

## Adhesion at Al-hydroxide-polymer interfaces: Influence of chemistry and evidence for microscopic self-pinning

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### ABSTRACT

We present a combined chemical (auger electron spectroscopy) and microscopic (optical microscopy, scanning electron microscopy and scanning probe microscopy) study of the work of adhesion and delamination mechanisms at interfaces between a glassy polymer (glycol-modified polyethylene terephthalate) and Al covered with different types of surface hydroxides. A clear correlation between the measured work of adhesion and the chemical nature of the Al surface, specifically the hydroxyl coverage and the iso-electric point is found. The magnitude of the work of adhesion points to important contributions from plastic deformation in the glassy polymer for some cases. Delamination is shown to be accompanied by the formation of microscopic shear bands at such interfaces. The non-monotonous stress-strain behaviour of the glassy polymer that gives rise to the shear bands is also shown to lead to peculiar pinning events at the crack front. Evidence indicates that the occurrence of protrusions in the crack front deriving for example from the presence of stress concentrators and crack initiation sites ahead of the front, combined with mode and rate dependence of the local energy release rate along the front may pin the front at positions adjacent to a protrusion. It is believed such microscopic mode-dependent pinning phenomena may be relevant for the adhesion on patterned interfaces.

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### 1. Introduction

The adhesion of organic coatings on aluminium is an important industrial topic for example in the packaging of food and beverages. The native oxide on aluminium is stable only in neutral environments (pH 4–8) where no chlorides are present. In the case of aluminium alloys precipitates form cathodic or anodic sites where localized corrosion can initiate. One way of protecting aluminium alloys from corrosion is by using an organic polymeric coating and for effective protection it is essential that such coatings adhere well to the alloy substrate. The general aim of the work presented here is to increase the understanding of de-adhesion at interfaces between a glassy polymer and oxide- or hydroxide-covered metals. To accomplish the aim both the correlation between interface chemistry and work of adhesion, and between work of adhesion and delamination mechanisms is studied in detail. The specific

interfaces that are treated exist between glycol-modified polyethylene terephthalate (PETG) and oxy-hydroxide layers on pure and low alloyed Al (Al (99.999%) and AA1050) and an Al–Mg alloy, AA5182. This paper studies the influence that acidic, alkaline and boiling water pre-treatments have on these interfaces. It presents data on surface chemistry and bonding to a model compound and formulates a hypothesis on the expected bonding to PETG. It then extends those studies by determining the interface chemistry and work of adhesion of such interfaces and by studying the associated microscopic de-adhesion mechanisms in microscopic detail using *in situ* techniques. The materials and surface treatments used may be relevant for industrial practice, however the adhesion treatment and the thickness of the PETG layer were optimised for the experimental work carried out here.

In delamination or de-adhesion along interfaces between glassy polymers and metals different types of bonds interact. The metallic bonds are (in general) much stronger than the interchain van der Waals interaction in the glassy polymer, as can be judged from their respective moduli that typically differ by 2 orders of magnitude.

The bonding across the interface itself depends on the chemistry of both metal and polymer. Which types of bonds exist across the interface is not clear *a priori* because in general oxide or hydroxide

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**Table 1**  
Hydroxyl coverage (OH) and effective surface area ( $A/A_0$ ) determined by XPS and BET. From ref. [22].

AA1050	Alkaline	Acid	H <sub>2</sub> O
OH	43	35	47
$A/A_0$	1.6	1.4	15

layers cover a metal surface and both their chemical and physical nature depend on the pre-treatment of the metal surface.

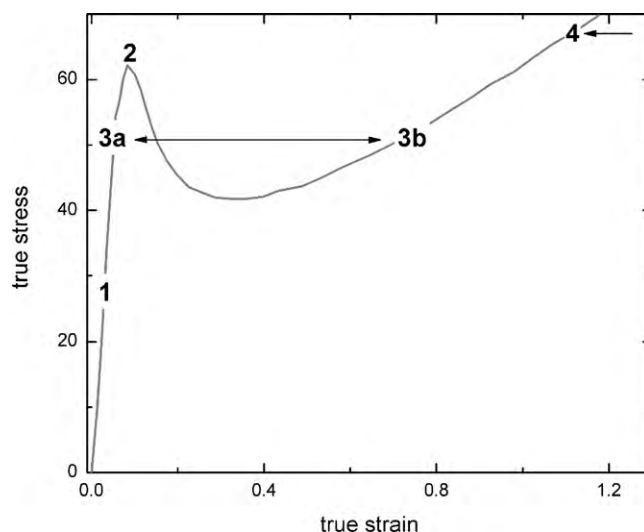
For an atomically flat interface the bond chemistry and density at the surface is important in determining the measured energy release rate. The interaction between polymers and metals is thought to be due to relatively weak hydrogen bonds the strength of which depends on the chemical nature of the interface. Assuming 10 hydrogen bonds per nm<sup>2</sup> and 4–100 kJ/mol [1] as bounds on the bonding energy this would lead to a energy release rate  $G$  of 1.7 J/m<sup>2</sup> at maximum, which is a rather low value. Such low values will only be measured if the interface bonds are very weak compared to those in the surrounding materials and both bond stiffness and maximum bond strength are relevant. But importantly the stiffness and strength of H-bonds can be of the same magnitude as those of the secondary bonds within a glassy polymer. This means that if a H-bond “connected” to a glassy polymer is loaded it may lead to substantial (visco-)elastic or potentially plastic deformation in the glassy polymer.

The chemical character of the native oxide layer on Al and Al alloys can be influenced by surface treatments and a distinction between acidic, alkaline and boiling water surface treatments is useful. Of particular relevance here are studies that deal with the bonding of the ester functional groups (C(=O)O) that occur in PETG. For AA1050 the influence of pre-treatments on the bonding of ester-based model compounds was studied by van den Brand et al. [22]. The carbonyl groups in the ester are positively charged and form so-called Lewis acids. The groups are able to accept electrons from electron donors. Hydroxyl groups present on the aluminium surface are able to donate electrons through the negatively charged O, and thus act as a Lewis base. Hydrogen bonds may be formed between the acid and base. van den Brand et al. [22] were able to determine the chemical nature of the bonds as well as the area fraction of the surface covered in –OH groups. Their results are shown in Table 1.

Using XPS measurements they found minor differences in the chemical behaviour of the aluminium cations for surface oxides after acid and alkaline pre-treatment. It was shown that the hydroxyl fraction is significantly higher after alkaline pre-treatment than after acid pre-treatment. Acid and alkaline pre-treated substrates showed an increase of effective surface area  $A/A_0$  with a factor of 1.4 and 1.6 as shown by BET techniques [22].

In case of AA5182 differences in surface chemistry come into play. The strength of the hydrogen bonds is positively correlated with the difference in iso-electric point (IEP) between the bonding species, which offers a way of qualitatively establishing interface bond strengths in these cases [14]. The IEP of a surface (that can be measured with colloid titration) is defined as the pH at which it has no net electrical charge. A low IEP indicates an acidic surface and a high IEP indicates an alkaline surface. The values of the IEP are 12 for magnesium oxide (MgO) and 8 for aluminium oxide (Al<sub>2</sub>O<sub>3</sub>), respectively [15]. Using inverse gas chromatography it has been determined that PETG is a weak base [10]. It is therefore expected that the hydrogen bond between MgO and PETG is stronger than between Al<sub>2</sub>O<sub>3</sub> and PETG.

On the surface of AA5182 oxides of both Mg and Al may be expected and considering their different IEP a surface treatment that influences the relative surface coverage of these oxides may also be expected to influence the adhesion to ester containing poly-



**Fig. 1.** True stress in MPa vs. true strain for PETG (after [5]). Numbers are used in the text to discuss the properties of PETG and again in Fig. 7 to discuss microscopic delamination mechanisms.

mers. Di-methylterephthalate (DMT) as a probe is expected to be especially relevant. With DMT as a probe on AA5182 it was found that alkaline and boiling water pre-treatment lead to a bonding interaction whereas acid pre-treatment does not. Similar findings were obtained for AA1050 [3].

The pre-treatment with boiling water cannot be easily compared to the other two since it dramatically changes the interface geometry. Using BET techniques van den Brand concluded that the effective surface area of AA1050 increased by a factor of 14.6 after a boiling water treatment [22] associated with the formation of a nano-structured pseudo-boehmite oxi-hydroxide layer (see Fig. 4). Such pseudo-boehmite layers are known to be particularly effective in increasing adhesion between metals and polymers such as PET and PE [19]. Rider reported [18] a boiling water pre-treatment to an aluminium substrate and effects on adhesion and the durability of an applied epoxy coating. Strålin and Hjertberg [20] found that an ethylene vinyl acetate polymer has a stronger bonding with a pseudo-boehmite aluminium hydroxide layer than with a dehydroxylated aluminium oxide.

The effects of substrate surface roughness on the adhesion of polymer coatings were extensively studied by [4,13,12,16,9,26,6]. It was found that adhesion at a rougher surface can indeed lead to an increased energy release rate. Often, dissipative mechanisms are triggered near the interface in the bulk of the metal and the polymer. By concentrating stress in the polymer at tips of fibers or along ridges of flakes for example, local plastic deformation may be induced that adds to the total work of adhesion. For glassy polymers this is an especially relevant issue because the (macroscopic) stress–strain curve of these materials generally shows initial softening behaviour after a yield stress before hardening occurs (see Fig. 1).

The peculiar shape of the stress–strain curve means that after the yield stress (point 2 in Fig. 1) is reached the material can deform spontaneously to a much higher strain level while at the same time reducing the local stress (e.g. points 3a and 3b in Fig. 1). Energy is then dissipated in the polymer by the formation of shear bands and no large scale de-adhesion needs to take place. If the ultimate stress in the polymer (e.g. point 4 in Fig. 1) is higher than that of the interface de-adhesion may take place along the polymer–oxide interface, or possibly through the oxide layer or along the Al–oxide interface. Dissipation in the polymer is known to be important in determining the work of adhesion since measured values are often

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