Etching of carbon fiber-reinforced plastics to increase their joint strength

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Graphical abstract

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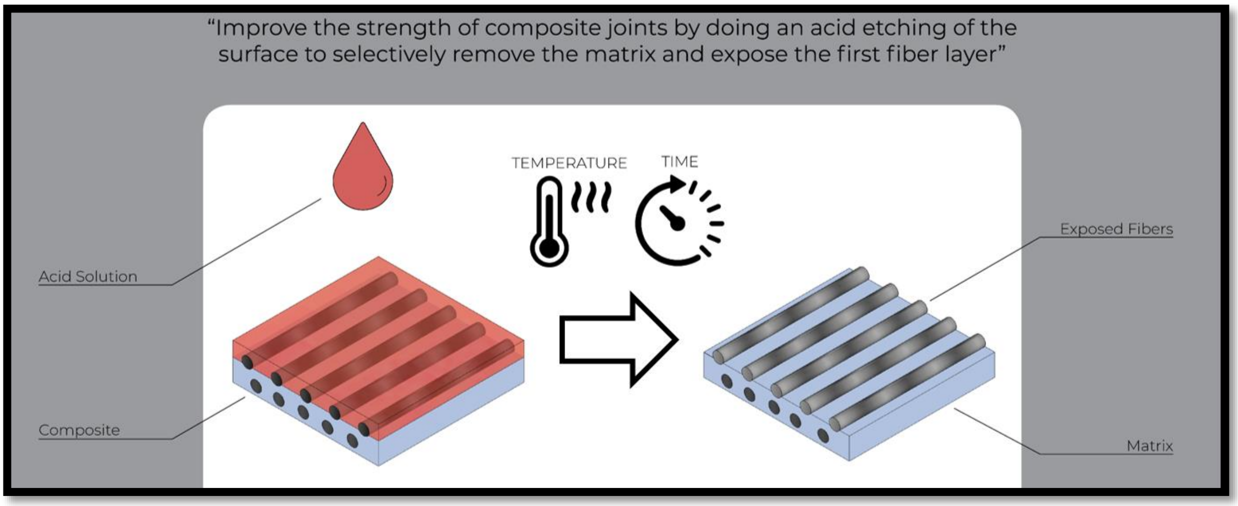


Abstract

An original method to increase the mechanical strength of adhesively joined Carbon Fiber Reinforced Plastics (CFRPs) and Honeycomb (HC) CFRP sandwich structures by etching is proposed, based on sulfuric acid etching of the CFRP surface.

Etched composites are joined by a novel phenolic resin based adhesive, cured and their cross section observed by FESEM.

Etching of CFRP was aimed to obtain a "*brush*" like composite to be infiltrated by the adhesive, giving a fiber reinforced, stronger composite joint.

This method gave a 100% increase of lap shear strength for the adhesive joined etched CFRP, compared to the non-etched ones.

Keywords: CFRP, etching, joining, adhesive, lap shear, honeycomb, sandwich

1. Introduction

CFRPs (Carbon Fiber Reinforced Plastics) are widely used in several applications ranging from sporting goods such as golf club, tennis racket and fishing rod, to aerospace, racing cars, drones, unmanned autonomous vehicles and other transportation fields because of their unparalleled mechanical strength coupled to low density [1]. Their joining and integration is a key issue and a wide range of solutions, mainly based on adhesive bonding, are available in the literature [2].

Adhesive bonding is the most popular option, first of all because adhesives can be used at temperatures compatible with CRFP matrices (about 150-200 °C), but also because of the robustness of the procedure, the possibility of disassembly in case of maintenance and their excellent fatigue life [3]. The use of adhesive allows saving weight by eliminating fasteners and introducing a more uniform load transfer: stress distribution is more uniform than with other conventional methods of joining [4], the load is transmitted from one CFRP to the other one through the adhesive layer in the overlap region, therefore the adhesive works as a medium for load transmission, which is important to achieve high strength joints.

There are different strategies to enhance the joint strength, starting from the proper selection of the adhesives [5], the adhesive thickness [6], and the surface preparation [7], among others.

The surface preparation is the most important parameter to improve the joint strength : mechanical abrasion is one of the most widely used surface treatment [8], while a totally new approach is the chemical etching of the CFRP surface to promote the adhesive penetration into it, thus improving the interaction adhesive/ CFRP, also by changing the CFRP surface tension. Other methods to reinforce joints have been also proposed, among them Comeld ™ and other similar options from TWI [9], or bio-mimetical approaches [10].

In this work, we propose an original method to increase the mechanical strength of adhesive joined CFRP by etching of their surface: the idea is to chemically remove only a few microns of the matrix while keeping the carbon fibers unaffected.

The chemical etching proposed here was inspired by some works aimed to recycle CFRP by dissolving their polymeric matrix [11] and by the international standards UNI EN 2564 [12] and ASTM D 3171 – 99 [13], used to completely dissolve the CFRP matrix in order to measure their fiber content. In [11] authors used potassium phosphate tribasic (K_3PO_4) as a catalyst and benzyl alcohol as a solvent to depolymerize cured epoxy resin and unsaturated polyester resin in CFRP: e.g. it took up to 8 hours to completely dissolve a tennis racket.

In ASTM D 3171 – 99 [13] and UNI EN 2564 [12], methods based on sulfuric acid (96-98 %) and hydrogen peroxide (30-50%), nitric acid (70%), ethylene glycol/potassium hydroxide or hydrochloric acid (5-10%), heated up to 160 °C, according to the given procedures, were proposed to measure the composites' fiber content.

The original etching procedure described in the following parts of this paper is based on controlled sulfuric acid etching on the surface of CFRP. After surface etching the CFRP were joined and the effect of etching time and temperature on joint strength was evaluated.

2. Materials and Methods

2.1 Materials

The CFRP plates and honeycombs (HC)CFRP used in this study were supplied by Thales Alenia Space (TAS - Cannes, France) and produced by North Thin Ply Technology (NTPT, Switzerland), from composite pre-impregnated (prepreg) made of carbon fibers having a diameter of about 7 microns and a cyanate ester matrix. They are manufactured by using proprietary spread tow technology. This involves the spreading of untwisted fibre tows into thin, flat unidirectional tapes which are then combined with resin to obtain prepreg tapes of 40 microns and 47% fiber volume fraction; the CFRP plies layout for plates and honeycombs is (0°/+60°/-60°, top layer in 0° direction) with an ILSS (Interlaminar Shear Strength) of about 33 MPa [14].

The HC(CFRP) have 10 mm or 20 mm cell size, each honeycomb wall is built with 6 plies (0°/+60°/-60°), and an overall thickness of 0.21 mm, the same fiber volume fraction (47%) as above.

The CFRP plates were cut by a disc saw to obtain slabs of 25 mm x 25 mm x 4 mm to be used for Single Lap Offset (SLO) shear test [15] (*adapted from ASTM D905-08* [16]) and 25 mm x 12 mm x 3 mm for bending tests [17]. (HC)CFRP were cut by scissors to 50 mm x 50 mm samples (thickness = 12 mm).

2.2 Etching Procedure

Before etching, all CFRP slabs and (HC)CFRP were cleaned with ethanol in ultrasonic bath for 10 minutes, 40°C, then dried with compressed air. The CFRP slabs sides not to be etched were masked with PTFE tape.

The CFRP slabs (25 mm x 25 mm x 4 mm) were put inside a Petri dish on a hot plate together with a beaker containing concentrated sulfuric acid (H_2SO_4, 96%, Sigma-Aldrich) and heated up to the selected temperature. The CFRP surface in contact with the hot plate was reversed upside-down and a few acid droplets (about 4 mL) were put on the CFRP surface until it was completely covered with a thin film of acid solution, then left on the hot plate for the selected time. (Figure 1 a, b)

The role of acid concentration (96%, 76 %, 33%), etching time (ranging between 5 and 20 minutes, multiple steps of 5 minutes each) and temperature (ranging between 80-150 °C) were investigated.

The etching process was also used on (HC)CFRP to be joined in a sandwich structure between two soda-lime or two CFRP skins (Figure 2) by dipping the (HC)CFRP 1-2 mm inside the acid 96%: the process was as described above, but with a time of 5 or 10 minutes, at a temperature range of 100 - 150 °C.

A *modification* of the etching process was done by preparing a suspension of alumina powder in sulfuric acid: 15 g of alumina (particle size 20-50 µm, Alfa Aesar) added to 18 mL of sulfuric acid and magnetically stirred for 5 min; then about 1 mL of hydrogen peroxide (H2O2 30%, ITW reagents) was slowly added to the stirred suspension and everything was kept at 150 °C (10, 15 and 20 minutes); this modified etching process was used to etch the CFRP *side* faces, as shown in Figure 3 b, c , to obtain the "brush" joints as in Figure 1 (c).

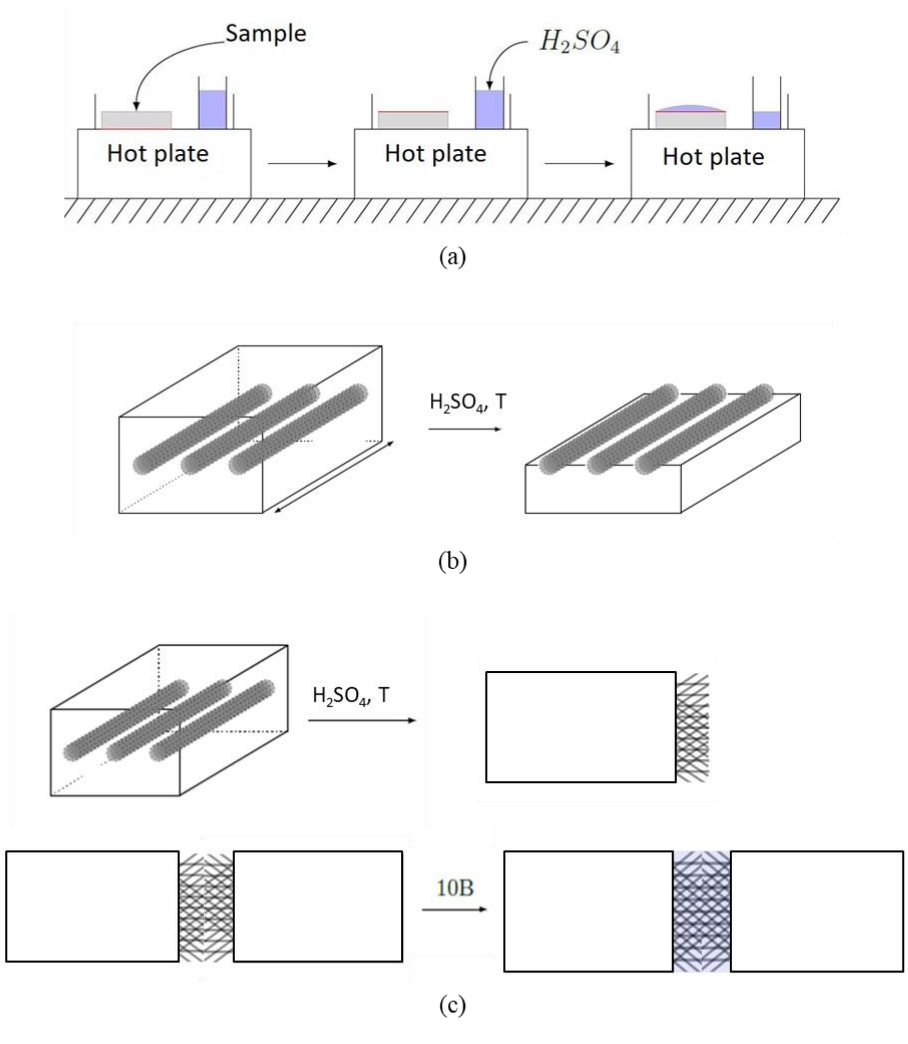


Figure 1: etching process sketch (a), etched CFRP surface (b), etched CFRP side (c)

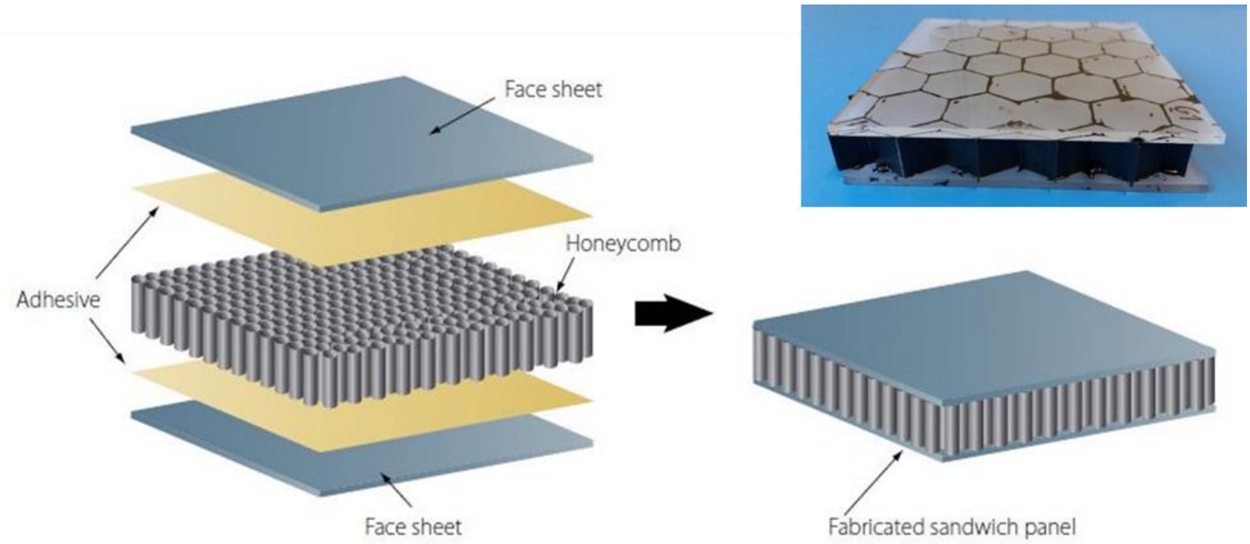


Figure 2: sketch of the sandwich panel made of honeycomb CFRP, (HC)CFRP, core joined to two skins made of CFRP or soda-lime glass slabs (obtained sandwich panel with glass skins, inset)

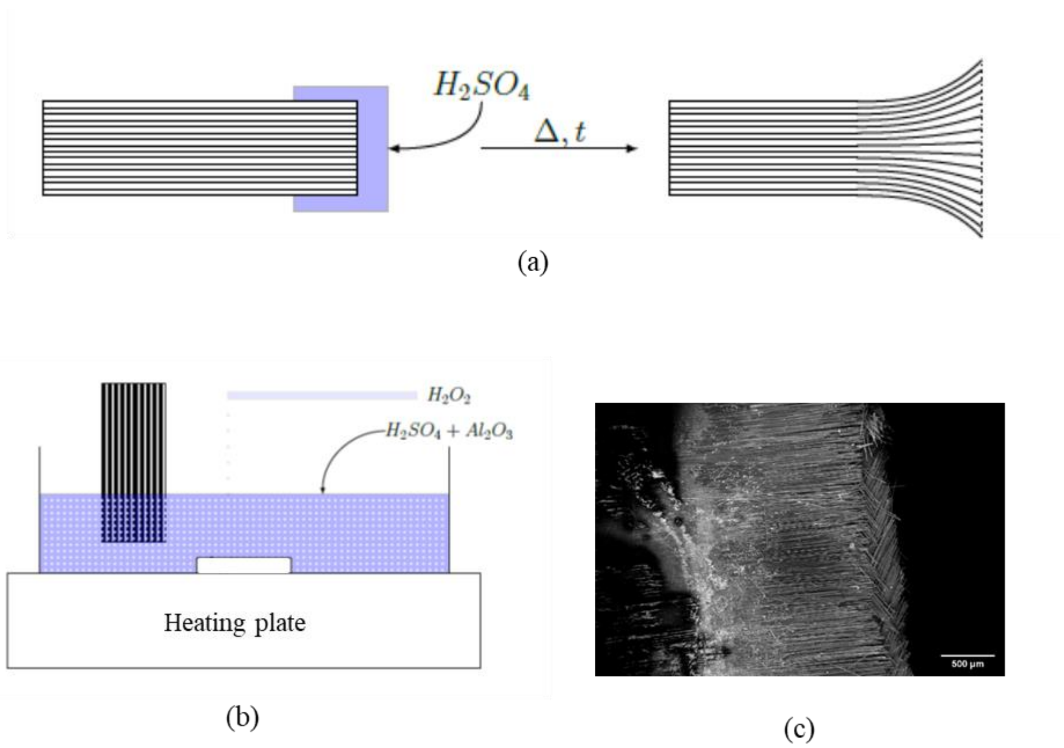


Figure 3: localized CFRP delamination due to excessive acid infiltration and matrix removal (a); etching protocol modified by adding alumina powders and oxygen peroxide to the acid (b); "brush" structure obtained (c) with the modified etching protocol

All the etching processes described above were performed multiple times at steps of 5 minutes each; at the end of each step, the samples were rinsed in distilled water to stop the reaction and ultrasonic cleaned for 10 min, then dried with compressed air. At the end of the whole etching process, samples were cleaned in ethanol in ultrasonic bath for 10 minutes at 40°C, then let dry in air before joining. Profilometry (FTS Intra with Ultra, Taylor Hobson, Ametek, USA) and mass loss were done on etched samples.

2.3 Joining

The adhesive used to join CFRP was provided by M.D.P. Materials Design & Processing S.r.l., Italy and labelled as 10B: it is an inorganic loaded phenolic adhesive especially formulated to join carbon based composites: it contains carbon fibers, graphite powders and other fillers. [18]. The curing treatment was set at 130°C (4 hours), followed by another step at 150°C (10 hours), heating rate 0,3 °C/min, in order to preserve the CFRP properties, as these composites cannot be heated at temperature higher than their Tg, 150°C. A minimal pressure (few kPa) was applied on each joined sample to keep them in the correct position during curing. The joint thickness was about 240 ± 40 µm microns, measured *ex-post* after joining and curing.

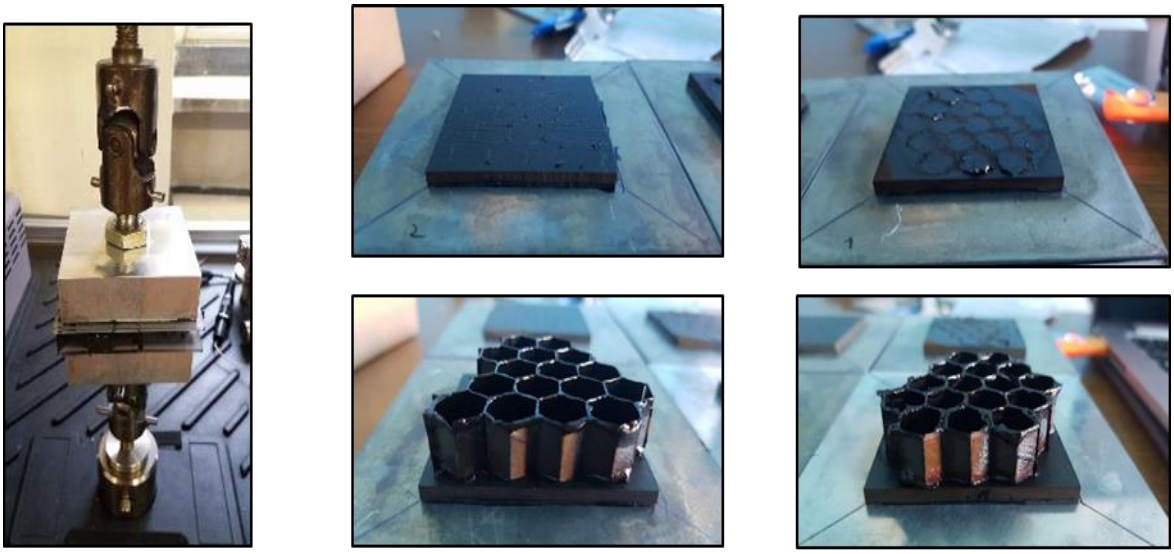
2.4 Mechanical tests

The surface etched CFRP (Figure 1 b) were joined for Single Lap Offset (SLO) tests, with a joined area of 25 mm x 12.5 mm = 312.5 mm^2; the side etched CFRP (figure 1 c) were joined for 4 point bending tests with a joined area of 12 mm x 3 mm = 36 mm2 [17]; both tests were done on six samples.

The sandwich structures were tested in tensile mode on a (HC)CFRP sandwiched between a soda-lime glass or a CFRP skin, with joined area of 50x50 mm = 2500 mm^2 by an in-house build set up (Figure 4 a), which consists in two steel plates connected to a universal tensile machine by a ball-joint; the sandwich is glued between the two steel plates and tested in tensile mode.

According to an internal TAS standard, tensile strength was calculated dividing the max load at failure by the overall honeycomb wall area, i.e. the area of a single wall multiplied by the total number of walls in the honeycomb. Non-etched CFRP and (HC)CFRP were also joined and tested for comparison purposes.

Joint cross-sections and fracture surfaces after mechanical tests were observed by Field Emission Scanning Electron Microscopy (FESEM- ZEISS Supra 40) with Energy Dispersive Spectroscopy (EDS- SW9100 EDAX).



(a) (b) (c)

Figure 4: tensile test on the (HC)CFRP sandwich panel with CFRP skins (a); fracture surfaces of the sandwich panel after mechanical tests: adhesive failure for non-etched (HC)CFRP (b); cohesive with partial (HC)CFRP delamination for the etched (HC)CFRP (5 minutes, 125 °C) (c).

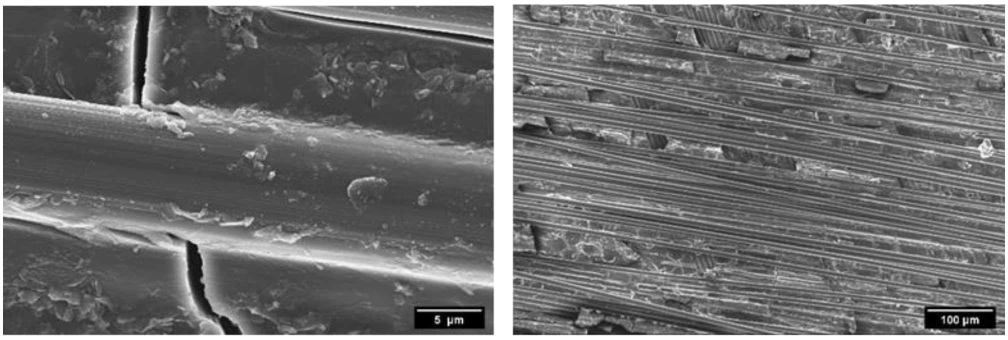
3. Results and discussion

3.1 Etching

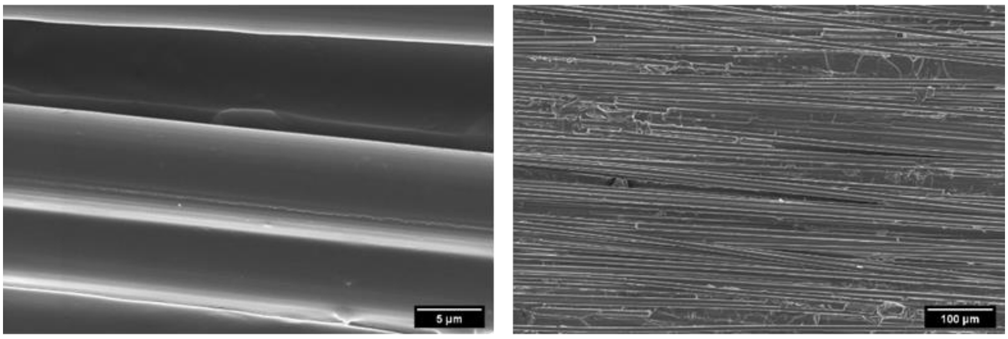
With the aim of chemically remove only a few microns of the matrix while keeping the carbon fibers unaffected H_2SO_4 was selected and tested to minimize temperature, time and acid concentration, in order to remove *only a very thin layer of the CRFP matrix, while keeping the carbon fibers unaffected and thus exploiting their mechanical strength in the adhesive joints.*

The experimental procedure sketched in figure 1 a was used to optimize the etching process for CFRP top surface (figure 1 b) or the CFRP side surface (figure 1 c).

Figure 5 shows the typical morphology obtained by SEM analysis of the CFRP surface after etching 10 minutes (two steps, 5 minutes each) with H_2SO_4, 96% at 100°C (a) and 125°C (b), (higher magnification pictures on the left): after etching at 100°C (Figure 5 a), the fibers are still partially embedded in the matrix and part of the matrix is still visible on the surface, making it unsuitable for a sound joint; on the contrary, etching at 125°C (Figure 5 b) gave much better results, fibers are completely clean and no matrix is visible on the etched surface. Etching at 115 °C gave similar results as at 100 °C, while etching at 150 °C resulted in an excessive removal of the matrix with loose fibers on the surface (SEM pictures not reported here), again, unsuitable for a sound joint.



(a)

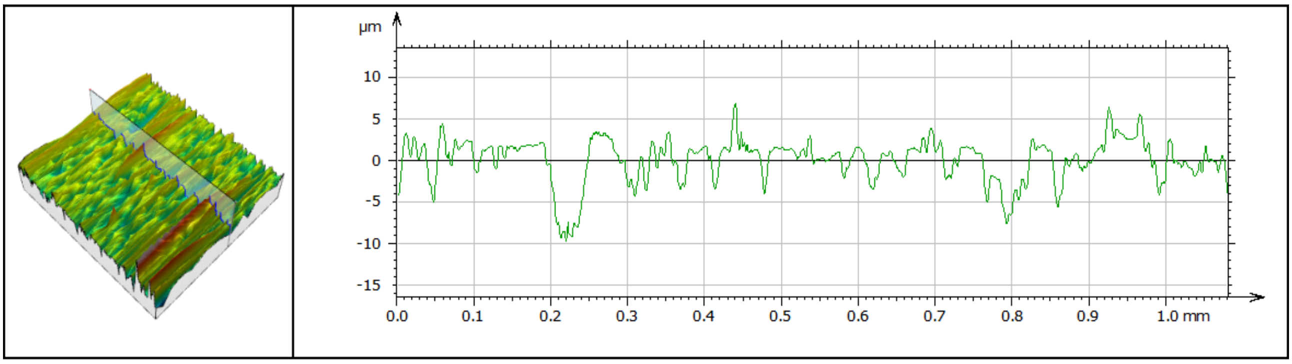


(b)

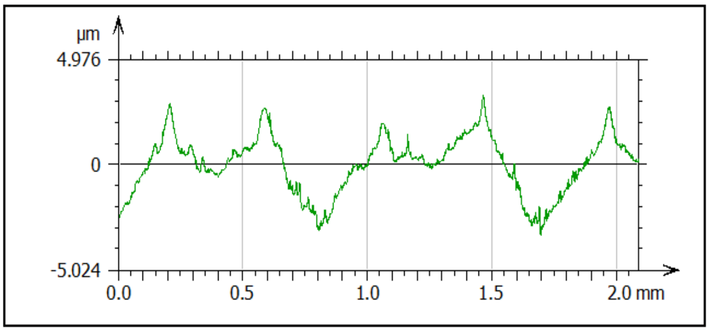
Figure 5: SEM of the CFRP surface after etching at 100°C (a) and 125°C (b), 10 minutes, higher magnification pictures on the left: after etching at 100°C (a), fibers are still partially embedded in the matrix, while with etching at 125°C (b), fibers are completely clean and no matrix is visible.

The CFRP mass loss after etching was measured (in triplicate) by weighting each sample before and after etching and was found to be 0,16 % ± 0,05 for samples etched at 125 °C, 10 minutes, and 0,13 % ± 0,01 for samples etched at 100 °C, 10 minutes.

Figure 6 shows the profilometry done on the surface of etched CFRP (125°C, 10 minutes) (a) and on as received CFRP surface, as comparison (b): as expected, the profile ranged from ±5 microns for the non-etched CFRP surface to a ±10 microns for the etched one. The overall etched surface shows a uniform etching, with room between fibers for the adhesive to infiltrate and giving a composite joint.



(a)



(b)

Figure 6: Profilometry of etched CFRP (125°C, 10 minutes) surface (a); as received CFRP surface profilometry, as comparison (b)

The same etching process was used and adapted to (HC)CFRP to be joined in a sandwich structure between two skins, as in Figure 2: in this case the etching was done with less aggressive conditions, such as 5 minutes at 125 °C, 96%. Even though their matrix is the same one (cyanate ester), etching at temperature higher than 125 °C and longer than 5 minutes resulted detrimental for the (HC)CFRP integrity.

Etching of the *side face* of CFRP was aimed to obtain a "*brush*" like composite to be butt-joined to another "*brush*" like one (figure 1 (c)): the adhesive joint should infiltrate fibers, giving a stronger, composite joint.

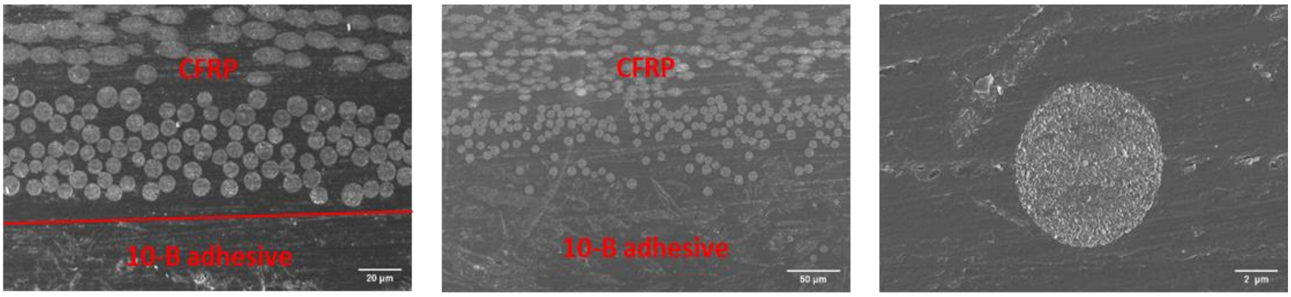
Actually, etching the CFRP side face was much more difficult than expected: Figure 3 (a) sketches the localized and excessive CFRP delamination occurred after etching at 150 °C, 10 minutes; the reason for that is most likely due to excessive acid infiltration and matrix removal due to capillary forces originating inside the uncontrolled cracks in the matrix following the composite cutting process.

The etching process was then modified by adding alumina powders to the acid: the alumina-acid thick suspension was effective to reduce the acid infiltration inside the composite; in order to locally remove the suspension to keep the etching reaction going on, some hydrogen peroxide drops were added during the process: the “brush” structure was successfully obtained (Figure 3 b, c).

3.2 Joining, mechanical tests and etching optimization

All the etched composites (CFRP slabs surface or side etched, (HC)CFRP were then joined by the 10B adhesive, cured and their cross section polished and observed by FE-SEM. Not etched composites were also joined and observed for comparison purposes.

Figure 7 shows the polished cross-sections of adhesive joined CFRP slabs, not etched (figure 7 a) and surface etched (sulfuric acid, 96%) at 125 °C, 10 minutes (figure 7 b): the adhesive infiltration inside the etched region is evident in Figure 7 (b) where the interface between adhesive and CFRP is not distinguishable. The not etched interface adhesive/composite is, as expected, a straight discontinuity between the two materials (Figure 7 (a)), while the adhesive perfectly infiltrates the etched CFRP surface replacing the removed matrix, as shown in figure 7 (b). The high wettability between fibers and adhesive, especially synthetized for this purpose, is evident in Figure 7 (c).



(a) (b) (c)

Figure 7: SEM cross-section of adhesive joined CFRP slabs: not etched (a) and etched at 125 °C , 10 minutes (b): the infiltration of the adhesive inside the etched region is evident. The interface between adhesive and CFRP is highlighted in red. The high wettability of the adhesive with carbon fibers is shown in (c)

Mechanical tests confirmed the influence of the adhesive infiltration inside the etched surfaces discussed above: *a 100% increase in mechanical strength was measured by SLO test versus etching temperature, after etching at 125 and 140 °C, 10 minutes,* respect with the non-etched samples (Figure 8). A plateau in lap-shear strength was found for etching temperature higher than 125 °C. Notably, samples etched at temperature higher than 140 °C were not suitable for mechanical test, due to the excessive etching.

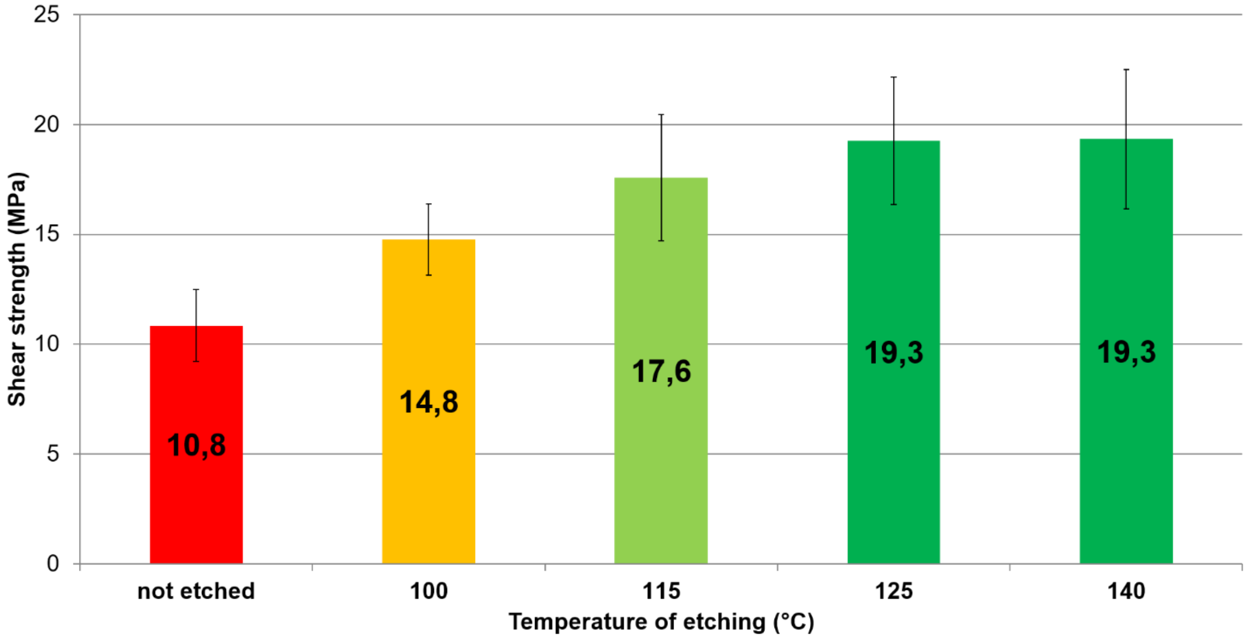


Figure 8: Results of SLO test for adhesive joined CFRP versus etching temperature (10 min, 96% H_2SO_4,) non-etched samples for comparison purposes.

Figure 9 shows the Load/Displacement curves of the joined CFRP after SLO test: non-etched, etched at 100 °C (10 minutes), etched at 125 °C (10 minutes); the deviation from linearity of samples etched at 125°C, 10 minutes, is *due to the composite nature of the joining itself, obtained by etching and adhesive infiltration*; this is in agreement with the fracture surface in figure 10 (c), where the fiber pull-out and composite delamination are evident. This is not the case for the other Load/Displacement curves in figure 9, where the adhesive does not infiltrate fibers (non-etched, figure 9) or the etching is not sufficient (etched at 100 °C, 10 minutes, figure 9).

The fracture surfaces (Figure 10) after SLO tests for joined CFRP (a) non-etched, (b) etched at 100 °C, (c) etched at 125 °C further confirm the differences discussed above due to etching and adhesive infiltration: while fractures in (a) and (b) are mixed adhesive/cohesive, with only part of the two fracture surfaces covered by adhesive, in (c) CFRP delamination and fiber pull-out is evident.

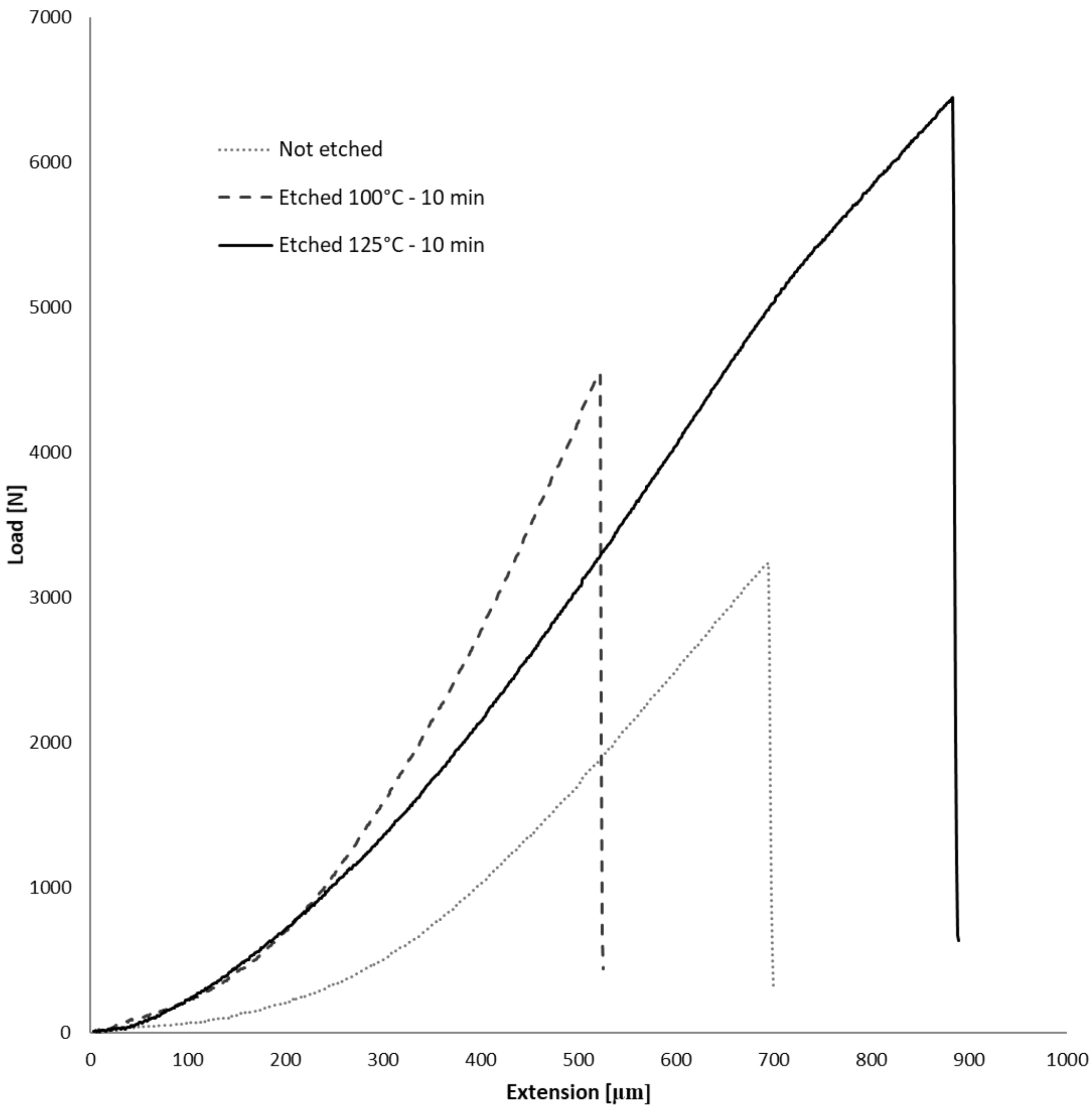


Figure 9: Typical load/displacement curves of joined CFRP after SLO test: non-etched, etched at 100 °C (10 minutes), etched at 125 °C (10 minutes); the deviation from linearity of samples etched at 125°C, 10 minutes showing the composite nature of this joint (c)

(a) (b) (c)

Figure 10: Fracture surfaces of joined CFRP after SLO test: (a) non-etched, (b) etched at 100 °C (10 minutes), (c) etched at 125 °C (10 minutes); fractures in (a) and (b) are mixed adhesive/cohesive, while in (c) CFRP delamination and fiber pull-out is evident.

Etching at 100 °C was found to provide a slight improvement in mechanical strength and the fracture is still mixed adhesive/cohesive; the same for samples etched at 115°C (fracture surfaces not reported here).

Remarkably, the adhesive infiltration and substitution of the removed CFRP matrix after etching 10 minutes at 125°C, showed in Figure 7 (b), corresponds to a 100% increase in lap-shear strength (Figure 8), respect to the non-etched sample: in case of suitable CFRP etching (125 °C, 10 minutes) the joint is reinforced by unaffected carbon fibers and its strength is high enough to cause the composite delamination.

It must be considered that, even if the CFRP ILSS is about 33 MPa [14], the value of about 19 MPa measured by this lap-shear in compression is only an *average one* and it doesn't take into account the stress concentration peaks for this test: stresses higher than 33 MPa were probably reached at the two extremities of the lap joint, causing delamination and an average lap-shear of 19 MPa.

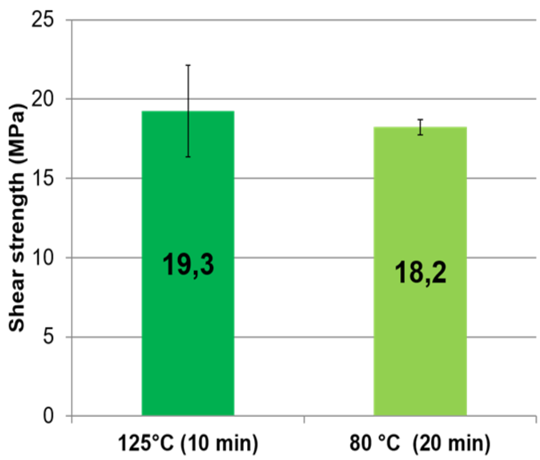
Different mechanical tests should be done to have a more reliable information about the effectiveness of this etching process: tensile tests, for instance, on etched and non-etched joined CFRP are under consideration.

In order to make the etching process more industrial-friendly, we tried to reduce acid concentration (96%, 76 %, 33%), etching time (ranging between 5 and 20 minutes) and temperature (ranging between 80 and 150 °C). Several surface etched CFRP were tested by the same SLO tests: Figure 11 (a) and (b) summarize the etching conditions optimized to have a 100% increase of the mechanical strength for the etched CFRP:

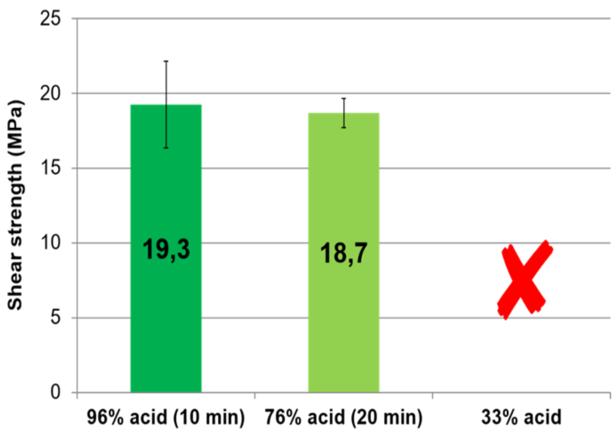
- the etching temperature can be lowered from 125 °C to 80 °C, but it requires a longer etching time (20 minutes) to give the same lap-shear strength (Figure 11 (a).
- the acid can be diluted from 96 to 76%, but it requires a longer etching time (20 minutes) at 125 °C.

The attempt to further reduce the acid concentration to 33% gave a non-effective etching and lower mechanical strength.

It can be concluded that this H_2SO_4 etching is effective when done between 80-125 °C, 10-20 minutes, with 96 or 76 % H_2SO_4.



(a)



(b)

Figure 11: Influence of etching time (a) and acid concentration (b) on lap shear strength of the joined CFRP

The etching process for (HC)CFRP gave interesting results when done for 5 minutes, at 125 °C: longer time and higher temperatures had detrimental effects on the (HC)CFRP (results not reported here).

(HC)CFRP joined in sandwich structures with CPRP skins as in Figure 4 were tested in tensile mode (figure 4 a): Figure 4 (b) and 4 (c) show the sandwiches fracture surfaces after tensile tests: an adhesive failure with most of the adhesive attached to the (HC)CFRP was found for non-etched (HC)CFRP (figure 4 b); a completely different fracture surface showing cohesive failure with the adhesive on both sides and with partial (HC)CFRP detachment was found for the etched (HC)CFRP. The tensile strength of sandwiches with not etched HC(CFRP) gave 21.4 MPa (maximum load at failure = 1708.5 N divided by the overall HC wall area = 80,02 mm^2), while for HC(CFRP) etched 10 min at 125°C it was 29.1 MPa (maximum load at failure = 2289.0 N divided by overall HC wall area = 78,75 mm^2).

Sandwich panels made of CFRP honeycomb joined to two soda-lime glass skins (figure 2, inset) gave fracture in the glass and results are not reported here. These results can only give preliminary information, but they demonstrate that this etching process can be also effective on (HC)CFRP: the effectiveness in term of mechanical strength and overall properties of the sandwich structures is still to be assessed.

Finally, the “brush” CFRP, successfully obtained by the alumina/hydrogen peroxide modified etching process (figure 3 b,c) were butt-joined by the 10B adhesive and tested in four point bending according to ASTM D7264: up to now, no substantial improvement in the bending strength was measured, compared to the joined non-etched CFRP.

Four point bending strength of 28,8 ± 6,1 MPa were obtained for the non-etched joined “brush” CFRP and 14,3 ± 2,6 MPa, 27,0 ± 1,9 MPa, and 24,4 ± 2,5 MPa for those etched 10, 15 and 20 minutes, respectively, all of them at 150 °C. These results might be due to a still to be improved infiltration of the adhesive in the "brush" joint. Research is ongoing to optimize also this modified etching protocol and made it suitable to etch CFRP side surfaces. Also in this case, tensile tests on etched and non-etched joined CFRP are under consideration.

4. Conclusions

The original etching procedure described in this paper, based on controlled sulfuric acid etching on the CFRP *surface*, was found effective in increasing up to 100% the mechanical strength (lap shear) of adhesive joined etched CFRP slabs.

Also the etched Honeycomb CFRP based sandwich structures showed an increased tensile strength compared to the non-etched ones.

The "brush" CFRP, successfully obtained by the alumina/hydrogen peroxide modified etching process is still to be optimized in term of adhesive infiltration in the brush structure.

Tests are ongoing to test these etching protocols at the industrial scale: even though the use of acids is more complex to manage than mechanical abrasion commonly used to increase adhesive joint strength, this method has the advantage of leaving fibers unaffected. Furthermore, the proposed etching can be useful to join CFRP with other adhesives such as, for instance epoxy-based ones.

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Figure Captions

Figure 1: etching process sketch (a), etched CFRP surface (b), etched CFRP side (c).

Figure 2: sketch of the sandwich panel made of honeycomb CFRP, (HC)CFRP, core joined to two skins made of CFRP or soda-lime glass slabs (obtained sandwich panel with glass skins, inset).

Figure 3: localized CFRP delamination due to excessive acid infiltration and matrix removal (a); etching protocol modified by adding alumina powders and oxygen peroxide to the acid (b); "brush" structure obtained (c) with the modified etching protocol

Figure 4: tensile test on the (HC)CFRP sandwich panel with CFRP skins (a); fracture surfaces of the sandwich panel after mechanical tests: adhesive failure for non-etched (HC)CFRP (b); cohesive with partial (HC)CFRP delamination for the etched (HC)CFRP (5 minutes, 125 °C) (c).

Figure 5: SEM of the CFRP surface after etching at 100°C (a) and 125°C (b), 10 minutes, higher magnification pictures on the left: after etching at 100°C (a), fibers are still partially embedded in the matrix, while with etching at 125°C (b), fibers are completely clean and no matrix is visible.

Figure 6: Profilometry of etched CFRP (125°C, 10 minutes) surface (a); as received CFRP surface profilometry, as comparison (b).

Figure 7: SEM cross-section of adhesive joined CFRP slabs: not etched (a) and etched at 125 °C, 10 minutes (b): the infiltration of the adhesive inside the etched region is evident. The interface between adhesive and CFRP is highlighted in red. The high wettability of the adhesive with carbon fibers is shown in (c).

Figure 8: Results of SLO test for adhesive joined CFRP versus etching temperature (10 min, 96% H2SO4,) non-etched samples for comparison purposes.

Figure 9: Typical load/displacement curves of joined CFRP after SLO test: non-etched, etched at 100 °C (10 minutes), etched at 125 °C (10 minutes); the deviation from linearity of samples etched at 125°C, 10 minutes showing the composite nature of this joint (c)

Figure 10: Fracture surfaces of joined CFRP after SLO test: (a) non-etched, (b) etched at 100 °C (10 minutes), (c) etched at 125 °C (10 minutes); fractures in (a) and (b) are mixed adhesive/cohesive, while in (c) CFRP delamination and fiber pull-out is evident.

Figure 11: Influence of etching time (a) and acid concentration (b) on lap shear strength of the joined CFRP.

Table Caption

none