

## Summary: The Formation and Degradation of Interactions at Polymer/Metal Oxide Interfaces

### Scope

Hybrid polymer/(hydr)oxide/metal systems such as adhesive bonding and organic coatings are established industrial technologies. However, these important technologies suffer of several technological problems of strategic importance. The most important problem includes the loss of adhesion strength in the presence of humidity and ionic compounds. The durability of the entire system is largely determined by the interface between the organic layer and the metal oxide. Unfortunately, the investigation of the binding and degradation mechanisms occurring at the interface region is not an easy task as this region is masked by a  $\mu\text{m}$  thick polymer layer on one side and a thick metal (oxide) on the other. Therefore, this region is often called the buried interface. Current state-of-the-art methodologies risk to modify this region or use a destructive way of analysing the interface. Therefore, it is the aim of this PhD project to unravel the interface of hybrid organic/metal oxide systems by obtaining local chemical state information while simultaneously probe the effect of moisture and ions of an electrolyte without the risk of modifying the chemical state of the interface by the utilized analysis approach or destructive techniques.

In this work, model systems are chosen of which the interface is in situ studied under varying environmental conditions, without exposing the interface to the atmosphere. For the metal oxide substrate aluminium is selected because it is an important structural engineering metal. It is the most widely used non-ferrous metal and has applications in transportation, packaging, machinery, building, construction, etc. Pure aluminum forms spontaneously an ultrathin surface oxide and oxyhydroxide film under ambient conditions, a so-called native oxide layer. Surface adhesive and corrosion properties are thereby determined not only by the bulk composition but by the surface of the native oxide that is formed. In order to simplify the complex delamination processes that might occur, the environmental conditions during the experiments are selected to be in the passive region of aluminum oxide. This to prevent the occurrence of any corrosive de-adhesion processes and solely investigate molecular interfacial interactions. As a polymer, two types are chosen to investigate and to compare.

The first type is a carboxylic acid model system, more specifically polyacrylic acid (PAA). A second model coating is an ester model coating: polymethyl methacrylate (PMMA). Carboxylic acid based polymers are often used as adhesion promoters in nowadays coating formulations. The reason for their use is that empirical observations showed that they actively promote adhesion, especially in wet conditions. Ester based polymers are also often used in primer applications to increase adhesion properties. By the application of a new generation of techniques, the influence of external conditions such as changing ambient conditions like the direct influence of water or ionic compounds will be investigated.

### Short term aqueous exposure at the interface of carboxylic acid and ester model coatings on aluminium oxide

The reactive adsorption of the carboxylic acid model polymer polyacrylic acid onto the surface of the native aluminum oxide is studied in situ from a PAA/methanol solution by infrared spectroscopy. Afterwards, the system is exposed to humid conditions to monitor the short term effect of water on the interface. First, the polymer layer is made sufficiently thin to access the interface by means of X-ray photoelectron spectroscopy (XPS). We characterized the formation of a carboxylate ionic bond at the interface with ambient pressure XPS (APXPS). When water is dosed in the APXPS chamber up to 5 Torr ( $\pm 28\%$  relative humidity), an increase in the amount of ionic bonds at the interface is observed in the C 1s spectrum (Figure 1). The combination of the thin film approach with APXPS opens up the possibility to expose hybrid systems to a wide variety of gas mixtures, simulating near-realistic conditions in the XPS analysis chamber. The only disadvantage of this technique is the upper gas pressure limit. The maximum attainable pressure in the analysis chamber is limited since the gas phase attenuates the photoelectrons that are detected, currently this limit is approximately 20 Torr. The obtained results show that water has a mediating role at the interface, leading to the formation of more ionic bonds.

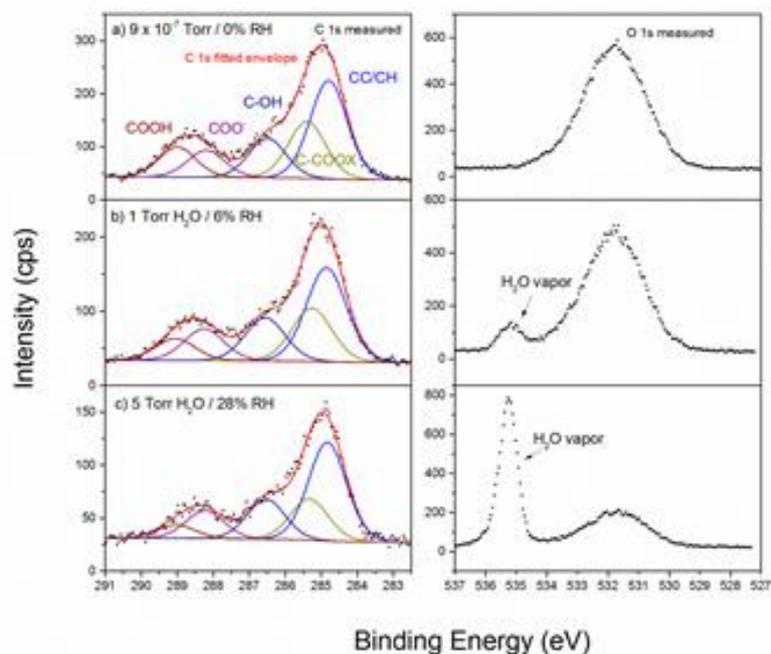


Figure 1: C 1s (left) and O 1s (right) APXPS spectra of an ultrathin PAA film on native aluminum oxide at varying water vapour pressures.  $9 \times 10^{-7}$  Torr (a), 1 Torr H<sub>2</sub>O (b), 5 Torr H<sub>2</sub>O (c).

The interfacial interactions of ultrathin polymer films were also investigated with ATR-FTIR in the Kretschmann geometry. This technique allows to create an infrared spectrum of the near-interface region, giving valuable information on the chemical state of species located at the interface. An electric field can still pass through a thin metal oxide film, which opens up the possibility of investigating the interface by infrared spectroscopy. This is possible when the metal oxide film is deposited on an Internal Reflecting Element (IRE) crystal and not thicker than 50 nm (otherwise the metal film will absorb the infrared light). ATR-FTIR Kretschmann is an excellent technique to characterize interfacial interactions in situ, when a metal oxide film is in contact with a dilute polymer solution. We investigated a PAA adsorption from a PAA/methanol solution. The formation of ionic bonds was shown, more specifically carboxylate anion bonds, with the aluminum oxide surface during the reactive adsorption process. The thin film depositions were also exposed to an aqueous electrolyte while the interface was investigated in situ. This allowed to observe the initial increase of ionic bond formation due to the diffusion of water molecules arriving at the hybrid interface. These observations were in accordance with the APXPS measurements.

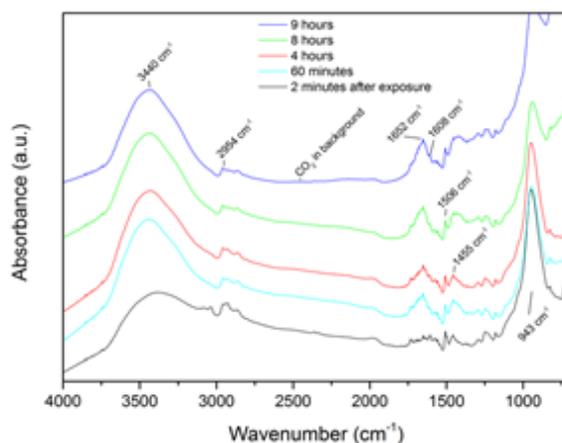


Figure 2: ATR-FTIR Kretschmann spectra of PMMA on native aluminum oxide. Spectra were taken at different times after exposure to a 0.1 M borate buffer solution. Showing the formation of carboxylate bonds and the build-up of water.

The effect of water on the interface of ultrathin PMMA and aluminium oxide were also shown with APXPS and ATR-FTIR Kretschmann (see PhD manuscript) and additional molecular structure information was obtained by using ToF-SIMS analysis (shown in Figure 3).

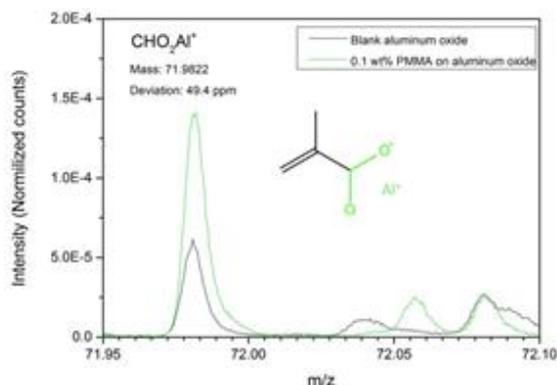


Figure 3: ToF-SIMS spectra showing a fragment ( $\text{CHO}_2\text{Al}^+$ ) that indicates the carboxylate bond between PMMA and aluminum oxide.

The combination of the obtained results from ToF-SIMS, APXPS and ATR-FTIR Kretschmann on both PAA and PMMA coated aluminum oxide resulted in the proposal of adsorption mechanisms showing the mediating role of water molecules in the bond formation and degradation.

### Long term aqueous exposure at the interface of carboxylic acid and ester model coatings on aluminium oxide

The bonding states of the carboxylic acid model and the ester model polymer onto the aluminum oxide surface are compared after long term aqueous exposure. An integrated setup, combining Fourier transform infrared spectroscopy in the Kretschmann configuration with odd random phase multisine electrochemical impedance spectroscopy (ORP EIS) allows us to characterize the bonds formed at the interface, while simultaneously monitor changes induced by the effect of water diffusion at the interface both chemically and electrochemically. By using the odd random phase multisine approach, it is possible to obtain information of the whole hybrid system in the same time frame as when the interfacial infrared spectra are collected. This allows us to make a direct comparison between the recorded impedance and infrared data (Figure 4). Moreover, the integrated setup is used to monitor aqueous influences on the interface over long exposure times. The onset of disbonding and delamination of the organic coating is investigated. The effect that a different pretreatment step of the aluminum oxide has on the formed bonds at the interface, and thus on the overall interfacial stability, is also investigated.

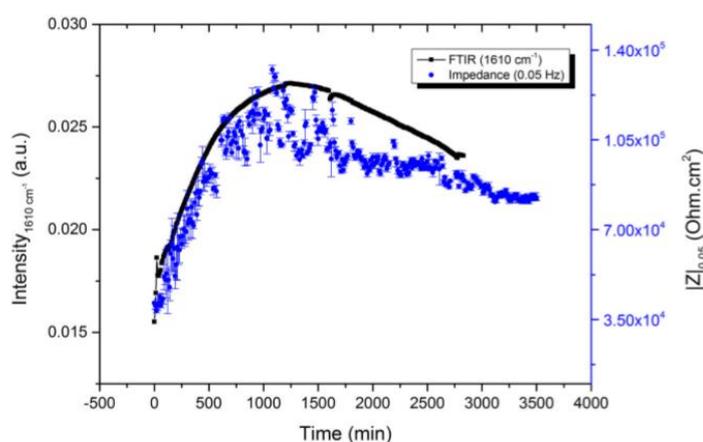


Figure 4: Overlay of FTIR and Impedance data. The intensity of the asymmetric  $\nu_{\text{as}}(\text{COO}^-)$  carboxylate stretch located at  $1610\text{ cm}^{-1}$  and baseline corrected as a function of electrolyte exposure time (black dotted line) obtained with FTIR in the Kretschmann geometry; Magnitude and error values of the impedance at 0.05 Hz (blue dots). A direct link is observed between the carboxylate bond at the interface and the impedance magnitude from the low frequency region.

## Effect of the solvent on the aluminum oxide interface

In literature, the possibility of interactions occurring between the used solvent and the metal oxide surface are often overlooked. Therefore, the integrated setup is used to study the effect of a common organic solvent (methanol) onto a physically vapor deposited aluminum oxide. It is shown as a function of exposure time that initially, physisorbed methanol and adventitious carbon are replaced at the aluminum oxide interface, followed by chemisorption of methanol to form methoxide species. It is thus important to take into account the solvent/metal oxide interactions since this interaction might lead to a decrease in available bonding sites on the metal oxide surface when depositing polymers from polymer solutions.

## Conclusions

From the observations made in this work, we are able to elucidate the **adsorption mechanisms of PAA and PMMA on aluminum oxide**. Moreover, we were able to monitor **enhanced adhesion** and **bond breakage due to water** at the interface that eventually leads to macroscopic delamination.

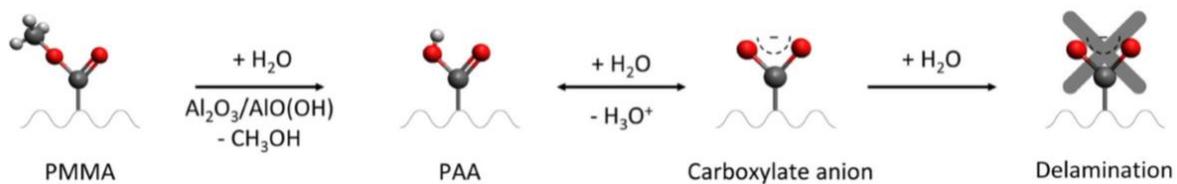


Figure 5: Reactions occurring at the polymer/metal oxide interface, highlighting the mediating role of water.

We have shown that four parameters are largely contributing to the interfacial interactions and stability between a polymer and a metal oxide. These are the **functional groups of the polymer (1)**, the **surface oxide properties (2)** and external influences such as the extent of **adventitious carbon (3)** and **solvent interactions (4)**.

Carboxylic acid based polymers are often used as adhesion promoters in modern coating formulations. The reason for their use is that empirical observations showed that they actively promote adhesion, especially in wet conditions. The observations made in this thesis explain this phenomenon of enhanced adhesion from a molecular point of view. However, an important aspect that must be taken into account is the onset of corrosion. From the integrated FTIR/ORP EIS setup we observed that the borate buffer actively compensates the deprotonation of the PAA coating during the diffusion of the electrolyte. Also at the interface itself, deprotonation occurs as a result of hydrolysis. This creates very acidic conditions locally at the interface, and thus at the metal oxide substrate. The adhesion promoter might in this case become a corrosion promoter. Overall, the findings of this PhD will help to bridge the gap between fundamental science and macroscopic behavior in order to eventually predict and engineer the durability of industrial hybrid systems under realistic, day-to-day conditions.