STUDY OF MECHANICAL AND PHYSICO-CHEMICAL SURFACE PROPERTIES OF COMPOSITES AND THEIR IMPACT ON BOND STRENGTHS IN REPAIR TECHNOLOGIES

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Keywords: adhesive bonding, surface treatment, surface characterization, bonded repairs

Abstract
The mechanical performance of bonded joints is critically dependent on mechanical, physical and chemical characteristics of its individual constituents and the interfaces between them. Adhesion, with respect to the subject matter, requires a profound knowledge of the chemical, physical and geometrical state of the adherend's surface and can be individually tailored by surface treatment. In the present study, detailed optical and physico-chemical surface characterization is performed on different pre-treated composite surfaces to define a suitable set of testing methods to assess adhesion mechanisms. The impact of the surface parameters on global bond strength is evaluated by single-lap shear tests. The results provide data to correlate global bond strength with surface related parameters in order to predict and improve bonded repairs for aircraft structures.

1 Introduction

The growing use of composites in today`s aircraft structural parts reasonably leads to an increase of damage and failure of these structures. Accordingly, the life-cycle-costs of composites in aerospace remain enormously high. For that purpose, maintenance and repair strategies have to be studied in greater detail in order to optimize state-of-art techniques and to develop approaches towards new repairs for aircraft structures. In terms of lightweight design and damage tolerance, bonded repairs would be the preferred strategy [1]. Nevertheless, durability and structural integrity of bonded composite repairs cannot be ensured after the repair has been installed. In fact, the key factors for functioning of repairs on aircraft structures are proper adhesion and bonding, respectively. Regarding surface properties, adhesion can be tailored via mechanical and chemical functionalization of the composite surface [2]. This work studies the effect of different mechanical surface pre-treatment techniques (sanding, grit blasting etc.) and physico-chemical methods (corona treatment, wet chemical methods etc.) on composite surfaces prepared for bonding. Some aspects of adhesion are addressed by detailed surface characterization of the pre-treated laminates. Unfortunately, there is no unifying 'theory of adhesion', and no direct correlation between perfect adhesion and bond strength [2] can be drawn. Some common adhesion theories in literature [2-6], e.g., are based on adsorption, diffusion, electrostatic, mechanical interlocking and chemical bonding aspects. In the present study adhesion is assessed by

clarifying adsorption mechanisms (physical surface state, surface energy), mechanical interlocking (surface topology) and the chemical composition of the surface. The evaluated surface parameters are further correlated with mechanical performance of bonded coupons to demonstrate their impact on global bond strength. A basic concept for an appropriate testing methodology of composite bonded joints, including optical and physico-chemical techniques of surface analysis, is presented.

2 Experimental- Materials and testing methods

2.1 Materials

Coupons were cut out from carbon fiber reinforced composite laminates. The laminates were composed of 12 plies of a commercially available epoxy prepreg material (epoxy resin / amine hardener) with unidirectional (UD) fiber orientation (total thickness 2,4 mm). An epoxy structural adhesive film with a nominal thickness of 1,4 mm was used for bonding. All materials used within this research are commercially available and generally employed for aerospace applications.

2.2 Surface pretreatment techniques

2.2.1 Mechanical pre-treatment

Conventional abrasive techniques (sanding, grit blasting) were performed for mechanical surface preparation. The coupons were sanded with an angular grinder using two different grits (grit 60 and grit 100). Grit blasting was performed with a silica sand (grit 0,1-2 mm) at a pressure of 9 bar. Furthermore, one coupon plate was cured with a polyester peel ply for surface roughening.

2.2.2 Physico-chemical treatment

Corona discharge treatment was used for surface activation and to attach oxygen moieties onto the sample surface. The samples were treated in the laboratory corona station PG 3001 (Ahlbrandt System GmbH, Lauterbach, Germany) at 600 W. Additionally, some samples were chemically modified after corona-treatment by attaching mercapto (-SH)- moieties onto the surface (wet chemical method).

2.3 Surface characterization techniques

2.3.1 Optical techniques

Optical surface characterization techniques can be basically divided into image capturing methods (2D) techniques (e.g light micrography) and topographic surface analysis (3D) (e.g. confocal microscopy). Prior to bonding, light microscopy with a reflecting light microscope (Olympus BX51, Olympus Soft Imaging Solutions GmbH, Münster, Germany) and stereo light microscopy (Olympus SZX12, Olympus Soft Imaging Solutions GmbH, Münster, Germany) were performed to obtain a rather descriptive image of the individually pre-treated surfaces. The surfaces were analyzed in greater detail by scanning electron microscopy (SEM) (Zeiss DSM 962, Carl Zeiss MicroImaging GmbH, Germany). Additionally, the topology was addressed by confocal microscopy. For that purpose, the surface roughness R_a (arithmetic average of profile height) and R_q (root mean squared), according to DIN4768 [7] and DIN4762 [8], are evaluated as representative topology parameter from line scans performed with the confocal microscope (FRT MicroProf® MPR 1080, Fries Research and Technology GmbH, Bergisch Gladbach, Germany). A special light microscopical device (Alicona Infinite Focus®, Alicona Imaging GmbH, Graz, Austria) was used to establish the 3D- topology of the pre-treated surfaces.

2.3.2 Physico- chemical techniques

In order to assess the surface energy, contact angle measurements were performed with a Krüss DSA 100 goniometer (Krüss GmbH, Hamburg, Germany). Contact angles of two different liquids (water and diiodomethane) were determined for the pre-treated surfaces, to calculate both, the polar and the dispersive parts of surface energy [6]. The drop shape

analysis and the determination of the contact angle α were performed accordingly to Young's equation [9],

$$\gamma_{LV}\cos\alpha = \gamma_{SV} + \gamma_{SL} \quad (1)$$

where S, L, V denote the solid, liquid, vapor phases, and γ_{SV}, γ_{LV}, γ_{SL} are the interfacial energies. The contact angles in the subject matter are determined by the circle fitting method (Krüss GmbH, Hamburg, Germany). The polar and dispersive parts of the surface energies of the solid (γ_{SV}) were calculated correspondingly to the Owens-Wendt-Rabel-Kaelble (OWRK) method [10]. The determination of surface free energy by contact angle measurements solely provides repeatable results for rather 'smooth surfaces'. Most abrasive treated surfaces are too rough for detailed drop shape analysis. Therefore, the wettability of the pre-treated composite surfaces was further verified by wetting tests. For that purpose, a common epoxy structural adhesive resin (epoxy resin / amine hardener) was applied on pre-treated specimens, and during curing in an oven the wetting was observed by taking photographs at different curing stages.

2.3.3 Surface elemental analysis

XPS (X-ray photoelectron spectroscopy) was performed to assess the chemical composition of the surface. An XPS instrument (Thermo scientific K-Alpha) from Thermo Fisher Inc., Waltham, USA, was employed. Survey scans (source type: Al K-alpha, line scans with 3 spots, spot size 400 μm, energy step size 0,1 eV) were run to obtain data on the elemental surface composition. The depth of XPS analysis is in the range of a few nanometers.

2.4 Mechanical testing

The global bond strength was characterized by single lap shear testing correspondingly to ASTM-D5868 [11]. The adhesively bonded coupons are demonstrated in Figure 1.

Figure 1. Single lap shear coupon with doublers for centric load application

Doubler tabs were bonded to their ends to establish a centric load application and thus pure tensile shear loading of the bonding area. The coupons were surface pretreated and then adhesively bonded by applying an adhesive film. Afterwards they were cured in a press. The tests were performed on the MTS 810 servohydraulic testing machine (MTS Systems GmbH, Berlin, Germany). The coupons were fixed with hydraulic wedge grips. The free clamping length was 127 mm. The tests were performed at 23 °C, 50 % RH at a testing speed of 13 mm/min. The displacement was measured with a 3D optical measuring system, Aramis HS (GOM mbH, Braunschweig, Germany; WestCam Datentechnik GmbH, Mills bei Hall, Austria). For that purpose, a stochastic dot pattern was applied on the coupons using an aerosol spray. Prior to testing the system was calibrated with similarily patterned plates to correct distortion of the lenses and to calibrate the position of the cameras to each other. The testing configuration is depicted in Figure 2 in greater detail. The 3D optical displacement analysis provides more detailed information on the deformation in the bond line/adhesive layer. Therefore, the displacement in y-direction (loading direction) of the upper and lower adherend near the overlap region was measured. The displacement of the upper adherend represents the neat adherend deformation incl. impacts of the testing device, whereas the lower adherend displacement also accounts for deformation in the adhesive layer. The displacement in the bond line was calculated by subtracting the upper adherend displacement from the lower adherend displacement.

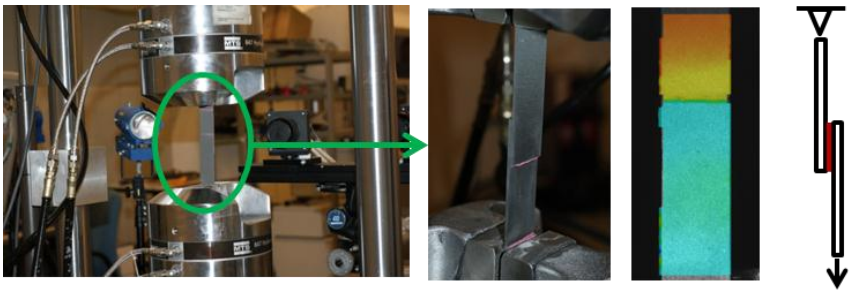


Figure 2. Lap shear testing configuration at MTS 810.22 with Aramis 3D optical measuring system

3 Results

3.1. Topology investigations by optical and microscopical techniques

In Table 1 an overview of the topologies of the pre-treated composite samples is presented. Light microscopical, SEM and InfiniteFocus® images are compared to broadly assess the surface profile. The untreated surface is mostly covered by the resin and slightly structured by the fiber alignment. Some scratches can be discerned. Both sanded surfaces are dominated by the sanding grooves perpendicular to the fiber direction. Fiber damage can be detected, henceforth. The grit blasted surface shows vast craters. Huge regions of fiber damage and break out can be found. The peel ply surface shows the typical pattern of the polyester fabric at the resin layer.

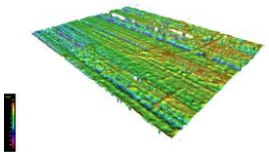
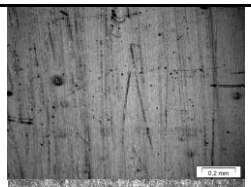
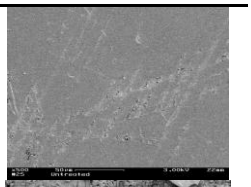
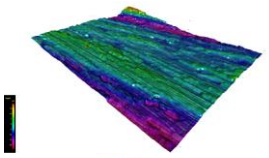
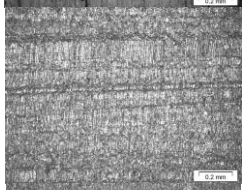
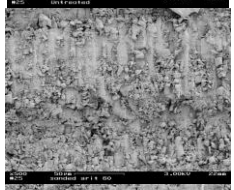
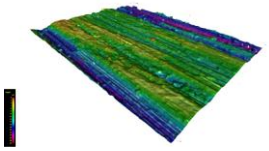
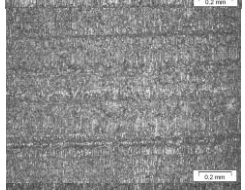
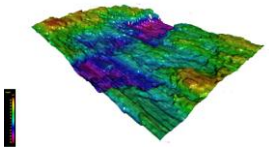
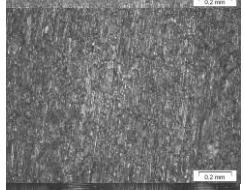
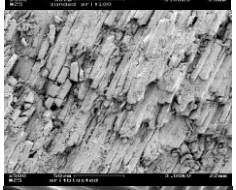
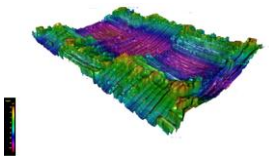
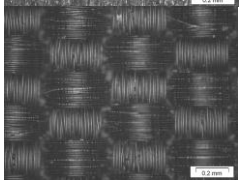
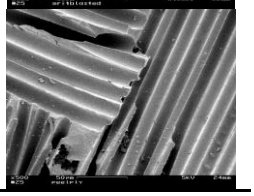
Surface treatment	**3D profile Infinite Focus®** 20x1	**Light microscopy** 100x1	**SEM** 500x1
Untreated			
Sanded grit 60			
Sanded grit 100			
Grit blasted			
Peel ply			

Table 1. Comparison of 3D- topology (Alicona IFM®) and micrographs (light microscopy, SEM) of the pre-treated composite surfaces

Surface roughness measurements are used to quantify the surface topology in order to assess the mechanical interlocking capability of the surface. The measurements are conducted each, in and perpendicular to fiber or sanding direction. The surface profiles and the corresponding roughness values (average value of five line scans) are compared in Figure 3 to better demonstrate the differences between the different treatments. As assumed, the untreated surface shows the lowest roughness, whereas the grit blasted one with the vastly structured profile shows the highest (~ factor 40). The peel ply surface shows medium roughness but a wavy profile. Regarding both roughness parameters R_a and R_q the pre-treated surfaces can be divided into low profiled (untreated), medium profiled (sanded grit 100, peel ply) and vast profiled (sanded grit 60, grit blasted), see Figure 3. The surface profile itself is expected to generate 'locking points' for the adhesive, but can also foreclose the fit of both adherents due to vast height differences in the profile.

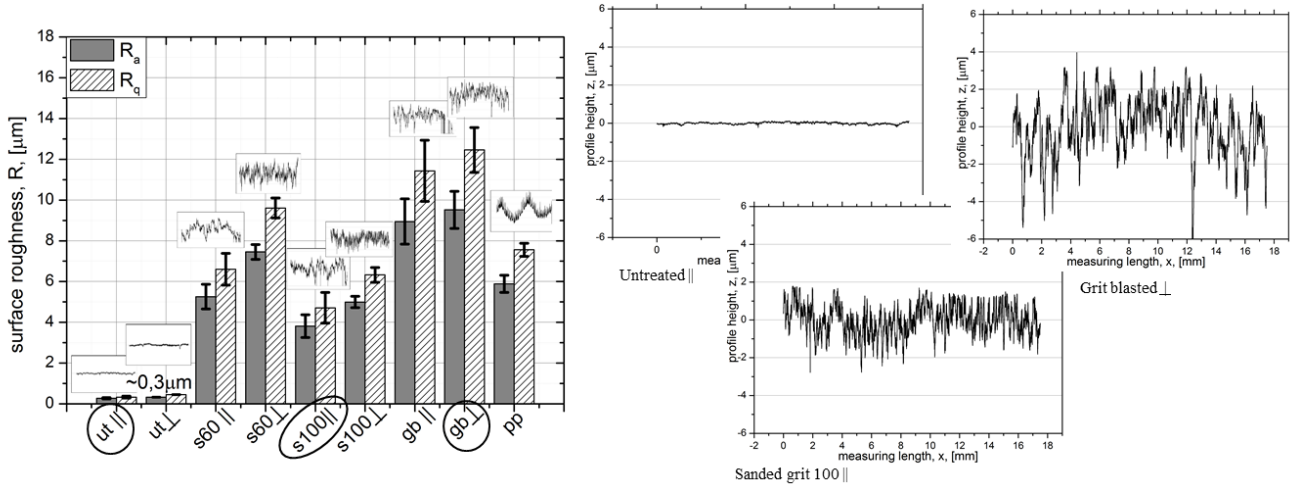


Figure 3. Comparison of surface roughness (R_a, R_q) and profiles of different mechanically treated samples

3.2. Surface tension and wettability

Contact angle measurements are performed to address the energetic state of the surface. The determination of the contact angle exclusively provides accurate drop shape formation in case of smooth surfaces. As a result, the contact angles are solely determined for the untreated and the non-abrasive treated surfaces (corona- activated, chemically modified). In Figure 4 the contact angles and the resulting polar and dispersive parts of surface energy are compared. The corona activated surface shows the lowest contact angles and the highest polar surface energies, thus. Unfortunately, the activation by corona (and also plasma) techniques suffers from short durability and is reversible, henceforth. However, the surface polarity can contrariwise be irreversibly improved by attaching functional groups onto the corona-activated surface, as it was performed with a reagent bearing mercapto(-SH)-moieties (chemically modified sample). This leads to a slight decrease of the polar surface energy compared to neat corona- activation, but still an increase compared to the untreated sample. Subsequently, wetting tests were further used to correlate surface polarity with their wettability and bonding performance, respectively. In Figure 5 the wetting of the adhesive on the completely cured samples is compared with the surface energies. It has to be highlighted, that the wettability for the corona-activated sample is poor. The adhesive peels off during curing, whereas it remains stable on the untreated sample and actually spreads on the chemically modified surface during cure. Additionally, the wetting characteristics of both, mechanically and physico-chemically, treated surfaces are opposed with each other, see Figure 5.

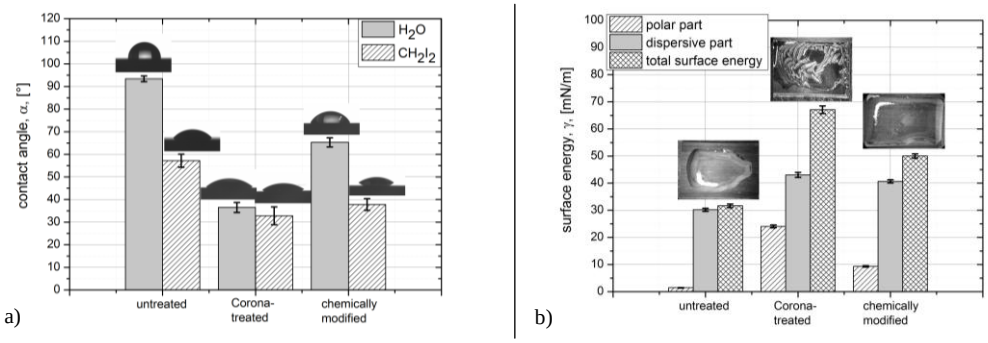


Figure 4. a) Results of contact angle measurements of untreated, corona-activated and chemically modified composite surfaces, b) Evaluation of surface energy and comparison with wetting behavior

Significantly, the abrasively treated samples show excellent wettability. Surface wettability in the subject matter is in no direct correlation with polarity. Concerning the wetting characteristics, surface roughness and texture seems to play a major role.

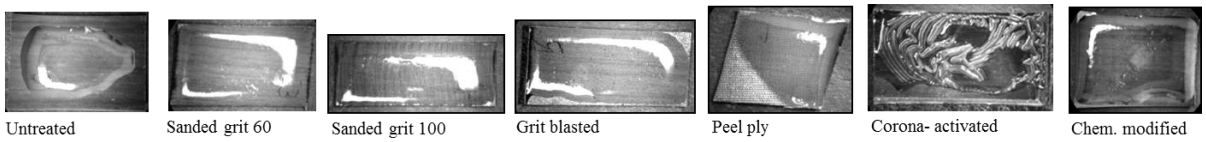


Figure 5. Comparison of wetting tests of different pre-treated composite surfaces

3.3. Study of chemical surface composition

XPS- measurements are performed to assess the overall chemical composition of the surface. Furthermore the existence of contaminants due to abrasive medium in mechanical treatment is evaluated. First, survey scans have been conducted. The corona –treated surfaces are excluded due to the instability of the activation. The results are demonstrated in Table 2 and Figure 6. The amounts (At-%) of C, N, and O (resin constituents) are compared. Significantly, the C content reaches maximum values for the abrasive treatments due to fiber exposure. The O content and, respectively, the O:C ratio increases for the abrasively treated surfaces and shows peak values for the chemically modified surface. An increased O:C-ratio is expected to improve surface wettability by improving polarity in the subject matter [2]. Additionally, the existence of other elements on the surface has been analyzed: the untreated samples show traces of fluorine due to lubricant residuals from processing. Furthermore, silicon can be detected as contaminant or constituent of the resin system with lower confidence, but no traces of metallic elements due to the abrasive medium are detectable. As it was expected, sulfur can be found on the chemically modified surface due to the attachment of mercapto (-SH) -moieties.

Surface treatment °	**C** [At%]	**N** [At%]	**O** [At%]	**Other** >1 At%	**O:C**
Untreated	69	3	8	F	0,12
Sanded grit 60	76	5	16	Si	0,22
Sanded grit 100	77	5	16	Si	0,21
Grit blasted	76	5	16	Si	0,22
Peel ply	76	5	16		0,21
Chemically modified	64	6	19	Si, S	0,30

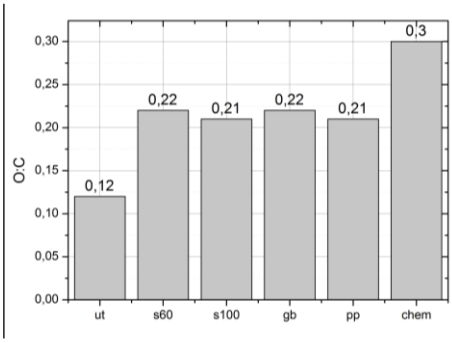


Table 2/Figure 6. Elemental composition and O:C ratio for various pre-treated composite surfaces

XPS- analysis can thus be applied to detect major chemical changes of the chemical surface composition. As XPS is extremely surface sensitive, this technique also provides information on the presence of contaminants at the surface.

3.4. Single lap shear testing of pre-treated adhesively bonded composite joints

In Figure 7a the results of the single lap shear tests of the bonded coupon joints are demonstrated. The displacement in the adhesive layer is approached by the difference between the upper and lower adherend displacement. The maximum force is chosen as parameter demonstrating joint strength (Figure 7b). The grit blasted and the peel ply coupons significantly show the lowest bond strength, whereas the force reaches maximum values for the sanded and the chemically modified coupons. The results generally demonstrate, that a slight roughening of the surface or the attachment of functional groups provides higher bond strengths. Concerning the chemically modified surfaces, a covalent bonding of the mercapto (-SH)- groups to the epoxy units of the adhesive resin is expected, contributing to an increased joint strength. The topographic improvement due to surface profiling is nevertheless restricted: A strongly structured surface (e.g. due to grit blasting or peel ply) results in lower bond strength, due to gaps between adhesive and adherend surface. The measured displacement- due to peel off processes and shear deformation in the adhesive layer- varies in the same matter as the bond strength. The failure mode is a mixture of cohesive and adhesive failure varying with the surface treatment (as it is exemplarily demonstrated for the untreated coupon in Figure 7c). A correlation between failure mode and wettability is assumed and should be further assessed.

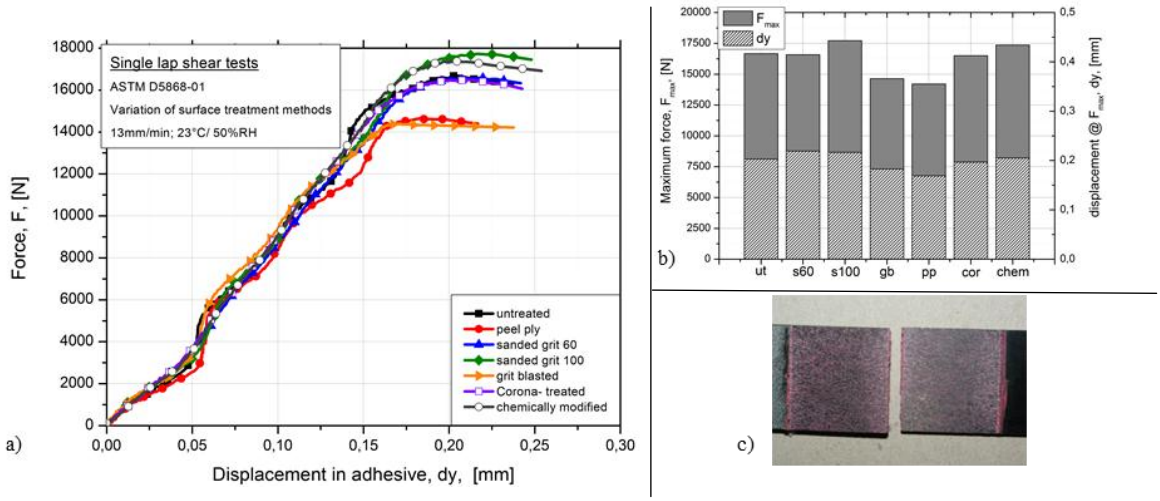


Figure 7. a) Average curves of SLS-testing of surface pre-treated bonded coupon joints; b) Comparison of maximum force, c) e.g. Damage analysis of untreated coupon

5 Conclusion

Tailoring surface properties by different pre-treatment techniques has great potential to improve strength and durability of bonded repairs. Therefore, the impact of the individual techniques on the surface 'state' has to be addressed. The actual key to success would be an improved understanding of the adhesion in dependence of the pre-treatment. The present study shows, that especially abrasive techniques and chemical surface functionalization have great potential to increase global bond performance. Abrasive techniques are proven to tailor surface topology and surface chemical composition of CFRP (carbon-fiber reinforced polymers) structures by e.g. exposing fibers or new resin layers, respectively. Chemical functionalization by means of attaching reactive groups onto the surfaces will additionally provide covalent bonding to reinforce adhesion between adherend and adhesive. A study of the overall chemical composition of the individually treated surfaces by e.g. XPS-techniques will therefore be of outmost importance. Furthermore, evaluation of bonding relations and

functional groups on surfaces would complement and verify the results. Moreover, correlations between wettability and global bond strength are of critical complexity. The study of different pre-treatment for CFRP establishes that- for the given material system- surface energy plays a complex role in describing the wettability of a surface. In brief, a high surface energy or, respectively, a high polarity does not automatically result in good wettability by adhesive resins: a careful balance between the polar and the dispersive parts of the surface energies both of the composite surface and the adhesive is required to achieve optimal adhesion. Surface topology in the subject matter crucially affects wettability and bond strength. Mechanical interlocking of the adhesive on the adherend profile seems to play an important role in bond strength. The wetting test shows excellent wettability for roughened surfaces, and the lap shear performance also reaches maximum values for slightly roughened surfaces. Surface roughness would be one possible parameter to describe and restrict the mechanical interlocking effect, but should be complemented with more detailed investigations- e.g. fracture mechanical testing and more detailed damage analysis. Understanding the failure mode corresponding to the surface 'state' is essential for an in-depth understanding of the functioning of a bonded joint in order to optimize and improve bonded repair strategies.

Acknowledgements

The present research work has been performed at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Austrian Ministry of Traffic, Innovation and Technology with contributions by the Chair of Materials Science and Testing of Plastics, Montanuniversität Leoben, Austria, and FACC AG, Ried im Innkreis, Austria. The PCCL is funded by the Austrian Government and the State Governments of Styria and Upper Austria.

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