

# 1 INTRODUCTION

## 1.1 General introduction

Surface modification of engineering materials by means of thin and ultra-thin films is an important issue in science and technology in a variety of application fields, such as

- corrosion protection of metals by organic coatings,
- adhesive bonding of polymers and metals,
- deposition of metal films on polymer substrates,
- design of biocompatible medical implants,
- deposition of low friction films in microelectronics,
- surface films for catalysis and energy conversion,

to name only a few.

In the field of surface engineering of metals such as steel, zinc, aluminium and magnesium and their alloys, by inorganic and organic thin films, mainly the corrosion protection, the adjustment of the surface energy, the adhesive and the tribological properties are in the main focus of investigations. Concerning corrosion protection a recent review by Grundmeier and Simoes illustrates the importance of the

- state of chemical bonding
- molecular ordering
- electrochemical reaction kinetics and
- transport properties

at polymer/metal interfaces on the stability of the system [1].

Only recently, the development of a new electrochemical technique for corrosion science, the Scanning Kelvin Probe, allowed the in-situ and non-destructive analysis of electrode potentials at hidden polymer/metal interfaces and thereby processes of de-adhesion in corrosive media. Mainly based on this technique, Stratmann et al. studied and revealed

principle mechanisms of corrosive de-adhesion processes on steel, zinc and aluminium alloys [2-4].

Parallel to mechanistic investigations of polymer/metal de-adhesion phenomena, research and development in thin film engineering e.g. based on conversion coatings on metals, organic coatings, sol-gel technology, self-assembled monolayers, physical vapour deposition, plasma polymer deposition and other forms of chemical vapour deposition has been done intensively within the last ten years with the aim to introduce new environmentally friendly processes with a high level of functionality into the production of surface finished metals.

A molecular understanding of thin film coated metals has been achieved for some chosen self-assembly processes, mainly for organothiols on gold and already much less for organophosphonates and organic carboxylic acids on aluminium oxide surfaces [5-9].

However, many surface processes of high technical importance were only empirically developed and the respective system complexity hindered a detailed structure-property correlation. Moreover, surface analytical techniques used so far which provide a molecular understanding, such as scanning tunnelling microscopy [6, 10-13] or reflection absorption infrared spectroscopy at grazing incidence could only be applied to few model systems [14, 15], where a direct link to the technical problem is missing.

There was thus a strong need to bridge the gap between new advanced surface modification processes and the detailed understanding of the involved surface chemistry, film formation processes and mechanisms of adhesion and de-adhesion as well as the correlation between structural aspects of thin films and their functional properties.

In this contribution the author tries to provide the reader with an overview on concepts for interface analysis and knowledge based surface engineering by thin films on engineering materials.

## **1.2 Adhesion at polymer/metal and polymer/oxide interfaces**

### **1.2.1 Aspects of materials science and physical chemistry**

The current knowledge of adhesion at interfaces between polymers and metals as well as polymers and oxides is based on completely different approaches in physical chemistry and materials science.

In materials science, adhesion is studied based on the microscopic analysis, adhesion testing and Finite Element simulation of polymer/metal composite systems such as adhesive joints or polymer/metal nanocomposites. Practical adhesion energies and criteria of failure can be deduced from these investigations [16-18]. Mainly, Kinloch and coworkers stimulated this field of research [19-25]. Moreover, an improvement of the composite system with regard to fracture toughness can be performed based on the mechanical characterisation of the materials as a function of the composition and the interface chemistry. Ageing studies accompany these studies and provide insight into the principal aspects of damaging mechanisms of composite systems such as adhesives [21, 22, 24, 26, 27].

Due to the complexity of the investigated systems an understanding of molecular adhesion forces and mechanisms of de-adhesion is not achieved by this approach.

In the case of layered systems such as organically coated metals and adhesive bonding, surface technology is one of the most dominating fields in materials chemistry. New surface technologies which lead to a change in surface topography, adjustment of the surface chemistry as well as the morphology of surface films are considered.

In the field of physical chemistry, the molecular understanding of adhesion and de-adhesion is in the focus of the current investigations. Especially, the establishment of techniques such as the surface force apparatus and the atomic force microscope have led to a much better understanding of the adhesion and friction between two solid surfaces or even between single organic molecules and model metal and oxide surfaces [28-31]. However, the measured adhesion forces can not directly be correlated to technical systems and destructive adhesion tests. They further neglect any mechanical properties and thus illustrate only a single aspect of the overall phenomenon, but this quantitatively and in great detail.

Further physicochemical investigations are focused on the spectroscopic characterisation of molecular adhesion by means of surface selective spectroscopic techniques such as

- Vibrational spectroscopy (Infrared and Raman Spectroscopy, Sum Frequency Generation)
- Mass spectroscopy (Thermodesorption Mass Spectroscopy, Time of Flight Secondary Ion Mass Spectroscopy)
- Electron spectroscopy (X-ray Photo Electron Spectroscopy, ...)

Electrochemical studies are sometimes combined with spectroscopic techniques such as vibrational spectroscopy. However, electrochemical investigations in most cases focus on the understanding of the de-adhesion processes and the adsorption of organic molecules on metal and semiconductor electrodes in liquid electrolytes.

Grundmeier and Stratmann recently reported on the application of spectroscopic, microscopy and electrochemical techniques to study adhesion and de-adhesion phenomena in-situ [32].

Finally, adhesion is studied based on theoretical methods [33, 34]. In this context, ab initio quantum chemistry methods and density functional theory are known and established for several decades now. However, their application to technologically relevant complex problems – complex either in terms of accuracy or in terms of the sheer size of the required atomistic models – was out of reach for a long time. It was only in the 1990s, driven by the advent of ever faster and faster computer hardware, that the predictive atomistic modelling and simulation based on quantum mechanics became applicable to a wide class of problems. Today simulation has matured to the point where chemists, physicists, materials scientists and chemical engineers regularly apply it to practical industrial problems like optimising polymer blend formulations, increasing the efficiency of organic crystallization processes, or improving the performance of catalysts. Many of these researchers are studying a set of problems which affects virtually every industrial product or process – in particular those connected to the behaviour at surfaces and interfaces.

Total energy calculations are based either on what is often called “molecular mechanics” or on quantum mechanics. Molecular mechanics approximate the energy of a system of atoms by summing a series of empirical functions representing components of the total energy such as bond stretching, van der Waals forces, or electrostatic interactions. Although only semi-quantitative, it has the advantage of being very fast. On the other hand, quantum mechanical methods apply various degrees of approximation to solve the many electron Schrödinger equation for a given spatial arrangement of atoms. Extremely accurate, although much more

computationally expensive, these methods yield not only the total energy but also the electronic structure of a system – enabling researchers to characterise chemical reactions.

### 1.2.2 Basic principles of polymer to metal adhesion

Adhesion is based on the chemical structure and microscopic structure of both the underside of the polymer and the surface of the metal or oxide covered metal substrate. The formed interfacial zone should be called an interphase rather than a sharp interface because it is three dimensional in nature [35-39].

Different theories have been developed to explain the origin of adhesion including [23, 40]

- the electrostatic theory, based on a charge transfer between the substrate and the coating
- the diffusion theory, based on the interdiffusion of polymer chains at the interface
- mechanical interlocking, based on the spreading of liquid paint into cavities of the surface leading to an anchoring of the paint after solidification, and
- the adsorption theory, based on covalent, polar and disperse interactions as well as acid base interactions between the substrate surface and the paint.

It has been argued that the formation of acid-base interactions between the polymer and the substrate may represent a major type of intrinsic adhesion force [41]. The acid may be an electron donor in the Lewis sense, or a proton donor in the Bronstedt sense. The base may be an electron donor, in the Lewis sense, or a proton acceptor in the Bronstedt sense. The acid-base theory has found widespread acceptance and an increasing number of papers deal with the understanding and application of these forces at the interface [42].

Covalent bonds at organic/metal interfaces have been observed for organothiols adsorbed on gold, silver and copper. For organosilanes a covalent bonding to oxide surfaces has been postulated but no convincing experimental prove has been published to date [43].

While the adsorption theory is the most accepted one, mechanical interlocking comes into play in case of substrates with a special kind of roughness where the liquid can spread into cavities and after curing thereby interlock with the substrate. The diffusion theory does not

play an important role for polymer/metal interfaces since the metal surface acts as a perfect diffusion barrier at temperatures significantly below the melting point. The contribution of the electrostatic theory is not easy to estimate. However, the electrical component of the adhesive force between the planar surfaces of solids becomes important if the charge exchange density corresponds to  $10^{17}$  electronic charges, meaning about 1% of the surface atoms [44].

Wetting of the surface is crucial for the formation of the interphase and is determined by the surface energy of the substrate and that of the liquid polymer or polymer solution in a solvent [45]. The basic step in the liquid coating process is the replacement of the substrate/air interface with the substrate/liquid and liquid/air interface. The wetting condition for static conditions can be described by the Young equation. Young expressed the conditions for equilibrium at a solid-liquid interface as

$$\gamma_1 - \gamma_{12} = \gamma_2 \cos \Theta_{21} \quad (1-1)$$

where  $\gamma_1$  and  $\gamma_2$  are surface energies of the solid (1) and liquid (2) in equilibrium with the saturated vapour of the liquid and  $\Theta_{21}$  is the contact angle at the three phase boundary.

The so-called spreading coefficient  $S$  is given by the difference in surface energy between the uncovered and the covered surface according to

$$S = \gamma_{s0} - (\gamma_{sl} + \gamma) \quad (1-2)$$

where  $\gamma_{s0}$  and  $\gamma_{sl}$  are the solid/air and solid liquid interfacial energies while  $\gamma$  is the surface tension of the liquid [44]. For complete wetting to occur,  $S$  must be positive. The greater the value of  $S$ , the more rapidly the liquid will rush to cover the substrate.

The adhesion strength of an interface between two materials  $\alpha$  and  $\beta$  can be defined by the work of adhesion. This is the work required to separate reversibly the interface to infinity per unit area

$$W_a = \gamma_\alpha + \gamma_\beta - \gamma_{\alpha\beta} \quad (1-3)$$

where  $W_a$  is the work of adhesion,  $\gamma_\alpha$  and  $\gamma_\beta$  the surface tensions of  $\alpha$  and  $\beta$  phases respectively, while  $\gamma_{\alpha\beta}$  is the interfacial tension between  $\alpha$  and  $\beta$ .

While the above mathematical treatment is true for equilibrium conditions, the real coating process is highly dynamic. Solvents and thinners strongly influence the wetting process and immediately after the paint application evaporation of solvents, orientation of macromolecules at the interface and crosslinking of oligomer chains start leading to nonsteady-state conditions [45]. During solvent evaporation adhesion-promoting groups can adsorb at the inorganic surface. Examples of these adhesion-promoting groups are hydroxyls, carboxyls, amides, isocyanates and epoxies.

When water molecules reach the interface between the coating and the inorganic surface of the substrate they may interfere with the adhesion between the polymer and the substrate. Eventually, in combination with intrinsic stresses in the coating this might lead to a loss of adhesion. The water molecules compete with and substitute the polar groups of the polymer at the metal surface. Moreover, accumulation of water at the interface caused by residual solvents or ions can lead to high osmotic pressures and subsequently to a hydrostatic disbonding. The degree to which permeated water may change the adhesion properties of paint/metal composite is referred to as wet adhesion [46, 47].

### **1.2.3 Molecular understanding of adhesion at polymer/metal interfaces**

#### **Experimental studies of molecular adhesion**

Spectroscopic studies of adsorbed monolayers and ultra-thin films on metals and metal oxides allow the characterisation of the type of interfacial bonding as well as the orientation and packing density in certain cases.

Especially vibrational spectroscopic techniques such as Surface Enhanced Raman spectroscopy and FTIR spectroscopy at grazing incidence have been applied to study the chemical bond between adsorbed organic molecules and metals as well as metal oxides. The peak position and shape of the adsorbed species in comparison to the state of the molecules in the bulk provide information about the interfacial bond and the orientation. The reader is referred to recent reviews in this field [32].

Measurement of the molecular ordering of self-assembly films on metal surfaces by means of a Scanning Tunneling Microscope has mainly been restricted to organothiols on noble metals [43].

As a means to measure adhesion energies of adsorbed molecules, Thermodesorption Mass Spectroscopy (TDS) has been applied. Especially Somorjai and co-workers considered the adhesion of organic molecules as model components of lacquers and adhesives [48]. The authors adsorbed epoxy group containing molecules and organosilanes on oxide covered surfaces under UHV conditions. The temperature at which the molecules desorbed could be used to estimate the adhesion energy. Moreover, the authors also co-adsorbed water on the metal surfaces to study the process of displacement under humid conditions.

Less fundamental work considered the application of ToF-SIMS for the detection of chemical bonds at interfaces between thin organosilane layers and metal oxide surfaces [49-51]. Wapner and Grundmeier recently showed that the application of ToF-SIMS for the detection of interfacial bonds is difficult since fragments such as Fe-O-Si are created by the impingement of Gallium ions on the surface [52].

#### *Theoretical understanding*

The interaction of layers of organic molecules, e.g. polycyanurates, with a surface is an interesting model system for the morphology of surface/adhesive interfaces. Here density functional theory (DFT)-based calculations have been successful in simulating vibrational and photoelectron spectra for small model adsorbants [53, 54]. Although in good agreement with experimental data, these calculations are restricted in length scales and cannot describe any effects beyond the first adsorbant layer, hence neglecting its embedding in a by far larger system of surface, interphase and adhesive interphase. Also the simulation of larger molecules or more complex surface structures remains impossible.

To optimise flotation processes as used in ore mining to separate and concentrate minerals, the interaction of so-called collector molecules (often xanthates) with the mineral surface has been studied. So far, atomistic simulation of the structures and processes involved was restricted to purely semi-empirical approaches for morphology and structure [55-58] and adsorption behaviour [59-61]. These semi-empirical methods were incapable of reliably predicting the atomistic bonding situation at the interface or of energetically differentiating competing mechanisms. As a consequence, the obtained theoretical data is of only limited value when it comes to interpret numerous spectroscopic experiments, and the predictive power in process optimisation is miniscule.



Surface analysis techniques, such as photoelectron (XPS and UPS) and vibrational (IR) spectroscopy have been used experimentally in trying to identify the nature of interfacial bonding and its role on the adhesion. Both spectroscopic methods lead to conclusions about the state of bonding. Thus intensity deficits or additions and energy shifts are used to infer changes in surface composition and to assign reaction sites.

Theoretically, one can estimate the changes in the binding energy of an electron in a core orbital as seen by XPS using the point-charge potential method. According to this model changes in the electronic population of one atom and its neighbours lead to core level shifts. Preliminary calculations using this method [62] reveal considerable core level shifts for atoms far from the reaction site. Therefore, one needs theoretical calculations in interpretation of XPS spectra since the correlation of core level shifts with reaction sites is not straightforward.

#### **1.2.4 Adhesion promoting bi-functional molecular layers on engineering metals**

Bi-functional molecules which bond with one end to the oxide covered metal substrate and with the other end to organic compounds of the organic primer or adhesive are on the one hand of technical importance and on the other hand they can act as model organic molecules for the analytical understanding of interfacial chemistry. Terryn et al. studied in detail the adsorption of organic carboxylic acids on oxide covered aluminium [63, 64].

Organophosphonates, organosilanes and organic carboxylic acids are currently the most promising so called coupling agents for oxide covered metals. They can be either applied directly on the oxide covered surface by adsorption from dilute solutions or they are incorporated in the organic phase and enrich as a monolayer at the polymer/metal interface.