ vi = 45 \] and \[ vii = 56 \] hours


Based C. Leygraf RTH Stockholm
Interfacial bonding of epoxy coating with ATR-FTIR

Zr conversion layer increase the interfacial bonding at epoxy/iron interface.

**EIS measurements**

![EIS measurements graph](image)

- Zr-treated cause changes in middle and low frequency range.

Study of the same molecular interface but buried under simple polymer films films

Polymer A

Polymer B
EIS study the interfacial bonding degradation in a Kretschmann geometry

Polymer A

Polymer B

Effective diffusion blockage by polymer B

relatively fast water ingress

Corresponding Nyquist plots of polymers collected at different exposure periods.

Water ingress for polymer A is followed by interfacial degradation (>10h) corresponding to disappearance of carboxylate bonding in FTIR analysis.

Study the interfacial bonding degradation in a Kretschmann geometry

Destruction of the molecular interface: disappearance of carboxylate bonding peaks

Little water ingress nor Zn hydroxide formation

No destruction of the molecular interface

Water at the interface and formation of Zn hydroxides

FTIR analysis

Chemical interface under polymers

- Adsorption
- Desorption
- Volta-potential shift

Model compounds

Interfacial bonding mechanism

Interfacial bonding
- formation
- degradation

Pretreatments:
- Composition
- Morphology
- Semiconductor properties

Form monomers to buried interface increase of complexity

Fe$_2$O$_3$/ZnO/ ZrO$_2$

Zn/Fe
PAA (polyacrylic acid)
- used for corrosion protective coatings

myristic acid
- single carboxylic acid group
- attached to CH₂/CH₃ tail

PP-MA model compounds on 5 different oxides:

- ring opening and formation of carboxylate for all types
- carboxylate anion bonded in a bridging bidentate manner

- some changes observed in peak distance
- mainly due to changes in shape of the symmetric stretching peak
- might be related to strength/stability of the carboxylate/Al bond?
Results; model adhesion molecules>

Bonding /reaction of PP-MA model compound
succinic acid with aluminium oxide surface>

- hydroxyls on oxide cause
deprotonation of acid
(COOH → COO⁻)
- water molecule formed
- desorbed from surface

- carboxylate ionically (very strongly!) directly bonded to Al cations

carboxylate anion (COO⁻) formed due to reaction between carboxylic acid groups
and oxide surface

van den Brand J, Terryn H., de Wit H. LANGMUIR 20 (15): 6308-6317 JUL 20 2004
Reactivity of oxides towards chemical bonding:

- Myristic acid ads. on oxides, rinsing-off non-bonding
- Amount strongly bonded (carboxylate anion) evaluated from integrated FTIR peak intensities

More OH groups → more bonding molecules!

The interactions between the three types of monomers and the zinc substrate resulted in the formation of a bridging bidentate coordination state implying the contribution of the same functional groups in the adsorption mechanism.

The frequency shifts of the carboxylate stretchings, $\Delta \nu$(COO)$=\nu_{as}$(COO$^-)$-$\nu_{s}$(COO$^-$), are 180, 82 and 169 for succinic acid, myristic acid and succinic anhydride.

Link with the hydroxide fractions.

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Figure 3. Proposed adsorption configuration of (a) succinic acid, (b) myristic acid molecules and (c) ring opening procedure of the succinic anhydride and formation of succinic acid molecules on zinc substrates.

Taheri P, Wielant T, Hauffman T, Flores J, Hannour F, de Wit JHW, Mol JMC, Terryn H
ELECTROCHIMICA ACTA 56, 4, 1904-1911 2011
FIB cross-section of 0.1 wt% PAA/ethanol deposition

TEM EMAT Antwerp

S. Pletincx; A. Head; O. Karslıoğlu; L. Fockaert; J.C Mol; Hendrik Bluhm; H. Terryn; T. Hauffman; in preparation
Polymer deposition: in-situ adsorption at the interface of polymer on aluminium oxide

0.01 wt% PMMA/toluene solution against Al oxide/air background

- Increase in peak area of OH (3426 cm\(^{-1}\)) at interface.
- Increased amount of carboxylate anion bond (1640, 1523, 1463 cm\(^{-1}\)).
- COO\(^{-}\) peak area increases, Al-O peak area decreases
In-situ effect of borate buffer on the PAA/aluminium oxide interface

Coating adsorbed from 0.01 wt% PAA/ethanol solution. Then exposed to 0.1 M aqueous borate buffer. Against coated aluminium oxide/air background.

- Increase in peak area of H$_2$O (3426 and 1655 cm$^{-1}$) at interface.
- Increased amount of carboxylate anion bond. Increased wet adhesion.
- COO$^-$ peak area increases, Al-O peak area decreases

![Graph and data](image-url)
Near Ambient Pressure XPS
Collaboration H. Bluhm Berkeley

- SPECS Phoibos 150 NAP

- Differential pumping allows pressure differences, 4 orders of magnitude between chamber and first stage.

- 100 W, large x-ray spot to reduce photon flux and prevent beam damage.
Interface of PAA/ native aluminium oxide in vacuum

Both C 1s and Al 2p peaks can be observed

→ Polymer film is deposited

→ Information of interface is present.
Normalized at $x = 282$ eV. Overlay PAA.

C 1s
Normalized at $x = 529$ eV. Overlay PAA.
Interface of PAA/ native aluminium oxide in vacuum

![Graph showing the binding energy of C 1s and O 1s](image)

- **O 1s**
- **C 1s**

**Data**
- Fit
- CC
- Beta C
- CO
- COO-
- COOH

**Intensity (a.u.)**

**Binding Energy (eV)**

Values range from 294 to 282 eV.
As the H₂O pressure is increasing more carboxylic acid functional groups are deprotonated and carboxylate anion groups are formed.

The amount of ionic bonds at the PAA/aluminium oxide interface increases in humid environments.

Conclusions

- In-situ FTIR Kretschmann measurements show formation of carboxylate bond at interface of both PAA and PMMA / aluminium oxide interface from the polymer solution.

- If an electrolyte is present, H$_2$O diffuses through the polymer layer and can immediately be detected at the interface. This leads to an increase in the amount of carboxylate bonds at the interface of both hybrid systems in the beginning.

- Near Ambient Pressure XPS can be used to investigate model hybrid interfaces by the use of ultrathin (< 10 nm) polymer depositions. Carboxylate anion bonds are observed at 3.4 eV binding energy shift w.r.t. 285 eV.

- Atmospheric conditions up till 5 Torr (30% RH) of H$_2$O were simulated in the chamber.
  - At the PAA/aluminium oxide interface, the amount of carboxylate anion bonds formed increased when water was added to the chamber.
  - Currently the same work is done on PMMA/aluminium oxides
New Approaches ToF-SIMS ion clusters
AFM combination

True 3-D chemical mapping!
Positive Ion Mass Spectra

Δ immersion time
0.001 wt.% SA

Zn – 3’ 0.001 wt.% SA
Zn – 5’ 0.001 wt.% SA
Zn – 7’ 0.001 wt.% SA
Zn – 9’ 0.001 wt.% SA
Zn – 15’ 0.001 wt.% SA

H⁺ peak widths
1.00 ns
1.03 ns
0.99 ns
1.02 ns
1.07 ns

Higher resolution and intensity compared to analysis BATCH 1

60s acquisition time
Can we model some of these approaches?

Combined Molecular Dynamics Simulations and Quantum Mechanics

Calculated interaction energy of aminoamide-modified epoxy resin adsorbate molecules with the hydroxylated Fe3O4(100) surface as a function of OH fraction.

“A Close-Up on Iron Oxide Type Effect on the Interfacial Interaction Between Epoxy and Carbon Steel: Combined Molecular Dynamics Simulations and Quantum Mechanics” Ghasem Bahlakeh, Mehdi Ghaffari, Mohammad Reza Saeb, Bahram Ramezanzadeh, Frank De Proft, Herman Terryn-Journal of Physical Chemistry C, 2016 DOI: 10.1021/acs.jpcc.6b03133
Molecular dynamics simulations using Reactive Force Fields (ReaxFF). Characterization of the adhesion and delamination of epoxy/alumina interfaces and how they are affected by water.
Chemical Interface between Organic Coatings and Metals

- Kelvin potential measurements show us that the delaminations is function of the prepration of the metal oxide in terms of nature of the oxide and termination groups
- In situ EIS combined with in situ IR show us that there is a link between electrolyte transport, arrival at the interface and in situ modifications under the coatings
- So there is a need to probe the interface under the coatings
- Step from ‘molecular adsorption’ to ‘coating’ is difficult from analytical point og view
- Buried interfaces can be studied by means of ATR-FTIR Kretschmann and we are trying by TOF-SIMS Ar gun clusters
- XPS on thin polymer films allows us to move to NAPXPS
- Combined in situ EIS ATR-FTIR Kretschmann and NAPXPS allows us to follow interface changes as function of electrolyte ingress in coatings
- Quantum chemical calculation can support some of the findings

- We think the approach is relevant for industrial applications as shown by other contributions during this week (Shoshan Abrami, Laura-Lynn Fockaert)
  - But we need to work on model systems this is a fight with the companies