INFLUENCE OF THE SURFACE PRETREATMENT ON THE DURABILITY OF ADHESIVELY BONDED COMPOSITE REPAIRS

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ABSTRACT

The effect of ambient conditions related to the aircraft industry on repair-specimens manufactured from epoxy-based carbon fiber reinforced prepreg material utilizing two different kinds of surface treatment in comparison to unrepaired (reference-) specimens will be investigated. The mentioned methods of surface preparation are sanding on the one hand and a combination of a corona with a wet chemical treatment by a functional organosilane on the other hand. The impact of conditioning in a de- and anti-icing fluid for 1 week at room temperature, in a hydraulic fluid for 6 weeks at 70 °C as well as under hot/wet conditions (70 °C/85 % r. h.) for 7 weeks on the tensile strength as well as the moisture absorption behavior will be discussed. During hot/wet conditioning, a substantial amount of moisture is absorbed, immersion in Kilfrost at room temperature leads to a lower amount of moisture absorbed. Moisture uptake in Skydrol could not be monitored. Tensile testing shows that the selected ambient conditions do not have a significant impact on the tensile strength of neither the repair-specimens produced with a scarf ratio of 1:30 nor on the reference-specimens. The analysis of the according failure modes of the repair-specimens reveals a failure normal to the specimens´ surfaces, no failure along the bondline is investigated.

1 INTRODUCTION

Since composite materials are increasingly used in e.g. the automotive and the construction sector [1, 2], but also as materials for load bearing structures in aircraft construction [1–4], these components need to be repaired after suffering damage [4–9]. Therefore, several repair strategies have been developed in the past, mainly divided into mechanically fastened and bonded repairs [6–8]. In comparison to mechanically fastened repairs, decisive advantages in terms of e.g. surface smoothness, the avoidance of the introduction of holes to composite structures, aerodynamic features and weight reduction can be achieved by utilizing bonded patch repairs [1, 4, 6, 7, 10, 11]. Despite these advantages, several challenges like durability of bonded repairs and advances in surface preparation techniques have to be addressed [4, 12, 13].

Within this work, the influence of selected, aircraft relevant media and environmental conditions on the moisture absorption behavior as well as on the tensile strength of reference- and repair-specimens according to AITM 1-0029 [14] will be investigated. The related fracture patterns will be analyzed as well. Besides sanding, which is commonly used for aircraft repair procedures [4], an alternative method of surface modification developed in previous studies with the intention of improving adhesion between the surface and the adhesive will be applied [9, 15]. This surface functionalization, described in greater detail in section 2.3 as well as [9, 15, 16], is achieved by a combination of a corona treatment in combination with a subsequent wet chemical treatment of the activated, tapered surfaces by a functional silane.

2 EXPERIMENTAL PART

2.1 Materials

A commercially available prepreg material, consisting of an epoxy-based resin reinforced with woven carbon fibers was used for the production of laminate plates and as repair-material. A supported, also commercially available epoxy-based film adhesive with a nominal thickness of 0.2 mm was chosen for bonding of the repair-joints. Curing of the laminate plates as well as of the repair-plies was achieved in an autoclave according to the material supplier's specifications. Pre-cured glass fiber reinforced epoxy resin functioned as tab material, Scotch-Weld^{TM} AF163-2L film adhesive with a nominal thickness of 0.14 mm supplied by 3M (Saint Paul, US) was used for the according bonding procedure.

For the surface functionalization (3-(2,3-Epoxypropoxy)propyl)trimethoxysilane, subsequently addressed as "epoxysilane", provided by Wacker Chemie (Muenchen, DE) as well as 2-propanol and tetrahydrofuran supplied by Carl Roth (Karlsruhe, DE) were utilized.

2.2 Specimen manufacturing

A quasi-isotropic, symmetric laminate was produced from the prepreg material by following the stacking sequence $[+45/0/-45/90]_S$. All laminate plates were checked for voids with ultrasonic inspection and passed this assessment. Repair-specimens with a scarf ratio of 1:30 were manufactured via a soft patch repair approach according to AITM 1-0029 [14]. Tapering with respect to the scarf ratio was performed manually using an angular grinder (grit 100) resulting in taper-areas with sanded surfaces. The taper-area of a pre-defined proportion of the laminates was additionally functionalized by the previously mentioned corona treatment, which was followed by a wet-chemical treatment with the epoxysilane. After tapering/chemical functionalization, a layer of the film adhesive was laid-up in the taper-area. Subsequently, the repair-plies were deposited on the film adhesive with a slight overlap. Curing of these repairs was performed under the same curing conditions as used for the production of the original laminate plates and was followed by a final ultrasonic inspection, which was passed as well.

Individual specimens cut from the laminate plates with a diamond coated disk mounted on a water cooled circular saw (Diadisc 5200, Mutronic Praezisionsgeraetebau, Rieden, DE) are depicted in Figure 1. Specimens extracted from unrepaired laminate plates were used as a reference. All specimens were 280 mm in length and 25.4 mm in width.

Tapered end tabs were bonded to the laminate plates with the Scotch-Weld^{TM} AF163-2L film adhesive in a hot plate press (P300 E+, Dr. Collin, Ebersberg, DE) according to the cure cycle specified by the adhesive manufacturer. A second batch of identical plates without tabs ("traveler specimens") was manufactured for moisture absorption measurement in order to eliminate the influence of the tab material [17].

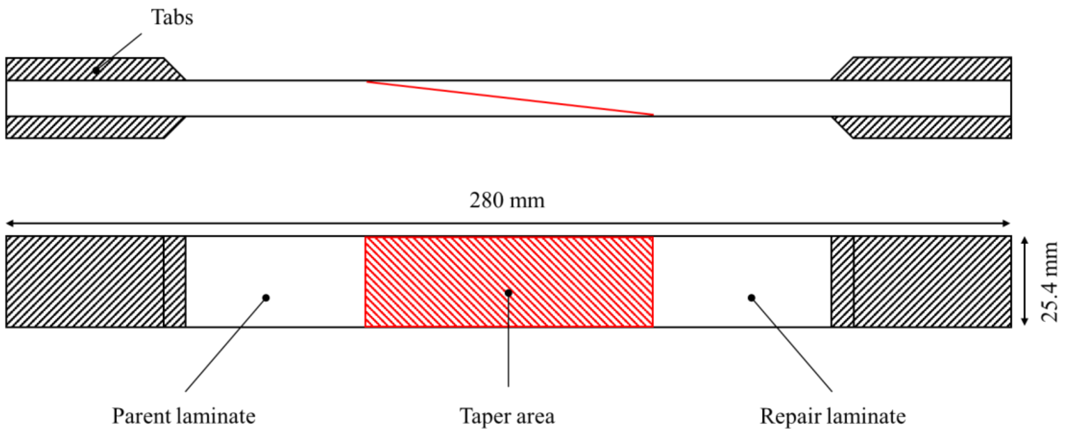

Figure 1: Schematic of the repair-specimens [16].

2.3 Surface functionalization

In an initial step, contaminants had to be rinsed off the tapered areas with 2-propanol before the corona (atmospheric pressure plasma) treatment commenced (Laboratory corona station PG 3001, Ahlbrandt System, Lauterbach, DE). Immediately after the corona treatment, the epoxysilane was applied to the surfaces with a brush. After an exposure time of ~24 h the epoxysilane was rinsed off with tetrahydrofuran for 3 times. It has to be noted that after each of these rinsing steps the surfaces were dried with compressed carbon dioxide. Finally, the surfaces were additionally dried at 70 °C for ~60 min in a heating chamber. The subsequent repair-procedure was started within ~2 days. Due to the functionalization procedure, an increase in surface energy was observed, which was stable for at least one week, as reported in [9, 16].

2.4 Specimens conditioning and moisture absorption measurement

Prior to specimens’ conditioning, all specimens were dried in a heating chamber for 4 days at 70 °C. In order to characterize the material behavior in the dried state, specimens dried at 70 °C for 4 days were prepared for tensile testing at 23 °C and 70 °C, respectively. Specimens conditioning and moisture absorption measurement were conducted in accordance with ASTM D5229 [17]. Conditioning was performed in a de- and anti-icing fluid (Kilfrost ABC-3, Kilfrost Limited, Haltwhistle, GB) for 1 week at room temperature (RT), in a hydraulic fluid (Skydrol LD-4, Eastman Chemical B.V., Capelle aan den Ijssel, NL) for 6 weeks at 70 °C and under hot/wet conditions (70 °C/85 % r. h.) for 7 weeks. Hot/wet conditioning was achieved in a climate chamber (CTC256, Memmert, Schwabach, DE).

Moisture absorption was monitored by iterative measurement of the traveler specimens´ mass gain, which were conditioned alongside the specimens with tabs attached. In order to determine the specimens´ mass, they were removed from the conditioning compartments, thoroughly wiped off and put into a sealed glass container in order to minimize the influence of the lab´s ambient conditions. Immediately after the weighing procedure, the specimens were put back into the conditioning compartments. The relative moisture content ΔM was calculated according to the following equation [17]:

$$\Delta M, \% = \frac{(W_i - W_b)}{W_b} \times 100 \tag{1}$$

Where W_i is the current specimen mass, g and W_b is the baseline specimen mass, g (after 4 days of drying at 70 °C).

2.5 Tensile testing and documentation of failure modes

Quasistatic tensile tests were performed according to AITM 1-0029 [14] on a universal tensile/compression testing machine (Z250, Zwick, Ulm, DE) equipped with a 250 kN load cell and wedge-screw grips (250 kN maximum load). The initial grip separation was 160 mm, the test speed was set to 2 mm/min crosshead speed. In order to determine the specimens´ moisture content immediately before tensile testing, the mass was measured as described. Subsequently the samples were transported to the testing machine in a sealed glass container. For the tests at 70 °C, specimens were put in the machine´s heating chamber for 10 min before the tensile tests were started. Tensile strength values were calculated from the maximum load divided by the thickness in the parent laminate area and the width of the specimen (each as a mean of three individual values per specimen).

The according failure modes were documented with a digital single lens reflex camera equipped with a macro lens (EOS 600D and EFS 18-55mm 0.25m/0,8ft, Canon Inc., Tokyo, JP) and were categorized according to AITM 1-0029 [14].

3 RESULTS AND DISCUSSION

3.1 Moisture absorption

In Figure 2 the relative moisture content and the according standard deviations as a function of the exposure time for the reference- as well as the repaired specimens with sanded as well as functionalized surfaces conditioned in Kilfrost and under hot/wet conditions is depicted. Due to the low amount of moisture absorbed, moisture absorption could not be monitored properly for the specimens immersed in Skydrol at 70 °C. In general, two observations can be made. Firstly, repaired specimens show a slightly higher amount of moisture absorption than the unrepaired ones. Secondly, moisture absorption for the two kinds of repair-specimens is similar, independent of their type of surface treatment (sanded or additionally functionalized via corona discharge and wet chemical treatment). Specimens conditioned under hot/wet conditions (70 °C/85 % r. h.) absorb a considerable amount of moisture up to 1.04 % in the case of the repaired specimens. A slightly lower amount of moisture (0.98 %) is found in the unrepaired reference-specimens. Conditioning for 1 week at RT in Kilfrost leads to a moisture uptake of up to 0.25 % for the repaired and 0.22 % for the unrepaired specimens. It has to be noted, that the equilibrium moisture content could not be reached after 1 week of exposure in Kilfrost at RT.

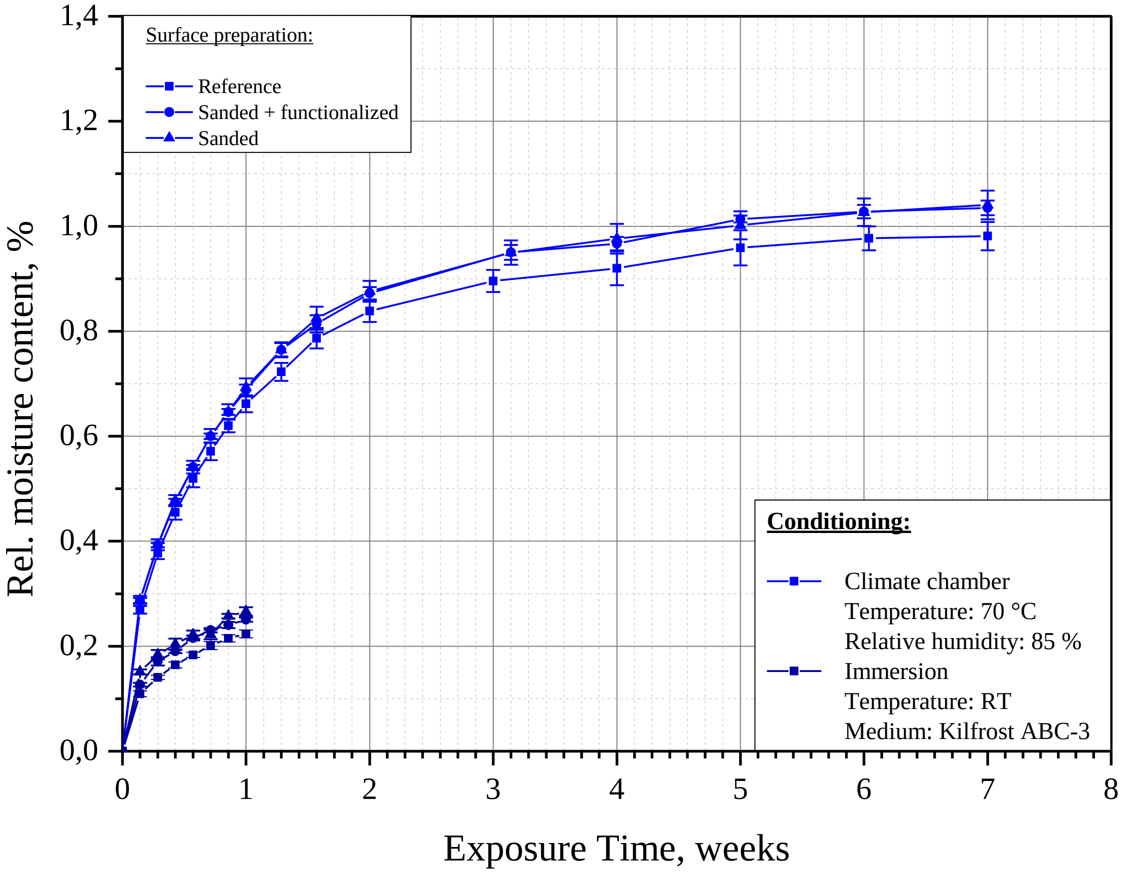

Figure 2: Relative moisture content and the according standard deviations of the reference- and repair-specimens as a function of exposure time for conditioning in Kilfrost and under hot/wet conditions (mean of 8 specimens).

3.2 Quasistatic tensile tests

Tests of the reference-specimens in the dried state at 23 °C and 70 °C show that the tensile strength for these specimens stays constant. Figure 3 and Figure 4 show the tensile strength of the reference- and repair-specimens normalized to the according dried reference at 23 °C / 70 °C, respectively, as a function of the ambient conditions.

In Figure 3 the mean tensile strength at RT of the reference- and repair-specimens after drying for 4 d as well as after immersion in Kilfrost is depicted. Concerning the repair-specimens in dried condition 93 % of the reference´s tensile strength can be restored with the functionalized surfaces, 81 % with the sanded surfaces. After immersion in Kilfrost, a slight increase in the unrepaired specimens´ tensile strength to 105 % can be observed. The values for repaired specimens with both surface treatments lie between 90 % - 93 %. It can be concluded that immersion in Kilfrost does not have a significant influence on the tensile strength of neither the unrepaired reference-specimens nor on the repair-specimens. Also, the surface functionalization with the combined corona and wet chemical treatment does not have a pronounced impact.

Figure 4 contains a similar plot as Figure 3 for the specimens tested at 70 °C. The repair-specimens in dried state show a slight decrease in tensile strength to 85 - 88 % when compared to the specimens with functionalized surfaces tested at RT. Conditioning in Skydrol as well as under hot/wet conditions does not significantly influence the reference- as well as the repair-specimens when compared to the specimens in dried state tested at 70 °C. The tensile strength values are 102 % for immersion in Skydrol and 97 % for the hot/wet condition for the reference-specimens and 89 % - 91 % (Skydrol) and 84 - 86 % (hot/wet) for the repaired specimens. As for the specimens tested at RT, the additional surface functionalization does not have a beneficial impact.

It is important to note that the failure mode of all specimens for the selected ambient conditions was tensile failure in the taper-area (normal to the specimen surface) [14]. Failure did not occur along the bondline, as exemplarily shown in Figure 5 for the tests performed at RT after drying as well as after conditioning in Kilfrost and in Figure 6 for the tests performed at 70 °C after drying as well as after conditioning at 70 °C/85 % r. h. Similar results for repair-specimens with scarf ratios ranging from 1:20 – 1:50 were found in previous studies, where other types of adhesives were used [16]. In this case, a shift to a failure along the bondline was found for repair-specimens manufactured with a scarf ratio of 1:9 [16].

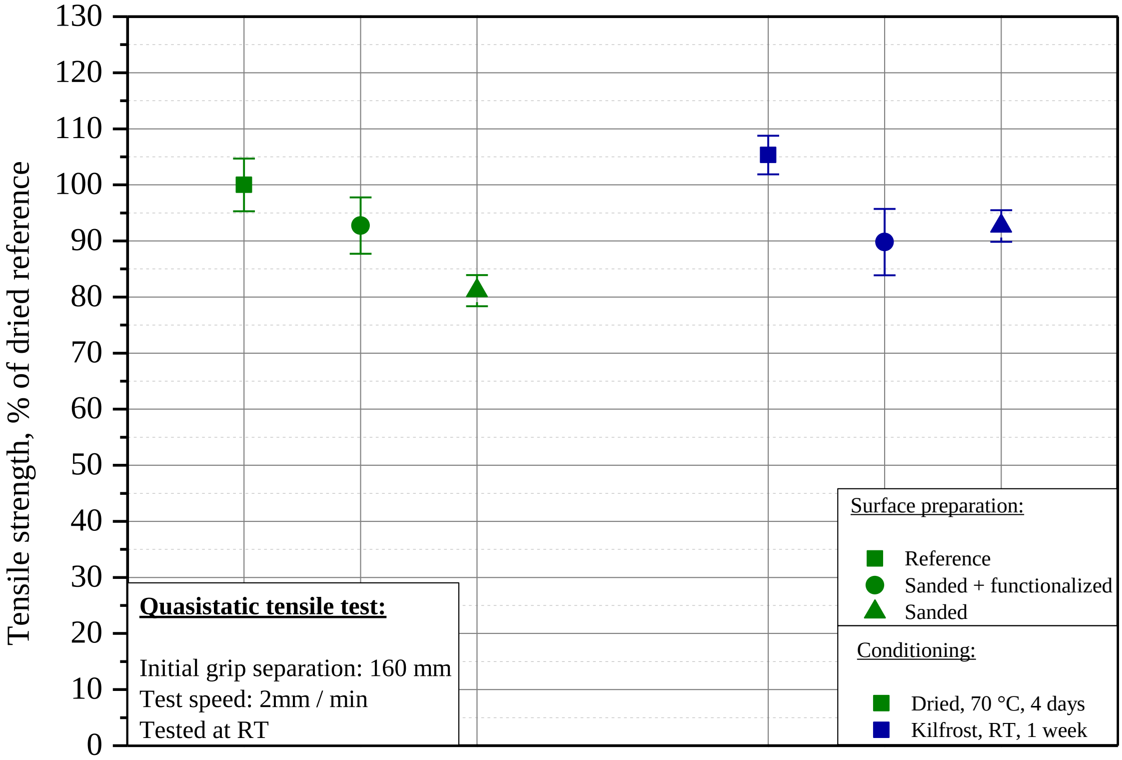

Figure 3: Mean tensile strength and standard deviation (normalized to the unrepaired, dried reference) of the reference- and repair-specimens with sanded as well as functionalized surfaces as a function of the according ambient conditions, tested at RT.

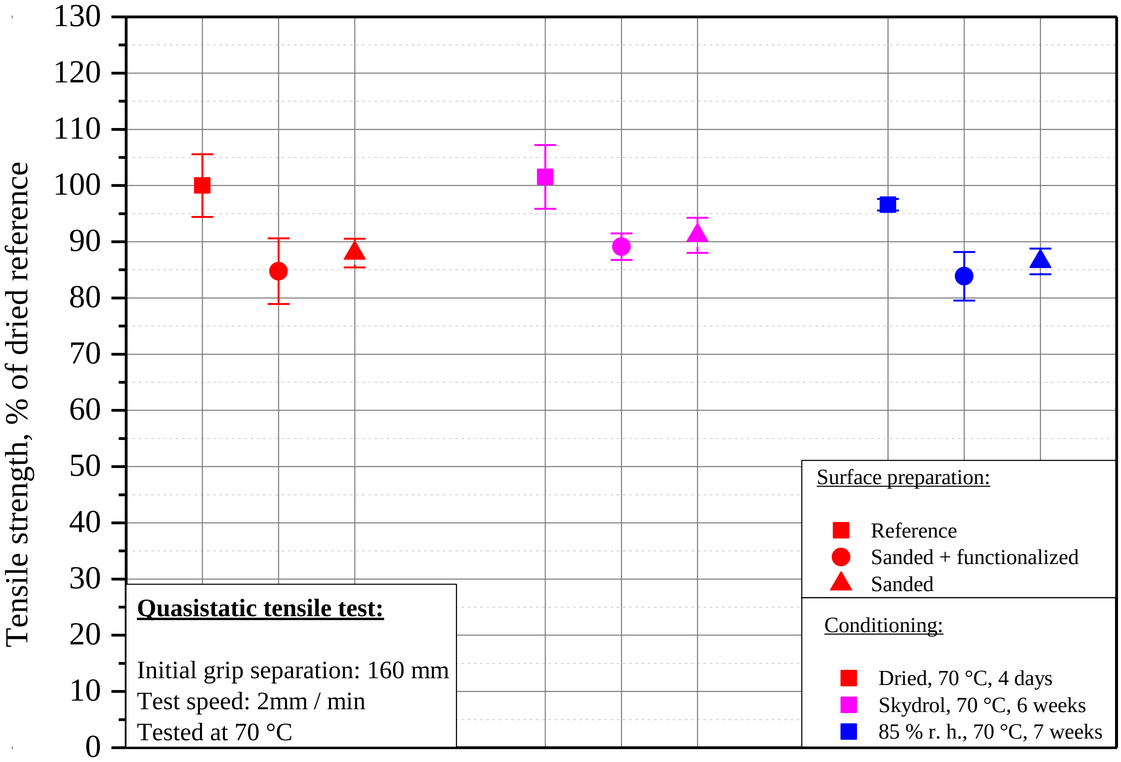

Figure 4: Mean tensile strength and standard deviation (normalized to the unrepaired, dried reference) of the reference- and repair-specimens with sanded as well as functionalized surfaces as a function of the according ambient conditions, tested at 70 °C.

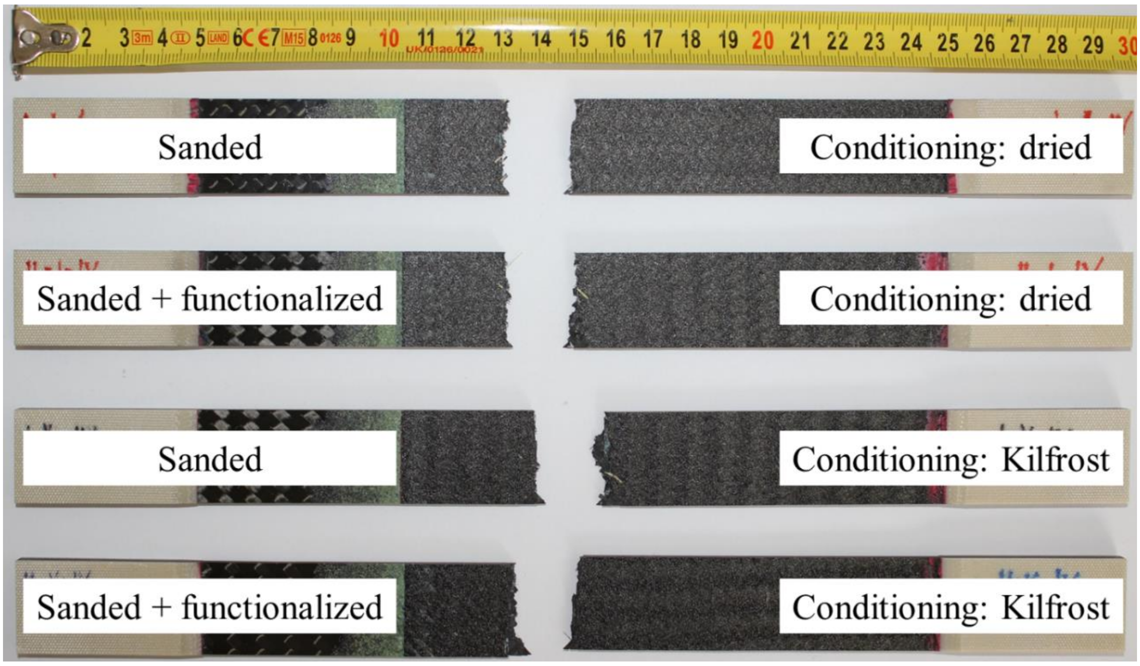

Figure 5: Failure modes (exemplary) of repair-specimens tested at RT

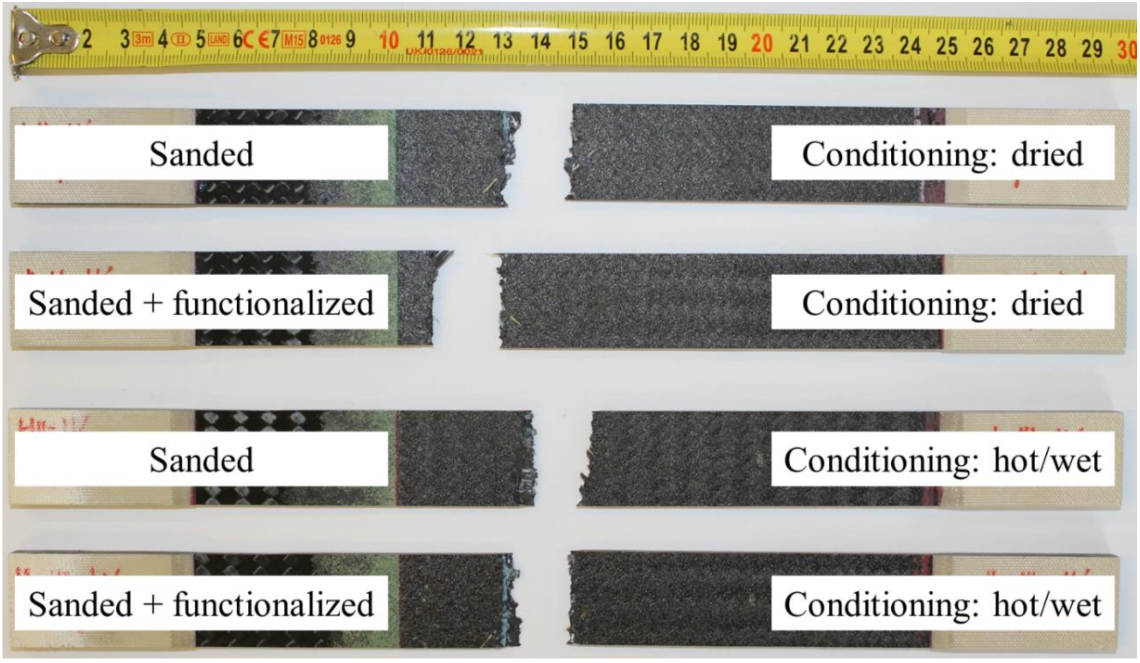

Figure 6: Failure modes (exemplary) of repair-specimens tested at 70 °C

4 CONCLUSIONS

Specimens conditioned for 7 weeks under hot/wet conditions absorb a considerable amount of moisture. The ones immersed in Kilfrost at RT absorb less moisture in one week, which does not lead to an equilibrium state. In both cases the repaired specimens absorb a slightly higher amount of moisture than the unrepaired reference-specimens, independent of the surface state (sanded or additionally functionalized). Analysis of the moisture absorption behavior was not possible for immersion in Skydrol.

Quasistatic tensile tests performed at 23 °C and 70 °C, respectively, show that the tensile strength of the unrepaired reference-specimens is not significantly influenced by the selected ambient conditions. The surface functionalization achieved by the combination of a corona with a wet chemical treatment with epoxysilane showed no significant improvement of the repair-specimens´ tensile strength. With the dried repair-specimens tested at 23 °C, 81 – 93 % of the dried reference-specimens´ tensile strength can be restored, with the ones conditioned in Kilfrost 90 - 93 % can be achieved. The dried repair-specimens tested at 70 °C show a relative tensile strength of 85 - 88 %. Repair-specimens after immersion in Skydrol reach 89 % - 91 % of the reference-specimens´ tensile strength (tested at 70 °C), the ones after hot/wet conditioning 84 - 86 %. Hereby it has to be noted, that the failure mode for all repair-specimens, independent of the previous conditioning, the test temperature as well as of the surface treatment, is tensile failure (normal to the specimens´ surface) according to AITM 1-0029 [14].

Further investigations will focus on the influence of selected ambient conditions on repair-specimens with steeper scarf angles, on single-lap-shear-specimens and on neat adhesive specimens with the goal of deepening the understanding of interactions of aircraft repairs with complex environmental conditions [18]. Moreover, damage tolerance and fatigue behavior of such repairs will be addressed. In parallel, alternative methods for surface functionalization will be analyzed.

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REFERENCES

[1] Y. Sugita, C. Winkelmann and V. La Saponara, Environmental and chemical degradation of carbon/epoxy lap joints for aerospace applications, and effects on their mechanical performance, *Composites Science and Technology*, **70**, 2010, pp. 829–839 (doi:10.1016/j.compscitech.2010.01.021).

[2] V. La Saponara, Environmental and chemical degradation of carbon/epoxy and structural adhesive for aerospace applications: Fickian and anomalous diffusion, Arrhenius kinetics, *Composite Structures*, **93**, 2011, pp. 2180–2195 (doi:10.1016/j.compstruct.2011.03.005).

[3] G. Gardiner, Aircraft composites repair moves toward maturity, *CompositesWorld*, **2**, 2016, pp. 30–37.

[4] K. B. Katnam, L. Da Silva and T. M. Young, Bonded repair of composite aircraft structures: A review of scientific challenges and opportunities, *Progress in Aerospace Sciences*, **61**, 2013, pp. 26–42 (doi:10.1016/j.paerosci.2013.03.003).

[5] S.-H. Ahn and G. S. Springer, *Repair of Composite Laminates*, Department of Aeronautics and Astronautics, Stanford University, Stanford, CA, USA, 2000.

[6] S. B. Kumar, I. Sridhar, S. Sivashanker, S. O. Osiyemi and A. Bag, Tensile failure of adhesively bonded CFRP composite scarf joints, *Materials Science and Engineering B*, **132**, 2006, pp. 113–120 (doi:10.1016/j.mseb.2006.02.046).

[7] H. Schmutzler, J. Popp, E. Büchter, H. Wittich, K. Schulte and B. Fiedler, Improvement of bonding strength of scarf-bonded carbon fibre/epoxy laminates by Nd:YAG laser surface activation, *Composites: Part A*, **67**, 2014, pp. 123–130 (doi:10.1016/j.compositesa.2014.08.029).

[8] K. B. Armstrong, L. G. Bevan and W. F. Cole II, *Care and repair of advanced composites*, SAE International, Warrendale, Pennsylvania, USA, 2005.

[9] I. Jölly, S. Schlögl, M. Wolfahrt, G. Pinter, M. Fleischmann and W. Kern, Chemical functionalization of composite surfaces for improved structural bonded repairs, *Composites Part B*, **69**, 2015, pp. 296–303 (doi:10.1016/j.compositesb.2014.10.020).

[10] M. Davis and D. Bond, Principles and practices of adhesive bonded structural joints and repairs, *International Journal of Adhesion and Adhesives*, **19**, 1999, pp. 91–105 (doi:10.1016/S0143-7496(98)00026-8).

[11] A. Baldan, Adhesively-bonded joints and repairs in metallic alloys, polymers and composite materials: Adhesives, adhesion theories and surface pretreatment, *Journal of Materials Science*, **39**, 2004, pp. 1–49 (doi:10.1023/B:JMSC.0000007726.58758.e4).

[12] A. Revathi, M. Sendil Murugan, S. Srihari, N. Jagannathan and C. M. Manjunatha, Effect of Hot-Wet Conditioning on the Mechanical and Thermal Properties of IM7/ 8552 Carbon Fiber Composite, *Indian Journal of Advances in Chemical Science*, **2**, 2014, pp. 84–88.

[13] A. Higgins, Adhesive bonding of aircraft structures, *International Journal of Adhesion and Adhesives*, **20**, 2000, pp. 367–376 (doi:10.1016/S0143-7496(00)00006-3).

[14] AITM 1-0029, Airbus Industrie Test Method - Fibre reinforced plastics - Determination of tensile strength of a tapered or stepped joint, Issue 1, 1995.

[15] I. Jölly, S. Schlögl, M. Wolfahrt, G. Pinter, W. Kern and M. Fleischmann, Characterisation and functionalization of composite surfaces to optimise structural bonding in aerospace, *Proceedings of Adhesion '13*, University of York, UK, July 04-06, 2013, pp. 1–4.

[16] F. Röper, M. Wolfahrt, G. Kucher, A. Bubestinger and G. Pinter, Effect of Repair Design and Surface Treatment on Adhesively Bonded Composite Repairs, *Proceeding of the 17th European Conference on Composite Materials*, June 26-30, 2016, pp. 5037–5043.

[17] ASTM D5229 / D5229M - 92 (2010), Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials, 2010.

[18] F. Röper and M. Wolfahrt, Geklebte Reparaturen von Faserverbundstrukturen in der Luftfahrt, *Carbon Composites Magazin*, **2**, 2015, pp. 79–80.