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The effects of severe temperature changes and high humidity on porous CFRP

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ABSTRACT

Purpose: A route to manufacture porous carbon fiber reinforced plastic (CFRP) for study purposes is described.

Design/methodology/approach: The porous CFRP is characterized using standard techniques such as matrix digestion as well as the more sophisticated method of high resolution Microfocus X-Ray Tomography (µCT). A comparison of the results of those methods is presented. The mass gains of specimens with a wide range of porosity have been measured both in constant humidity and in alternating environments.

Findings: It could be shown that severe temperature changes can temporarily increase the moisture content of porous CFRP. However, after the return to a constant environment, the moisture content returns back to saturation levels. Furthermore, it could be shown by X-Ray Tomography that even under severe climatic conditions no permanent liquid water condensates inside the pores.

Research limitations/implications: Using Microfocus Computed Tomography it could be shown that even after nearly a year under hot-wet conditions and more than 150 severe temperature cycles there is no liquid water detectable inside the pores.

Originality/value: In this paper the effects of severe temperature changes and high humidity on porous CFRP.

Keywords: Porosity; Voids; Computed tomography; CFRP

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PROPERTIES

1. Introduction

Whenever complex structures are made from CFRP, porosity cannot be ruled out. It has been known for a long time that porosity can influence the water uptake as well as the mechanical properties of CFRP [1,8]. It is a matter of high concern whether there is condensation within porous CFRP if it is subjected to sharp temperature changes in high humidity environments since this condensation might lead to ice and this might damage the material from within.

In literature, several ways to produce porous CFRP have been described, ranging from the reduction of

autoclave pressure to pores simulated by inserting PTFE monofilaments [1,7,10]. In order to be as close to real aircraft material as possible, the more intrusive methods such as spraying the individual prepreg layers with water during the lay-up of the laminate were of only limited usefulness. Instead, the parameters that can cause undesired porosity in real parts were used to produce the now wanted porosity on a specimen level. There are two main causes for porosity in real aircraft parts. The first type of pores stems from air that is entrapped during the layup. The other type of pores is formed during the cure cycle whenever the vapor pressure of any constituent of the matrix exceeds the countering outside pressure and therefore this substance starts to boil. Common sources of vapor pressure are residual solvents and water.

2. Material and method

2.1. Specimen manufacturing

Hexcel M18-1/G939 prepreg [6] was chosen as the CFRP base material due to its widespread use within the aviation industry. G939 is an orthotropic fabric material with similar properties in 0° and 90° direction. When laminated and cured under nominal conditions, this material has a fiber/volume content of 55% and a nominal single layer thickness of 0.227 mm. Stacking sequence for all specimens was $[[+45/0/-45/90]_x]_s$ and manufacturing was acc. to DIN EN 2565 [3].

For this study, entrapped air as the main pore source was not desirable since it is hard to control the amount of air and therefore to get reproducible results. Therefore, to ensure the absence of air, a vacuum compactation was applied after each prepreg layer. Only on one laminate this compactation step was not applied. This one laminate was meant to be a test on how much porosity is possible at all [11]. This resulted in very high porosity and a significant increase in thickness – Table 1.

In all the other laminates porosity was created only with the vapor pressure method. Curing of the laminates was done according to a modified cure cycle. The regular cure cycle was modified in three different ways. The soak phase under vacuum was skipped in order not to flush out the pores along with the resin flow. Autoclave pressure was varied between 8.2 bar and 0.96 bar_{abs}- Figure 1. No vacuum was applied during the whole cure cycle to further enlarge the amount of pores. The median atmospheric pressure in Erding is 0.96 bar_{abs} due to its elevation.

2.2. Measurement methods

After curing, the plates were stored at room temperature for > 24 h and then inspected with Ultrasonic Testing (UT).

After this initial inspection the plates were cut into 10 mm x 20 mm specimens with a water cooled diamond saw. The individual position of each specimen was noted. Therefore, it was later possible to compare the porosity results of the specimens with the UT data from the plates.

Table 1.
List of specimen plates

Plate Number	Length x Width, mm	Thickness, mm	Absolute Cure Pressure, bar
1	360 x 260	2.12	8.2
2	360 x 260	2.11	5.6
3	360 x 260	2.12	5.0
4	360 x 260	2.13	4.5
5	360 x 260	2.14	4.0
6	360 x 260	2.11	3.5
7	360 x 260	2.11	3.2
8	360 x 260	2.12	3.0
9	360 x 260	2.14	2.5
10	360 x 260	2.13	2.4
11	360 x 260	2.12	2.0
12	360 x 260	2.23	1.6
13	360 x 260	2.35	0.96
14*	360 x 260	3.52	0.96

*Plate 14 was not subjected to vacuum compactation during layup. As a result a lot of air remained between the prepreg layers. This was done on purpose in order to produce as much porosity as possible

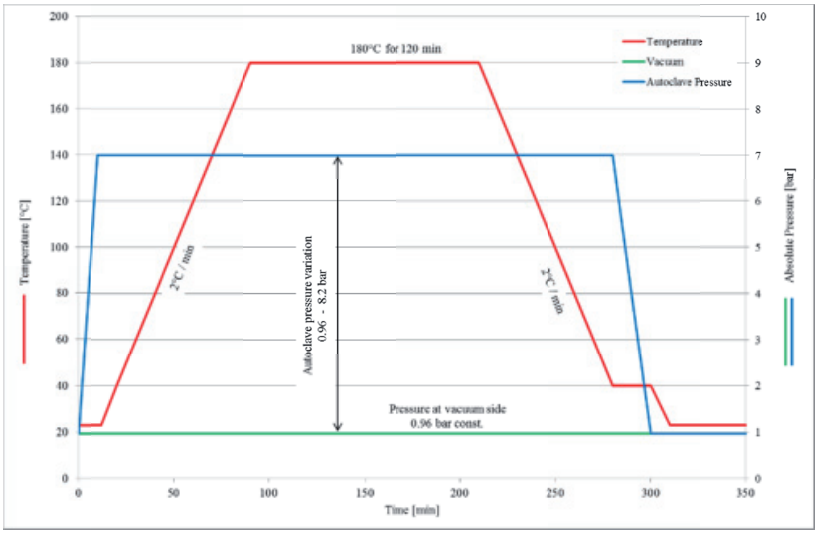

Fig. 1. Modified cure cycle to produce porosity [9]

The small specimen size was necessary for two reasons. First, it had to be ensured that porosity variations within a specimen are negligible. Since porosity distribution within a plate was not uniform due to the resin flow, large specimens would have shown an undesirable porosity gradient. By choosing a small specimen size this gradient could be minimized. This method divided each plate into a large number of specimens with different levels porosity that could later be sorted into groups of similar porosity.

Secondly, specimen size has a direct influence on CT resolution. The smaller the specimen, the higher is the achievable resolution.

After cutting, the specimens were characterized using Microfocus Computed Tomography (µCT) and matrix digestion according to DIN EN 2564 [4], with the parameters given in Table 2. The results of all methods were compared for consistency.

3. Results and discussion

3.1. Porosity measurement results

Whereas porosity can be detected non-destructively with UT, this technique can't deliver quantitative results by itself or even show small individual pores. Matrix digestion on the other hand is a well-established and standardized method but it destroys the specimen. Other techniques such as micrographs can deliver very high resolution 2D images but also destroy the specimen.

µCT can overcome all those limitations by directly detecting and analyzing the pores within the material in 3D. µCT has been used as the reference measurement method for porosity for several years [1,2]. However, even if individual pores can be shown and measured, the precision of quantitative measurements cannot be taken for granted.

There are different ways to analyze the 3D CT data. The simplest way to perform a volume analysis is a look at the gray value (GV) distribution of the voxels. The fraction of voxels with a GV, i.e. X-ray attenuation coefficient, lower than a certain threshold can be measured (threshold method). The theory is simply that voxels in pores have a much lower GV than voxels in solid material. For large pores in cast metals this method works excellently. In CFRP, the contrast between air and material is much lower. On top of that, most of the pores are much smaller than in metals, increasing the number of voxels that are part pore and part material. If that happens, the GV of such a voxel is between that of air and CFRP. This is called partial volume effect. This effect also prevents the use of other methods such as peak deconvolution to correctly separate the air and material peaks. However, even the threshold method can prove very tricky – Figure 2.

The threshold problem can be alleviated if a reference sample of known pore content is always scanned along with the unknown samples. If now the threshold is set to a level where the result for the reference sample is correct, all the other samples within the same volume are measured correctly as well. The reference sample was scanned with the highest achievable resolution (5 µm) and image contrast and was itself cross-referenced to other samples

that had been scanned along with it and then been measured with matrix digestion. Using this method, a good correlation between µCT and matrix digestion has been achieved - Figure 3a.

DIN EN 2564 states that the precision for porosity content is estimated to be 1% absolute. The good linearity of the correlation suggests a better precision. µCT precision in this study is estimated to be 0.2%. As it has been reported in literature [7,9,10] there was a linear correlation between ultrasonic attenuation and pore content – Figure 3b.

3.2. Influence of cure pressure

After establishing the accuracy of the porosity measurement process itself, it is possible to correlate the manufacturing data with the obtained porosity results. There was a clear link between autoclave pressure and average porosity content – Figure 4.

At an autoclave pressure of 8.2 bar, porosity could not observed within the given detection limit, although no vacuum had been used. However, if autoclave pressure was

Table 2.
Inspection parameters

Ultrasonic Testing	Microfocus Computed Tomography	Matrix Digestion
Impulse-Echo mode	Voltage: 70 kV	Acc. to DIN EN 2564 [4]
Sender damping: 33 Ω	Current: 65 µA	without any deviations
Pulse Width :1	Voxel size: 11 µm	
Step Size: 0.1 mm		
Frequency: 5 MHz		
Amplification: 40 dB		

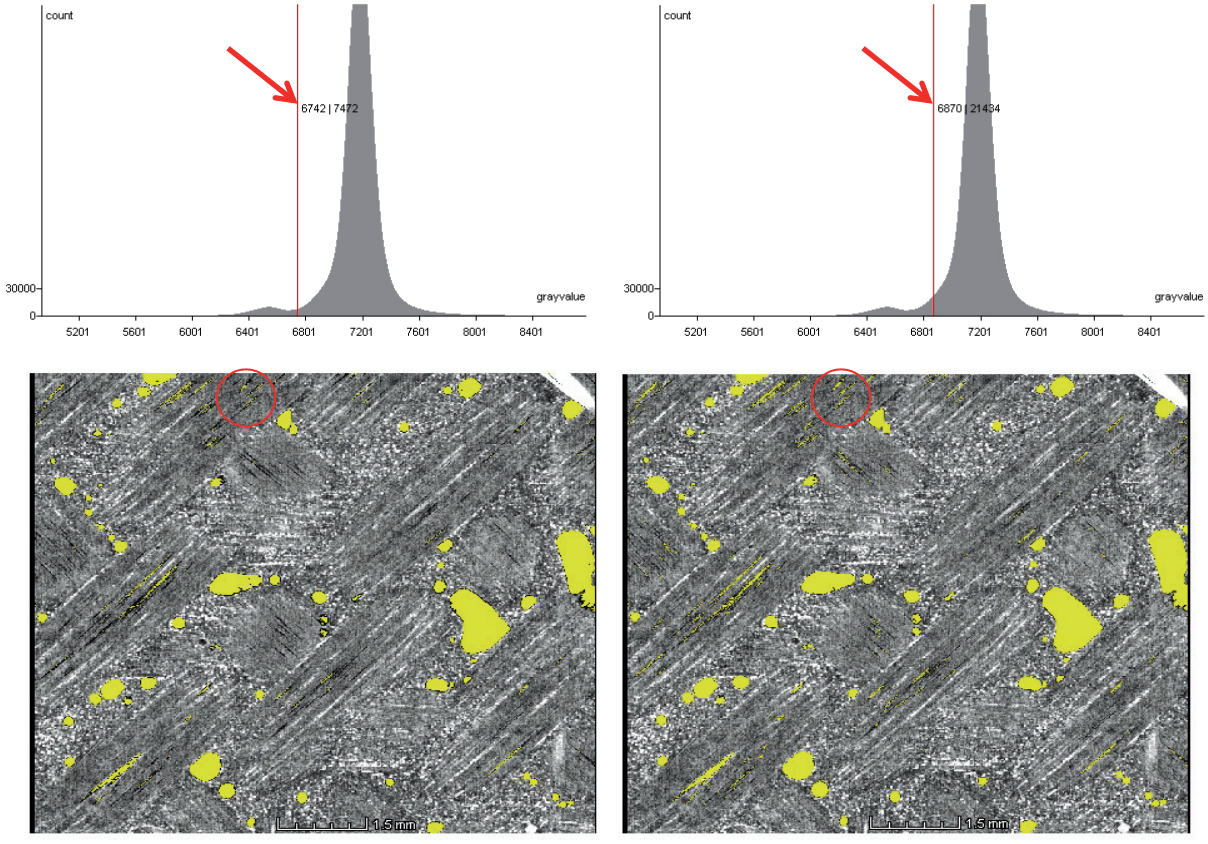

Fig. 2. A small variation of the threshold (arrows) leads to almost invisible changes in the marked voxels (circles). Yet the measured porosity content on the left side is 2.96 % and on the right side 4.63 % [5]

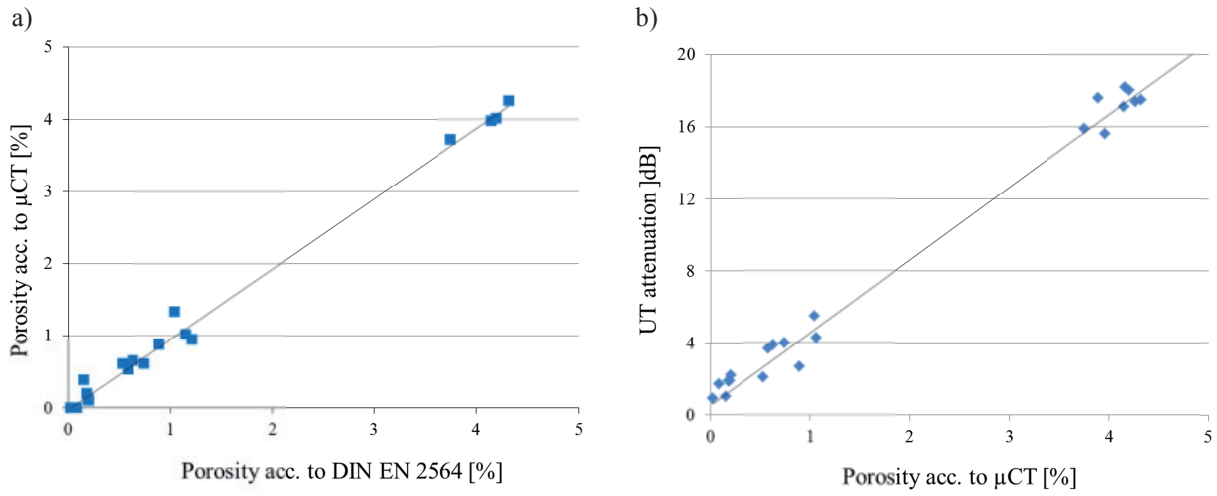

Fig. 3. a) Correlation between CT and matrix digestion porosity measurements, b) Linear correlation between CT porosity and UT attenuation

below 5 bar, average porosity rose exponentially up to about 6.5%. This correlation was also reported for older CFRP systems [8].

The data for plate 14 is not included in Fig. 5 since this plate was manufactured differently. The porosity of plate 14 exceeded 20%.

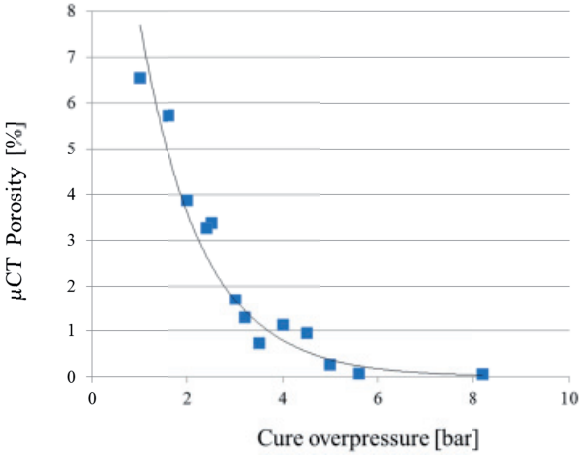

Fig. 4. Influence of autoclave pressure on the average porosity content of a plate

3.3. Water absorption

To measure the influence of porosity on the amount of water absorbed by CFRP, specimens were stored in a humidity chamber with forced convection at 70°C/85% r. H.. At irregular intervals the specimen were transferred into another chamber for temperature cycling. One cycle consisted of:

- Cooling down to -60°C in 30 min,
- Hold at -60°C for 30 min,
- Warm up to 20°C in 30 min and
- Hold at 20°C /85% r. H. for 30 min.

This cycle was repeated between 40 and 60 times before the specimens were put back into the humidity chamber. For each level of porosity, a group of five specimens was used. The average pore content for each group is listed in Figure 5. A group was considered valid when the porosity content of the five specimens was within ± 0.1% $_{abs}$.

The humidification and storage was done in two batches. Batch A had a very long storage time and the specimens had reached complete saturation before cycling began. Batch B was cycled before full saturation had been achieved [11]. The results of both batches are similar. All specimens were weighed immediately before and after cycling.

It can be seen in both specimen sets that the porous CFRP can absorb moisture faster than the non-porous CFRP. However, it also loses moisture faster when placed back into a constant environment. In the end, even after very long exposure times and a very large number of temperature cycles, there is no difference between the moisture content due to different levels of porosity.

In this study porous CFRP did not absorb more moisture in the long run as non-porous CFRP did. Therefore it is unlikely that liquid water accumulates inside the pores.

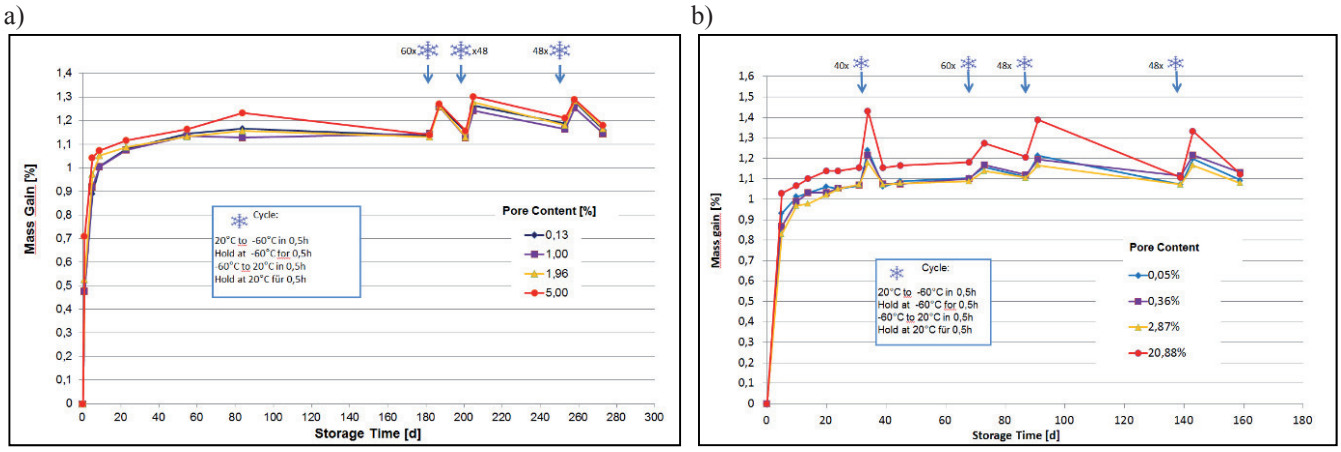

Fig. 5. Mass gain of batch A (a) and batch B (b) [11] during intermittent hot/wet and cyclic storage

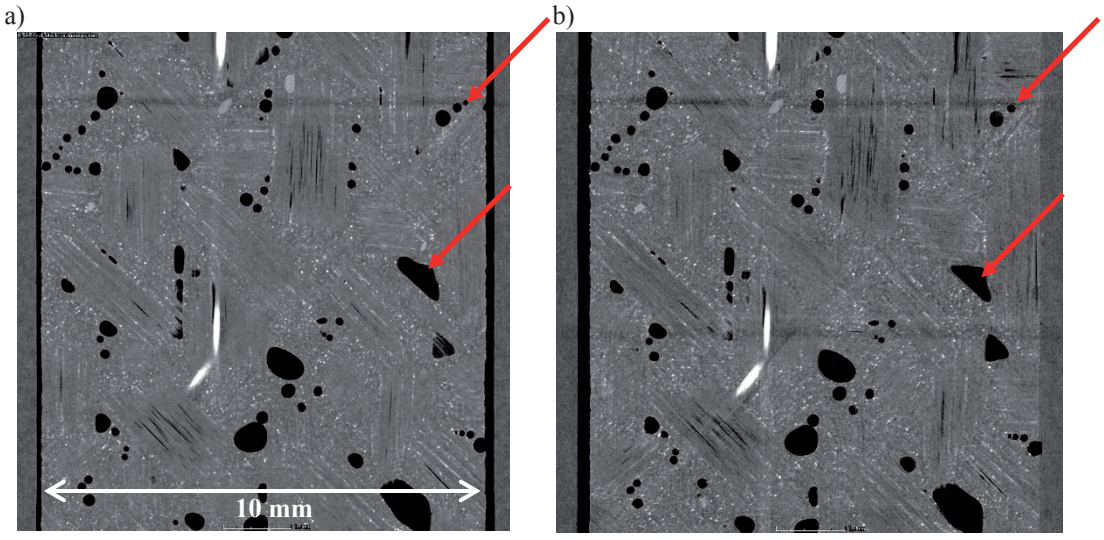

Fig. 6. CT cross-section through a specimen from plate 9. Specimen porosity is 5%. Image a) is after curing, image b) is after thermal cycling as depicted in figure 5 No water is detectable in any of the pores. The small variations between the images (arrows) are due to minor alignment errors

µCT was used to backup this result by comparing the 3D scans of freshly manufactured specimens with scans of exactly the same specimens after storage. It was possible to do CT- cross-sections at identical regions of the specimens and thus to search for any internal changes within the specimen.

However, no changes were detected, especially no liquid water. The very small differences that can be seen between cross-sections like in Figure 6 are due to the not absolutely perfect alignment of the scans.

In order to cross-check if liquid water would be detected in µCT cross-sections, a simple experiment was used. A few drops of water were put atop some specimens before the CT scan. This water was sucked into the narrow crevice between the conformal specimen holder and the samples by capillary forces. From there it could also enter those pores of the specimens that had an opening to the outside. The specimen holder was then sealed with a thin adhesive tape so that the specimens remained wet during the 2 h scan time.

The water inside those pores on the outside that had been reached by the capillary water can be clearly seen – Figure 7.

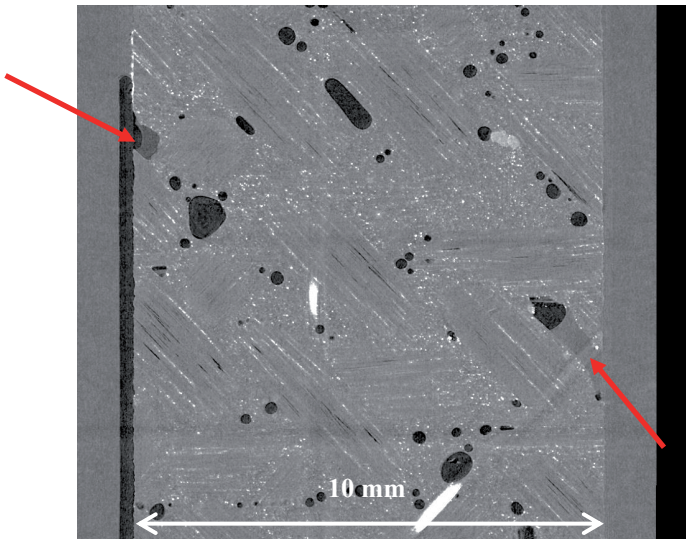

Fig. 7. Porous specimen after contact with liquid water. Pores that had a connection to the surface have filled up. This water is clearly detectable using µCT

4. Conclusions

In this study, it could be shown that porosity did speed up the absorption of moisture. This was to be expected since diffusion through the gas filled pores is much faster than through solid CFRP. However, under the parameters applied, porosity had no long term influence on the amount of absorbed water. In this regard, there was no significant difference between CFRP specimens ranging from pore-free to > 20% porosity.

Using Microfocus Computed Tomography it could be shown that even after nearly a year under hot-wet conditions and more than 150 severe temperature cycles there is no liquid water detectable inside the pores. This leads to the conclusion that for CFRP of this type and thickness, there is no danger of internal water filled pores and therefore also no danger of high internal pressure due to ice inside the pores.

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