SURFACE MODIFIED STEEL/EPOXY-BASED CFRP HYBRID LAMINATES UNDER MODE I, MODE II AND MIXED-MODE LOAD CONDITIONS

A. Monden[1], M. G. R. Sause[2] and S. Horn[3]

[1]Experimental Physics II, University of Augsburg, Universitätsstr. 1, 86159 Augsburg, Germany
Email: andreas.monden@physik.uni-augsburg.de,
Web Page: http://www.physik.uni-augsburg.de/de/exp2/mitarbeiter/Monden/
[2]Experimental Physics II, University of Augsburg, Universitätsstr. 1, 86159 Augsburg, Germany
Email: markus.sause@physik.uni-augsburg.de,
Web Page: http://www.physik.uni-augsburg.de/de/exp2/mitarbeiter/Sause/
[3]Experimental Physics II, University of Augsburg, Universitätsstr. 1, 86159 Augsburg, Germany
Email: horn@physik.uni-augsburg.de,
Web Page: http://www.physik.uni-augsburg.de/de/exp2/mitarbeiter/Horn/

Keywords: CFRP/steel hybrid laminate, surface modification, fracture energy release rate, DCB, ENF, MMB, mode mixity, digital image correlation, thermal residual stresses

Abstract

Planar hybrid laminates were investigated to quantify mode I, mode II and mixed-mode fracture toughness. These laminates were fabricated with a symmetrical layup consisting of unidirectional CFRP with a comparatively thin, surface treated steel foil in the center plane. A variety of surface treatments was applied to the steel surfaces, including sand blasting, Al_2O_3 grit blasting, silane treatment, an innovative approach based on DLC (diamond-like carbon) coatings and combinations thereof. Commonly used testing procedures like DCB (double cantilever beam), ENF (3-point end-notched flexure) and MMB (mixed-mode beam) tests were used to assess the fracture toughness at the interface. Delamination onset and movement were recorded using a digital camera system in case of DCB tests and digital image correlation (DIC) techniques in case of ENF and MMB tests. Specific laminate layup and thermally induced residual stresses affect the measured (apparent) fracture toughness values and intended mode mixities. Thus, corrections were applied during post-evaluation. All surface treatments resulted in individual fracture toughness values and proved efficient to increase fracture toughness significantly. The chosen test configurations allow consistent evaluation of interfacial fracture toughness values of hybrid laminates.

Excerpt from ISBN 978-3-00-053387-7

1. Introduction

Recent progress in the field of hybrid structures and materials has led to the development of mechanically and chemically stable joint technologies for combining fiber reinforced plastics (FRP) and metals [1–3], which also stimulated the need for mechanical testing procedures to determine the fracture toughness at the interface [4]. While combinations of lightweight metals and FRP are used in aerospace applications, steel is still the most widely used construction material in other fields of engineering, often due to economic reasons. Integration of structural FRP parts in such industrial areas leads inevitably to the challenge of joining these different material classes. Due to their different chemical structure, direct joints of steel and epoxy resin will result in poor adhesion, which leads to the requirement of surface treatments and modifications to achieve a mechanically and chemically stable joint [1–3]. To assess the effectiveness of different surface modification techniques on the bond strength between metal and epoxy resin, suitable test methods that allow evaluation of mode I (opening), mode II (sliding) or mixed-mode interfacial fracture toughness are necessary. To the authors' knowledge, no established standardized test methods exist for FRP/metal hybrid laminates for any of the mentioned delamination modes. Regarding pure FRP materials, standardized test methods are given by ASTM D5528 (DCB), ASTM D6671 (MMB) and ASTM D7905 (ENF), respectively. Their adaption and application to FRP/metal hybrid laminates appears promising, easing comparison of fracture toughness values without the need for specialized testing devices. Inhomogeneity originating from the specific, non-monolithic laminate layup and thermally induced residual stresses resulting from co-curing at elevated temperatures may strongly affect the measured fracture toughness values and intended mode mixities. The experimentally determined fracture toughness values of FRP/metal hybrid laminates are thus denominated as apparent fracture toughness values in the following, and corrections are needed to account for the influence of specific laminate layup and residual stresses to enable a direct comparison towards fracture toughness values of pure FRP specimens.

2. Surface modifications and specimen preparation

Sandwich plates were produced using a symmetrical layup consisting of 14 layers of SGL CE 1250-230-39 unidirectional epoxy-based prepreg with a nominal thickness of 0.22 mm per layer in cured state and X5CrNi18-10 cold-rolled steel foil of 0.1 mm nominal thickness laminated at the center plane (Fig. 1). At one side of the steel foil a precrack was built in using ETFE-foil of 25 µm thickness (Wrightlon® 5200). A standard curing cycle using 130 °C temperature for 90 min following the materials supplier's recommendations was used. A variety of surface modifications was applied to the steel foils prior to co-curing them with the prepreg material. Resulting thickness of the laminates was 3.4 mm, mainly due to the steel foil attenuating resin permeation in thickness direction.

Table 1. Properties of used materials.

Material	E_1 [GPa]	E_2 [GPa]	ν_{12} [-]	G_{12} [GPa]	α_1 [10^{-6} / K]	α_2 [10^{-6} / K]
steel X5CrNi18-10 (1.4301)	172.1	97.9	0.31	65.6	16.0 [5]	16.0 [5]
CFRP SGL CE 1250-230-39	129.0	6.9	0.33	6.1	0.3 [6]	30.0 [6]

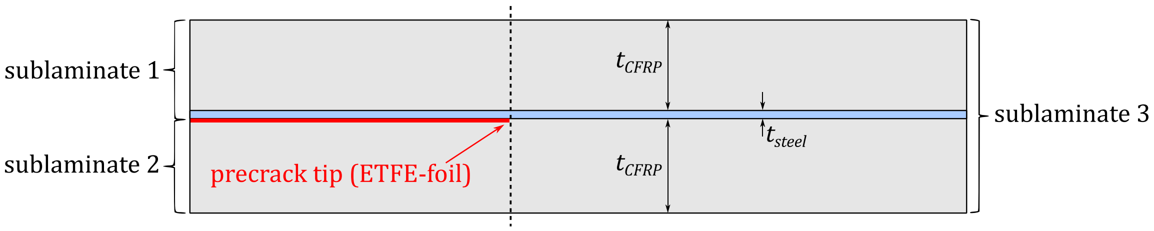


Figure 1. Schematic illustration of laminate layup.

We chose an "as received" cold-rolled steel surface as reference. The steel surface was cleaned in an ultrasonic bath for 10 min in acetone, 10 min in isopropanol, 10 min in deionized water and then dried using pressurized, oil-free nitrogen.

Grit blasted surfaces were fabricated to examine the influence of mechanical interlocking and increased surface area on the interfacial fracture toughness. Sand blasting was performed using a particle size distribution of 70 – 150 µm. Aluminium oxide abrasive (Al_2O_3) with particle sizes of

Excerpt from ISBN 978-3-00-053387-7

106 – 150 μm was used to produce coarse surfaces. It is well known that initial adhesion levels can be significantly increased by suitable grit blasting variants [7]. The underlying principle is discussed in literature: increased effective surface area resulting in increased intermolecular bonding [8], modification of the surface topology enabling mechanical interlocking and at the same time crack deflection away from the interface into the bulk [9], as well as introduction of physicochemical changes yielding an increase of wettability [10].

Silane treatment was applied to the cleaned and degreased steel surfaces. 3-Glycidyloxypropyl-trimethoxysilane ("Dynasilan® GLYMO", Evonik Industries AG) was hydrolyzed in aqueous solutions with a concentration of 10 vol%. To promote hydrolyzation and silanol formation, stirring in an ultrasonic bath was performed for 10 min. The steel foils were then dipped into the solution for 10 min (first 5 min in ultrasonic bath). After removing the steel foil from the solution, excess liquid was blown off the surface using pressurized, oil-free nitrogen before drying and curing the surface for 10 min at 110 °C. The silanes form a layer on the metal oxide surface via covalent bonds. At the same time functional groups of the silane layer promote chemical bonds to the epoxy resin. In literature, the possibility of an interphase formation featuring an intermediate modulus between polymer and metal facilitating stress transfer is also mentioned [11, 12]. Silane treatment was applied to the "as-received" steel surface as well as to sand blasted and Al_2O_3 blasted surfaces to investigate the effect of surface roughness.

Two different diamond-like carbon (DLC) variants were investigated regarding their effect on adhesion. DLC coatings in general are amorphous, metastable carbon-based materials exhibiting a significant ratio of sp^3-hybridized C-bonds, which account for the diamond-like properties like high hardness, low electrical conductivity and chemical stability [13, 14]. DLC coatings were applied using a PACVD (plasma-assisted chemical vapour deposition) process. With the choice of reactive gas (hydrocarbon precursor), the hydrogen content (C/H-ratio) of the coating can be influenced [13, 14]. DLC coatings may be doped with e.g. silicon to reduce residual stresses of the coating and thus improve adhesion to the steel substrate [14, 15]. Doping may be achieved by using a silicon containing hydrocarbon precursor. Further, Si-doping may change the surface chemistry regarding steel/DLC and DLC/epoxy adhesion. We investigated a "standard" DLC variant with relatively high hardness (abbr. DLC) and a silicon-doped variant (abbr. DLC:Si). In this study, DLC:Si was also applied to a previously Al_2O_3 blasted surface. Typical coating thicknesses are 2–3 μm.

Measured roughness values of the investigated surface modifications are listed in Table 2, where silane treatment is excluded as it is supposedly not affecting surface roughness. It can be seen that sand blasting and Al_2O_3 blasting increase surface roughness significantly, whereas DLC and DLC:Si coatings have a negligible effect on measured surface roughness values.

Table 2. Roughness values of modified steel surfaces.

Surface modification	R_a [nm]	R_{RMS} [nm]
untreated (reference)	180	225
sand blasted	389	504
Al_2O_3 blasted	995	1323
DLC	172	224
DLC:Si	196	251
Al_2O_3 blasted + DLC:Si	905	1135

3. Testing procedure

DCB tests were performed in accordance with ASTM D5528. Specimens of 200 mm length, 20 mm width and 50 mm effective precrack length were cut from the cured plates. Force during testing was applied via adhesively bonded load blocks and a crosshead speed of 5 mm/min. Crack tip propagation was recorded using a digital camera system (Zwick VideoXtens) enabling post-evaluation of initiation and propagation values.

In case of ENF tests in accordance with ASTM D7905, specimens of 175 mm length, 20 mm width and 48 mm precrack length (30 mm effective precrack length during fracture testing) were used. Tests were conducted with a crosshead speed of 0.8 mm/min. Delamination initiation was recorded and post-evaluated via DIC techniques (GOM ARAMIS 12M) [16].

MMB tests were conducted in accordance with ASTM D6671, and three different mode mixities (Eq. 1) were applied by variating the lever arm length of the MMB testing apparatus.

$$\frac{G_{\mathrm{II}}}{G} = \frac{G_{\mathrm{II}}}{G_{\mathrm{I}} + G_{\mathrm{II}}} \tag{1}$$

Specimens of 150 mm length, 20 mm width and 28 mm effective precrack length were used. Tests were conducted with a crosshead speed of 0.5 mm/min. Similarly to ENF tests, delamination initiation was recorded and post-evaluated via DIC techniques.

4. Evaluation and results

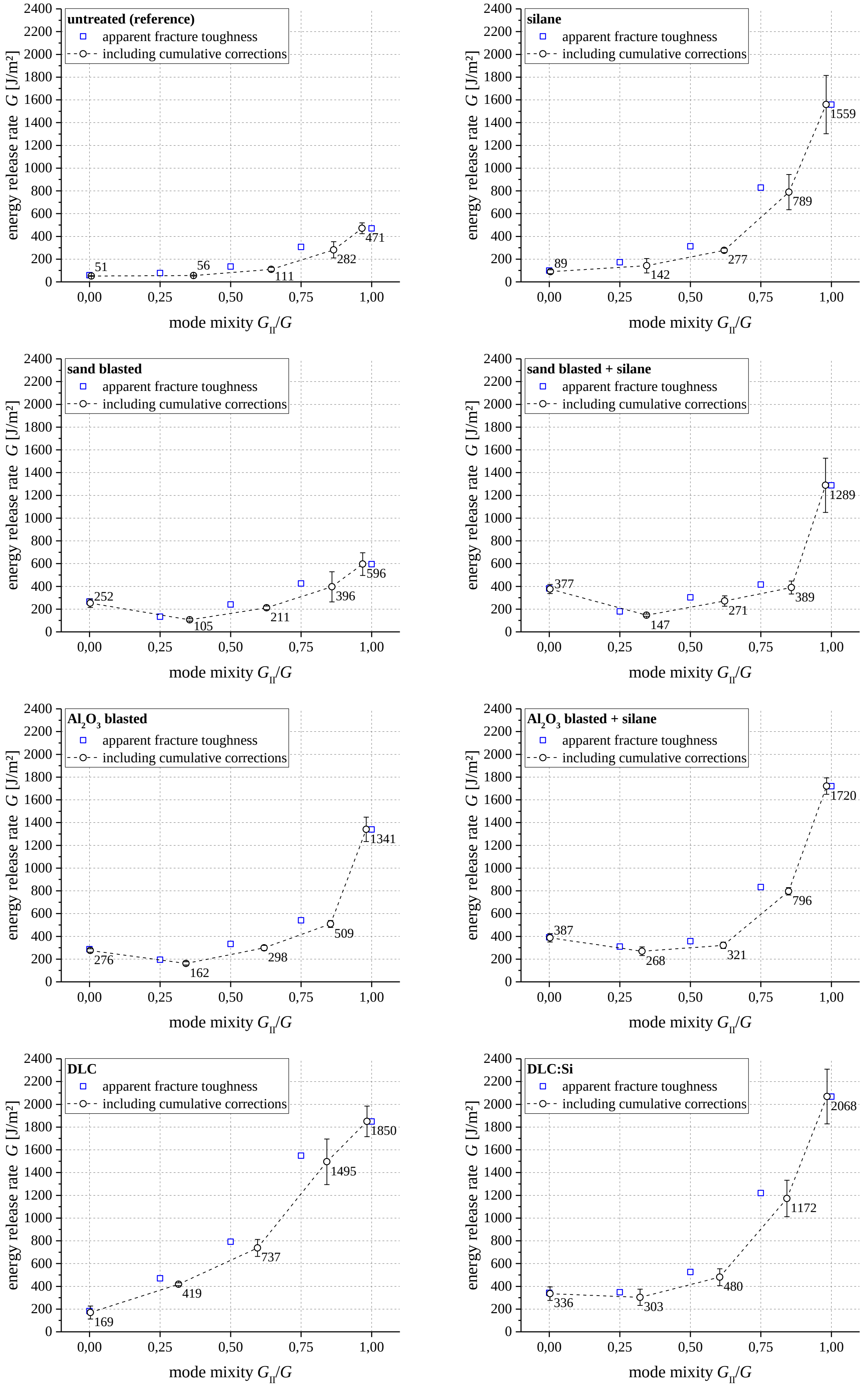
Corrections of the measured (apparent) fracture toughness values are necessary to account for a variety of effects. In case of DCB tests, corrections for large displacements and the stiffening of the specimen by the end blocks are performed according to ASTM D5528. For MMB tests, lever arm weight has to be taken into account and results in a shift of the intended mode mixities towards higher mode II ratios in the present case. The investigated hybrid laminates exhibit a macroscopically symmetrical layup, whereas failure is initiated at one of the CFRP/steel interfaces and thus asymmetry is introduced in the vicinity of the crack tip. For DCB tests, this asymmetry results in a minor mode II contribution, which can be estimated by the semi-empirical relationship established by MOLLÓN et. al. [17]. In case of MMB tests, similar effects on mode mixity result from the asymmetric failure behavior, which can be estimated using the formulations given by SHAHVERDI et. al. [18]. Thermally induced residual stresses resulting from curing at elevated temperatures affect the apparent fracture toughness values and intended mode mixities. This influence was quantified using the formulations given by YOKOZEKI et. al. [19], which are based on the general relationship introduced by NAIRN [20].

Results shown in Fig. 2 are based on a sample size of six specimens in case of DCB tests and three specimens in case of MMB and ENF tests, respectively. In case of untreated steel surfaces, purely adhesive failure at the interface was observed for the entirety of investigated mode mixities.

Mode I fracture toughness was significantly increased by sand or Al_2O_3 grit blasting, respectively, each combined with silane dip coating, as well as by DLC:Si coatings with and without previous Al_2O_3 grit blasting. Mode I fracture toughness in these cases exceeded the fracture toughness of pure CFRP. Observation of crack surfaces coincides with these findings, exhibiting purely cohesive failure within CFRP (Fig. 3–5).

All investigated DLC coatings exceeded the mode II fracture toughness of pure CFRP significantly, whereas DLC and DLC:Si coatings without previous Al_2O_3 grit blasting actually exhibit coating failure at the steel/DLC interface (Fig. 4–5). Significant increase of mode II fracture toughness could also be observed for the surface modifications including silane treatment, exhibiting mostly cohesive failure within CFRP (Fig. 3).

Excerpt from ISBN 978-3-00-053387-7


untreated (reference)
apparent fracture toughness
including cumulative corrections
51
56
111
282
471
silane
apparent fracture toughness
including cumulative corrections
89
142
277
789
1559
sand blasted
apparent fracture toughness
including cumulative corrections
252
105
211
396
596
sand blasted + silane
apparent fracture toughness
including cumulative corrections
377
147
271
389
1289
Al2O3 blasted
apparent fracture toughness
including cumulative corrections
276
162
298
509
1341
Al2O3 blasted + silane
apparent fracture toughness
including cumulative corrections
387
268
321
796
1720
DLC
apparent fracture toughness
including cumulative corrections
169
419
737
1495
1850
DLC:Si
apparent fracture toughness
including cumulative corrections
336
303
480
1172
2068
energy release rate G [J/m²]
mode mixity GII/G
0,00
0,25
0,50
0,75
1,00
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400

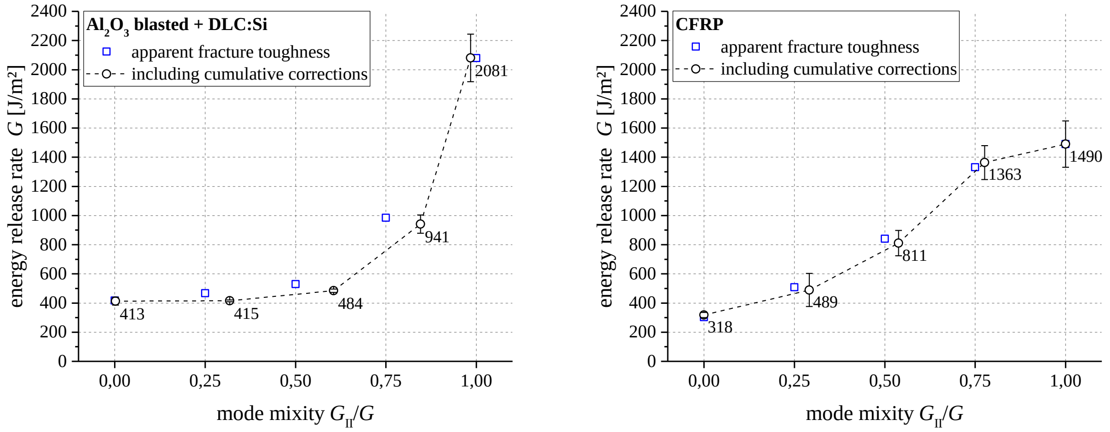


Figure 2. Results including cumulative corrections.

In the mixed-mode regime, fracture toughness values of pure CFRP were nearly reached by the non-doped DLC variant. Overall performance of the investigated DLC variants proved most suitable to improve fracture toughness in the mixed-mode regime.

Results shown in Fig. 2 indicate that scattering of the fracture toughness values was significantly reduced by Al_2O_3 grit blasting, both as a stand-alone treatment as well as a pre-treatment for subsequent silanization or DLC:Si-coating, respectively.

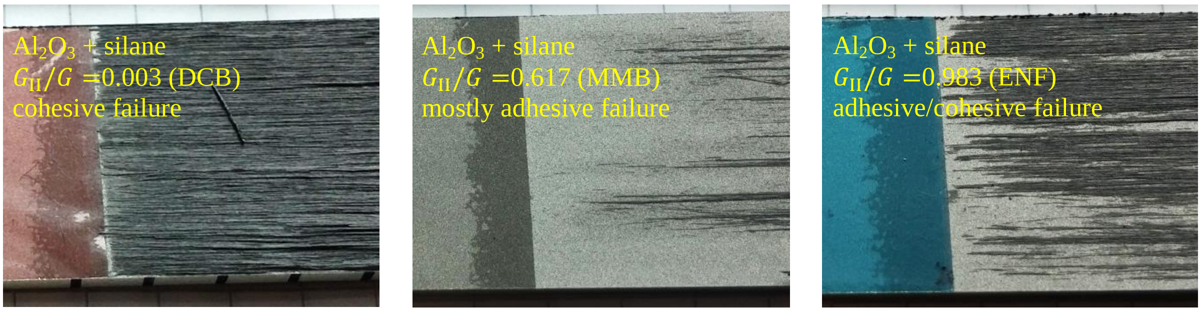


Figure 3. Fracture surfaces of Al_2O_3 blasted + silane treated specimens (representative examples).

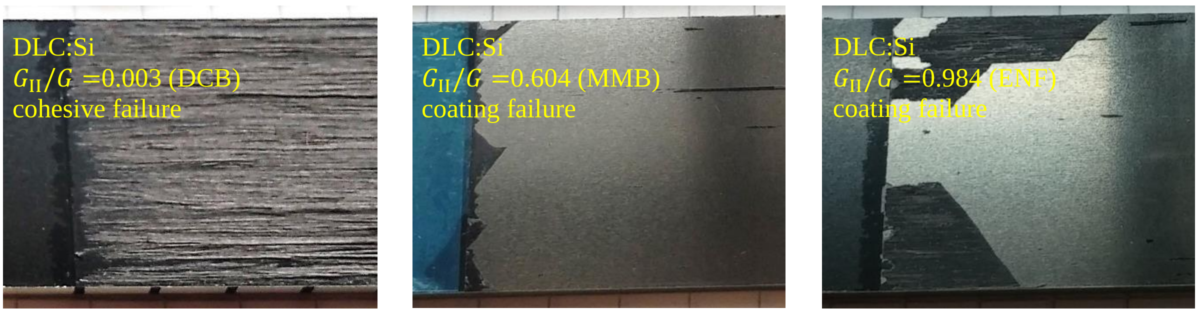


Figure 4. Fracture surfaces of DLC:Si coated specimens (representative examples).

Excerpt from ISBN 978-3-00-053387-7

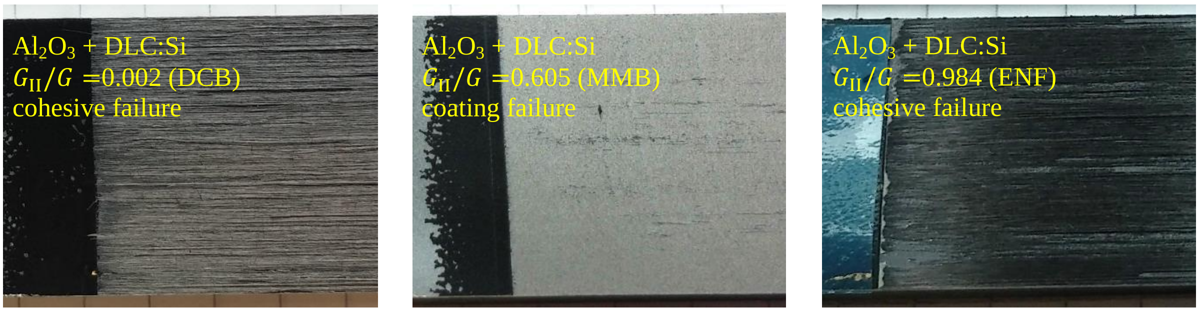


Figure 5. Fracture surfaces of Al_2O_3 blasted + DLC:Si coated specimens (representative examples).

5. Conclusion

We applied a variety of surface modification techniques to improve the interfacial failure behaviour in CFRP/steel hybrid laminates. Compared to untreated specimen, all surface modification techniques were found to improve the CFRP/steel interfacial fracture toughness, and each surface treatment resulted in characteristic fracture toughness values and failure modes of the laminate. DLC coatings showed a significant improvement of interfacial fracture toughness, which could be confirmed by examination of the fracture surfaces, revealing cohesive failure within the CFRP laminate or coating failure, respectively, depending on the applied load condition. Corrections were needed to account for asymmetric failure behaviour and residual thermal stresses, altering intended mode mixities and measured (apparent) fracture toughness values. The chosen test configurations allow consistent evaluation of interfacial fracture toughness values of hybrid laminates and enable comparison towards fracture toughness values of pure FRP materials.

Acknowledgements

This work was conducted within the project “FORCiM³A – Forschungsverbund CFK/Metall-Mischbauweisen im Maschinen- und Anlagenbau“, which is funded by the Bayerische Forschungsstiftung (BFS). The authors take this opportunity to gratefully acknowledge the collaboration with AxynTec Dünnschichttechnik GmbH, providing the DLC coatings.

References

[1] A. Baldan. Review: Adhesively-bonded joints and repairs in metallic alloys, polymers and composite materials: Adhesives, adhesion theories and surface pretreatment. *Journal of Materials Science*, 39:1–49, 2004.

[2] J.D. Venables. Review: Adhesion and durability of metal-polymer bonds. *Journal of Materials Science*, 19:2431–2453, 1984.

[3] T. Sinmazçelik, E. Avcu, M.Ö. Bora, O. Çoban. A review: Fibre metal laminates, background, bonding types and applied test methods. *Materials and Design*, 32:3671–3685, 2011.

[4] A. Baldan. Review: Adhesively-bonded joints in metallic alloys, polymers and composite materials: Mechanical and environmental durability performance. *Journal of Materials Science*, 39:4729–4797, 2004.

[5] Datasheet: Edelstahl 1.4301 (X5CrNi18-10). *Thyssen Krupp*.

Excerpt from ISBN 978-3-00-053387-7

[6] J. Both, D. Barfuß, H. Baier. Mode II Delamination of CFRP-Metal Laminates at Bolted Joints. *Proceedings of the 18th International Conference on Composite Materials*, Jeju Island, Korea, August 21-26, 2011.

[7] G.W. Critchlow, K.A. Yendall, D. Bahrani, A. Quinn, F. Andrews. Strategies for the replacement of chromic acid anodising for the structural bonding of aluminium alloys. *International Journal of Adhesion & Adhesives,* 26:419–453, 2006.

[8] J.M. Sykes. *Surface Analysis and Pretreatment of Plastics and Metals*. Applied Science Publishers, 1982.

[9] M. Shahid, S.A. Hashim. Effect of surface roughness on the strength of cleavage joints. *International Journal of Adhesion & Adhesives*, 22:235–244, 2002.

[10] A.F. Harris, A. Beevers. The effects of grit-blasting on surface properties for adhesion. *International Journal of Adhesion & Adhesives*, 19:445–452, 1999.

[11] P.M. Hobbs, A.J. Kinloch. The Computational Molecular Modelling of Organosilane Primers. *The Journal of Adhesion,* 66:203–228, 1998.

[12] M.-L. Abel, R.P. Digby, I.W. Fletcher, J.F. Watts. Evidence of specific interaction between γ-glycidoxypropyltrimethoxysilane and oxidized aluminium using high-mass resolution ToF-SIMS. *Surface and Interface Analysis,* 29:115–125, 2000.

[13] J. Robertson. Diamond-like amorphous carbon. *Materials Science and Engineering R*, 37:129–281, 2002.

[14] A. Grill. Diamond-like carbon: state of the art. *Diamond and Related Materials*, 8:428–434, 1999.

[15] J.C. Damasceno, S.S. Camargo Jr, F.L. Freire Jr, R. Carius. Deposition of Si-DLC films with high hardness, low stress and high deposition rates. *Surface and Coatings Technology,* 133-134:247–252, 2000.

[16] M.G.R. Sause. Fiber Reinforced Composites: In-Situ Monitoring. *Habilitation thesis, University of Augsburg,* 2015.

[17] V. Mollón, J. Bonhomme, J. Vina, A. Argüelles. Theoretical and experimental analysis of carbon epoxy asymmetric dcb specimens to characterize mixed mode fracture toughness. *Polymer Testing,* 29:766–770, 2010.

[18] M. Shahverdi, A.P. Vassilopoulos, T. Keller. Mixed-Mode I/II fracture behavior of asymmetric adhesively-bonded pultruded composite joints. *Engineering Fracture Mechanics,* 115:43–59, 2014.

[19] T. Yokozeki, T. Ogasawara, T. Aoki. Correction method for evaluation of interfacial fracture toughness of DCB, ENF and MMB specimens with residual thermal stresses. *Composites Science and Technology,* 68:760–767, 2008.

[20] J.A. Nairn. On the calculation of energy release rates for cracked laminates with residual stresses. *International Journal of Fracture*, 139:267–293, 2006.

Excerpt from ISBN 978-3-00-053387-7