Progress in Quantitative Adhesion Testing of Films and Coatings by means of Centrifuge Technology – Present State of the Art

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1. Introduction

Standardised conventional adhesion tests are time-consuming single-sample tests. Moreover, except for the pull-off test, all these tests provide only qualitative or semi-quantitative (ranking, respectively measurement of an adhesion-correlated quantity) information on adhesion. Sometimes, adhesion is evaluated even under compressive stress conditions (e.g. cross-cut and scratch test), which itself is a contradiction to adhesive strength as defined in terms of tensile force per area.
For optical coatings [1] it has been shown that the pull-off test in a centrifuge is definitely a promising alternative with respect to the reliable, fast and quantitative determination of adhesive strength in N/mm^2. The force-controlled centrifuge test is the only multiple-sample test which provides reliable quantitative information on the adhesive strength in agreement with DIN EN 15870 and DIN EN ISO 4624 on a statistical basis for up to eight samples simultaneously tested under identical testing conditions.

2. Experimental

The desktop testing system “Adhesion Analyser LUMiFrac®“ was introduced to the public at ACHEMA 2012 [2] and is shown in Figs. 1 and 2. By means of the software SEPView® any desired load-controlled testing sequence, i.e. load ramp or load modulation, can be realised.



Fig. 1: Desktop adhesion analyser LUMiFrac®



Fig. 2: Drum rotor equipped with eight testing units

The centrifugal force acts as tensile testing force for the pull-off test within the centrifuge. As the plug-in testing unit (Fig. 3), i.e. a test stamp bonded on the sample using a guiding sleeve, is also used prior to testing as adhesive application kit, the presence of shear forces can be avoided at both testing and preparation.

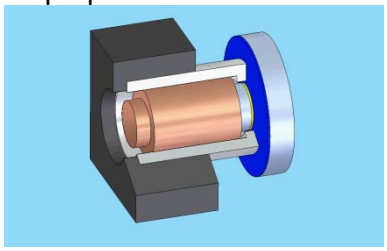


Fig. 3: Testing unit: sample (silver) with coating (blue) supported by the sleeve (grey), adhesive (yellow) connecting sample and test stamp (bright-brown), test stamp guided by the sleeve

By using test stamps made of WCu, the force range is extended to 6.5 kN corresponding to a tensile stress of roughly 80 N/mm^2 at a test stamp diameter of 10 mm. As bonding strength of adhesives is limited to approximately 30 N/mm^2 (cold-curing), respectively 100 N/mm^2 (warm-curing) this is not a severe limitation. In fact, for the lower test stamp diameters of 7 mm and 5 mm (corresponding to tensile stresses of roughly 160 N/mm^2 and 320 N/mm^2) there is no limitation at all.
Besides monolithic test stamps, modular test stamps have been investigated. One part of the test stamps functions as adhesive area usually made of stainless steel, the other part functions as mass body usually made of Cu or WCu. As a result, the cleaning effort for the reuse of test stamps is minimised and the number of material combinations is significantly higher.
Subsequent to testing, visual or microscopic inspection of the failure pattern in accordance with DIN EN ISO 10365 is recommended on both the substrate and the test stamp side. It could be shown that almost all fracture pattern, i.e. coating/substrate-related ones [substrate failure (SF), cohesive substrate failure (CSF), delamination failure (DF), partial delamination failure (pDF)] and adhesive-related ones [cohesive failure (CF), substrate-near cohesive failure (SCF), adhesive failure (AF), adhesive-cohesive failure (ACF), adhesive-cohesive failure with peeling (ACFP)], may be observed.

3. Application examples

3.1 Plasma pre-treatment of polypropylene

The effect of plasma pre-treatment of polypropylene (PP) regarding the bonding strength of adhesives is exemplarily shown in Fig. 4. According to the centrifuge test, adhesion is increased as a result of plasma pre-treatment by a factor of 10. For the pull-off test, a similar conclusion is impossible as the presence of shear forces prevents any measurement of low bonding strength values of the untreated surfaces and may generally result in apparently smaller tensile strength data as demonstrated for plasma-treated samples.

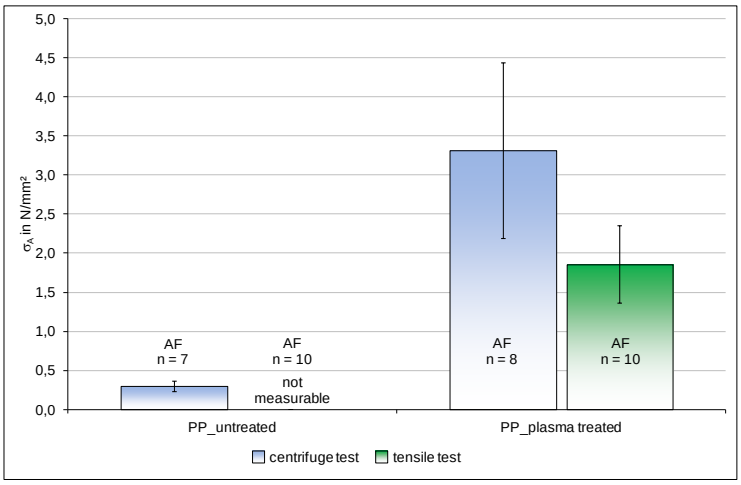


Fig. 4: Effect of pre-treatment of PP on bonding strength (3M DP 460), centrifuge vs. pull-off test

3.2 Plasma-metallised polymers

The adhesive strength of Al- and Cr-layers on polymers was investigated for polyvinylchloride (PVC) and polycarbonate (PC). Complete delamination was observed for 1 µm Cr-layers on PC already at 1.5 N/mm^2 (Fig. 5) whereas for 0.1 µm Cr-layers partial delamination occurs at only 4 N/mm^2. The thinner the Cr-layer, the lower the interfacial stress. For Al-layers, this behaviour is not as pronounced.

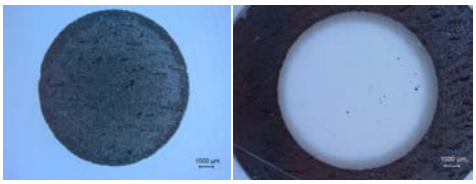


Fig. 5: DF-type failure for 1 µm Cr-layers on PC, substrate side (left) vs. test stamp side (right)

3.3 Rigid glass substrates

For glass substrates of thicknesses of 2 mm (A, B, E, F) and more than 15 mm (C, D), ACF-type failure was observed at very different tensile strength values (Fig. 6), i.e. at 10 N/mm^2 and 30 N/mm^2. This effect has to be considered for substrates without rear side reinforcement, in particular for different substrate materials or different substrate thicknesses. From the experimental point of view, it is demonstrated that adhesion is not only an interface property but also depends on plasto-elastic system features of both substrate and adhesive (Araldite 2011).

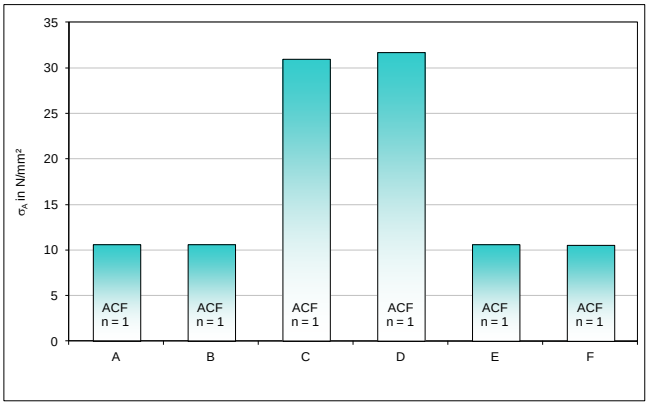


Fig. 6: Substrates without rear side reinforcement: thin (A, B, E, F) vs. thick (C, D) substrates

3.4 Flexible polymer foils

With regard to section 3.3 it is obviuos that the rear side reinforcement, e.g. by means of double-sided adhesive tape, is a prerequisite for correct measurement of flexible substrates. The effect of selective chemical reactions on plasma modified PP foils for improvement of adhesion of Al layers is described elsewhere [3]. A promising strategy is the chemical linking of functional groups by means of trialkoxysilanes. In this case, adhesive strength of Al is already beyond measurable peel strength values, i.e. no peeling of the Al-layer occurs. Within the centrifuge test, the Al-layer could easily be removed at about 2 N/mm^2, however, almost independent of the parameters of plasma treatment and the chemical modification strategy. Finally, it could be shown by XPS that the PP foil itself failed, i.e. the 2 N/mm^2 refers to the intrinsic strength of the PP foil and not to the adhesive strength of the Al-layer on PP.

3.5 Optical coatings

For optical coatings, adhesion tests according to ISO 9211-4 apply, namely the cheese cloth, the rubber, the tape and the cross-hatch (cross-cut) test. For an adhesive strength beyond several N/mm^2 it is almost impossible to discriminate adhesion by means of these tests. Fig. 7 provides one example of a protected silver mirror (CaF_2-Ag/Ta_2O_5) and shows that the centrifuge test is able to determine

adhesive strength as physical quantity to 7.5 N/mm^2 resulting from a rupture force of 600 N at a test stamp diameter of 10 mm.

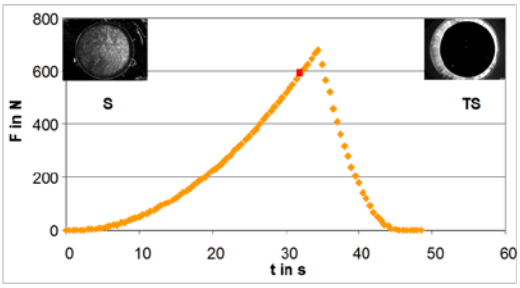


Fig. 7: Complete delamination at the CaF_2-Ag interface within the centrifuge test after 30 s

3.6 Areas of weak adhesion: TiN on 100Cr6 steel

By means of warm-curing adhesives, bonding strength can be increased to more than 100 N/mm^2. It is assumed that the adhesion of TiN and other hard coatings on steel is beyond this value. However, areas of weak adhesion, e.g. due to insufficient substrate cleaning, can be identified even for these layer/substrate systems (Fig. 8), however, adhesive-cohesive failure on the adhesive/layer interface already occurs for four samples.

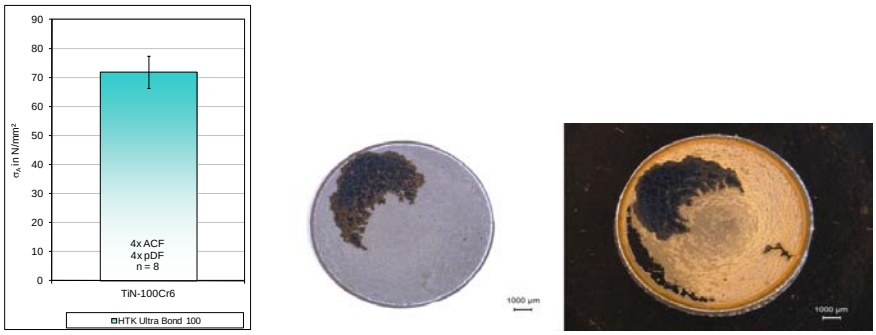


Fig. 8: ACF vs. pDF for TiN on 100Cr6 (left); pDF on test stamp (middle) and layer/substrate (right)

4. Summary and outlook

It has been shown that the pull-off test in a centrifuge has several advantages (fast and easy, no sample clamping, no shear forces, multiple sample test) and exceeds conventional tests despite the fact that in most of the cases a test stamp has to be bonded on the surface. Adhesive strength, bonding strength and composite strength as important quantities under tensile stress conditions can now be determined according to existing standards on a validated statistical basis.
Further research regarding the applicability of the centrifuge test under compressive stress conditions have already begun with regard to plasto-elastic properties, hardness in particular, densification, fatigue and others.
Of course, a new technology needs time for its dissemination, however, after several years of intense research and testing, the implementation of the new technology both to R&D and industrial QA has begun.

References

[1] U. Beck, G. Reiners, M. Weise, H. G. Niederwald, D. Lerche, U. Rietz, Surface & Coatings Technology 205 (2011) S182-S186
[2] Technical specification of Adhesion Analyser LUMiFrac, LUM GmbH
[3] R. Mix et. al., to be published