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Influence of the curing cycles on the fatigue performance of unidirectional glass fiber reinforced epoxy composites

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Abstract. During the manufacturing process of fiber reinforced polymers the curing reaction of the resin results in shrinkage of the resin and introduces internal stresses in the composites. When curing at higher temperatures in order to shorten up the processing time, higher curing stresses and thermal stresses are built up and frozen, as residual stresses occur. In the present work, a glass fiber reinforced epoxy composite laminate with an unidirectional architecture based on non-crimp fabrics with backing fibers is investigated. Three different curing cycles (time-temperature cycles) are used, leading to different levels of internal stresses. The mechanical properties, static strength and fatigue life time, are measured in three different directions of the material, i.e. the fiber direction, 0°, the 30° off axis direction, and the 90° direction transverse to the fiber direction. It is experimentally demonstrated that the resulting residual stresses barely influences the quasi-static mechanical properties of reinforced glass-fiber composites. It is found that the fatigue performance in the 0° direction is significantly influenced by the internal stresses, whereas the fatigue performance in the off axes directions so is not significantly influenced of these stresses. This is related to the observations that the damage mechanisms in the off axes directions are mainly related to shear failure in the matrix and in the interface between fiber and matrix and different from the damage mechanisms in the fiber direction, where the damage initiates in the transverse backing fibers and is directly related to fiber fractures in the load-carrying axial fiber bundles.

1. Introduction

The introduction is divided into two parts. Firstly, an overview over glass fiber reinforced materials and their manufacturing is given. Secondly, resin curing kinetics are described.

1.1. Glass Fiber Reinforced Materials

Epoxy resins are commonly used as matrix materials in glass fiber reinforced composites for rotor blades of wind turbines. To produce a glass fiber reinforced epoxy composite, the dry glass fiber fabrics (non-crimp fabrics) are build up in a mold and sealed in a vacuum bag. Two polymer components, resin and hardener, are mixed and the reinforcing glass fiber based structure is infused using vacuum assisted resin transfer molding (VARTM). During and after the infusion, the resin will undergo a curing reaction and transform to the solid state, the matrix. During



this reaction, internal stresses, which heavily depend on the time-temperature cycle during the curing, are built up in the composite.

Lower temperatures demand for longer times to fully cure the material and result in lower stresses whereas higher temperatures and shorter curing times increase these stresses. In manufacturing, it is attractive to reduce the mold time and thus increase the output by increasing the curing temperature. However, this is at the expense of the quality of the laminate.

The question is, how the material's properties are affected and the challenge is to find a compromise which meets the needs of production time and material quality. It is known that higher levels of residuals strains in a composite material reduce the fatigue performance of a glass fiber composite. This is particularly important for wind turbine blades as they are exposed to periodic loads and as repairs during service are difficult. Thus, the correlations between residual stresses and fatigue performance were studied manifoldly, showing that higher residual stresses cause a decrease in fatigue performance for composite materials. [1, 2, 3, 4] For this reason, three different panels are in the focus of this work, demonstrating the nexus between curing cycles, quality and properties.

In a previous study Pereira et al. investigated three unidirectional non-crimp fabric panels cured under three different curing cycles and the magnitude of the stresses was measured [1]. It was experimentally shown how these stresses have a large influence on the fatigue life time of the composite when loaded in the unidirectional fiber direction. It is the objective of the present work to measure if the curing cycles also influence the static properties and the off axes fatigue properties when the same panels are loaded in the off axes directions, that is load directions oriented 30° and 90° to unidirectional fibers.

1.2. Resin Curing Kinetics

The curing of an epoxy resin is the transformation from its liquid reactants to the cured, solid polymer. Thereby, the physical interactions between the initial molecules are partly substituted by covalent bonds. [5, 6, 7]

Before the reaction, each monomer occupies a volume larger than its real size due to physical interaction with its surroundings and other molecules and due to their atomic motion. As the chemical bonds are of a shorter range than the physical interactions, the molecules get packed closer together when transforming to the solid [8]. Macroscopically, this transformation is accompanied by a decrease in volume and thus an increase in density, referred to as shrinkage.[9]

A schematic and two-dimensional representation of this process is depicted in figure 1: In a), a monomer is represented by a hexagon. The inner, grey area is the size of the molecule, the outer contour is the space occupied due to physical interactions. In b), the curing process is sketched. Initially (i) the nineteen monomers can move freely but repulse each other due to physical interactions. During curing, chemical bonds are formed, and the molecules get packed closer together, with physical interactions only relevant on the surface of the formed macro molecule (ii)[8]. Although the total number of represented monomers is the same, the area of this flat macro molecule is reduced, as indicated by the black arrows. Transferred to three dimensions, this model demonstrates volumetric shrinkage during the curing process.

The total shrinkage is defined by the physical properties of the components and its reaction and is neither a function of time nor of temperature. As long as the molecules can move freely, shrinkage can cause a change in shape but will not impair the mechanical properties. However, when the polymer is in contact with stiffer material, such as reinforcing fibers, stresses can built up. This is demonstrated in figure 2: During the curing process, the resin material shrinks and gets attached to the fiber. Being the stiffer material, the fiber will undergo a compressive elastic deformation building up compressive stresses [10]. Further, the difference in the coefficient of thermal expansion of polymers and fibers has an effect on the residual stresses in a composite.

In the study by Pereira et al. a Fiber Bragg Grating (FBG) sensor is placed in a liquid,

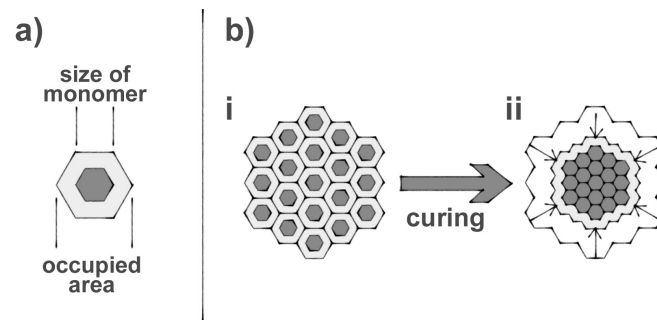


Figure 1. Simplified sketch of curing process. After curing, the molecules are packed closer together and thus the material's density increases (based on Shah and Schubel [8]).

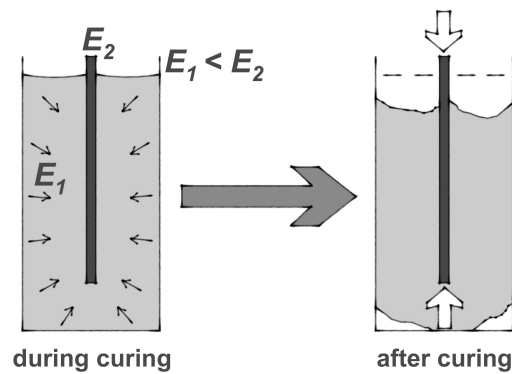


Figure 2. Shrinkage during curing around an obstacle, for instance a glass fiber (black). As Young's modulus of the fiber E_2 is significantly higher than Young's modulus of the resin E_1 , the fiber will be stressed, as indicated by the white arrows.

freshly mixed resin sample. Such, the evolution of strains can be measured directly and in situ[1]. A typical curve for strains measured by means of FBG sensors is displayed in figure 3. The strain evolution can be tracked over the course of time starting as liquid and then transforming to a gelled and solid state. While the resin system is in its liquid phase, no strains are measured. When the resin transitions into a gelled and later solid state, strains built up and can be detected. After curing is accomplished, the material is cooled to ambient temperature. The final strain value reading then gives a measure of the residual strain existent in the specimen. This value combines the strains due to chemical shrinkage $\Delta\varepsilon_{shr}$ and the strains due to thermal contraction $\Delta\varepsilon_{TC}$. [1, 4, 11, 12, 13]

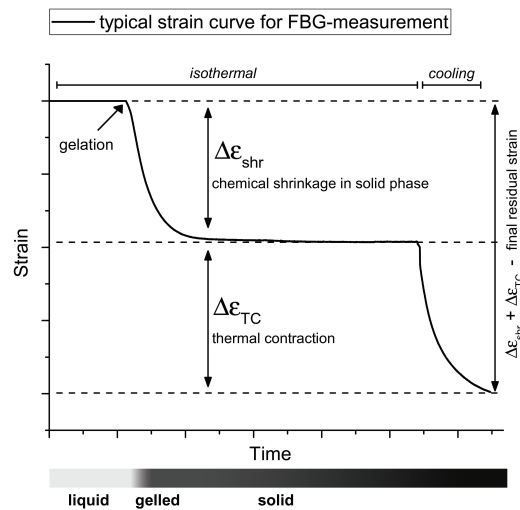


Figure 3. Schematic course of curve of the strain evolution during curing and subsequent cooling. The final strain value is the sum of strains due to chemical shrinkage $\Delta\varepsilon_{shr}$ and strains due to thermal contraction $\Delta\varepsilon_{TC}$.

2. Experiments

In this section, the used materials and experiments will be described.

2.1. Materials

Three panels were manufactured using VARTM under three different projected curing cycles according to figure 4. All cycles lead to a full cure of the material. The one-stage curing cycle at 110°C (EQA-03) exceeds the maximum glass transition temperature (84°C) of this system, the curing cycle at 75°C (EQA-02) remains below it. For the two-stage cycle (EQA-01), temperatures were chosen to be moderate but achieve a full cure.

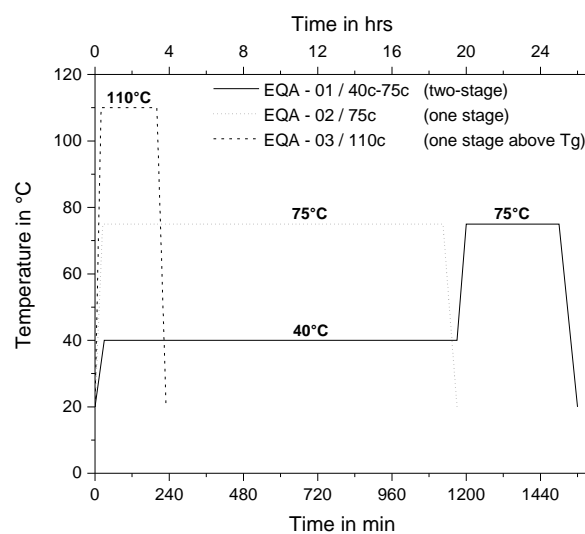


Figure 4. Projected time-temperature profile for the laminates from which specimens were cut.

Laminate built-up and the test specimen orientation and geometry are found in figures 5 and 6. Figure 5 represents the dry fiber layup of all laminates, figure 6 highlights the cutting directions. Hence in addition to the tests reported by Pereira et al., the new specimen are mainly reinforced with fibers in 30° and 90° to the specimen's longitudinal axis, which is also the axis of the load application.

The fibers were of type *Biax 600* and *UD1150+Biax100* and were vacuum-infused with the resin system *Araldite LY 1564 SP / hardener XB 3486* produced by Huntsman. Prior to the infusion, the resin system was mixed and degassed. The test laminates were cured in three different time-temperature curing cycles as depicted in figure 4.

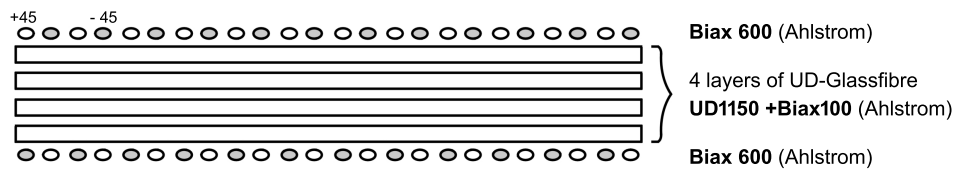


Figure 5. Layup of the glass fibers.

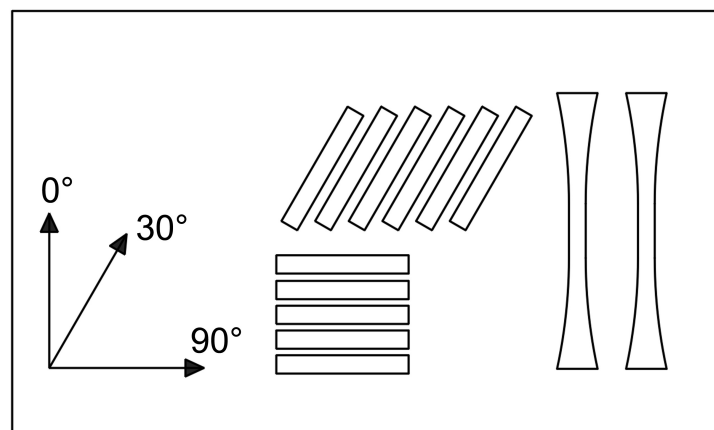


Figure 6. Cutting directions and specimen types.

2.2. Mechanical Test

The following test were performed:

- Static test of the matrix
- 0° -direction – Static, 2 test specimens from panel EQA-01 and EQA-02 and 3 test specimens from panel EQA-03
- 0° -direction – Fatigue, $R = 0.1$, 7 test specimens from panel EQA-01 and 6 test specimens from panel EQA-02 and EQA-03
- 30° -direction – Static, 3 test specimens from each panel
- 30° -direction – Fatigue, $R = 0.1$, 3 test specimens from each panel
- 90° -direction – Static, 3 test specimens from each panel
- 90° -direction – Fatigue, $R = 0.1$, 3 test specimens from each panel

Static tensile tests were performed using an universal servohydraulic test machine. Displacement rate was 2 mm/min. Fatigue tests were run using the same equipment and test were run at 4-5 Hz up to a run out level of $2 \cdot 10^6$ cycles in tensile-tensile mode with $R = 0.1$.

3. Results

In the following, experimental results are provided.

3.1. Residual Strains

As reported by Pereira et al. (refer to figure 3) values for the residual strain yield the results listed in table 1.

Table 1. Residual strains measured using FBG sensors

Material ID	Residual strain in %		
	specimen 1	specimen 2	mean value
EQA-01	0.44	0.44	0.44
EQA-02	1.31	1.44	1.38
EQA-03	1.24	0.82	1.03

3.2. Fiber Content

For quality assessment and to ensure the comparability of the different materials, the fiber volume content for each material was determined using pyrolysis and the results are given in table 2.

Table 2. Fiber volume content of all tested materials

Material ID	Fiber volume content in %
EQA-01	57.8
EQA-02	58.8
EQA-03	57.1

3.3. Quasi-static Test Results

The results of the quasi-static tests for composite specimens and neat resin specimens are displayed graphically in figure 7 (Young's modulus) and figure 8 (tensile strength) and are subsequently listed as tables (table 3 to 5). For composite specimen, the label indicates the cutting direction, that is, the tilting between the unidirectional reinforcement and the specimen axis. Pure resin specimen show no significant variation of quasi-static tensile properties as displayed in the right columns of figure 7 and 8. As for neat resin material, quasi-static properties of composite materials are not significantly influenced by the curing cycle.

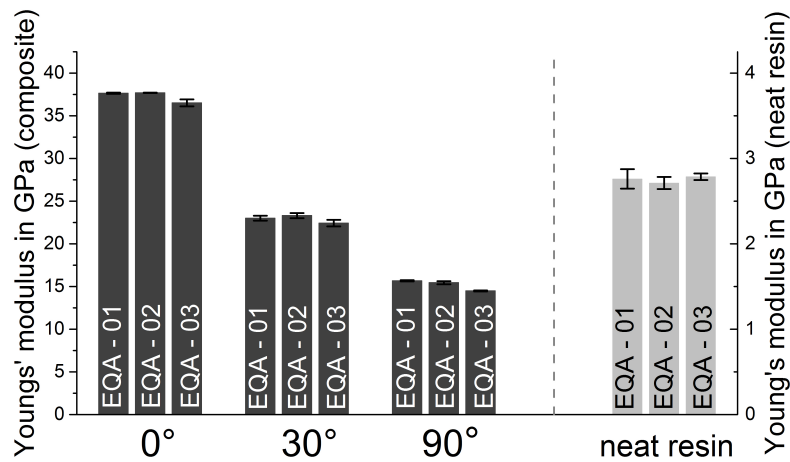


Figure 7. Young's modulus of composite and neat resin material; Right Y-axes (neat resin) adjusted with factor 10.

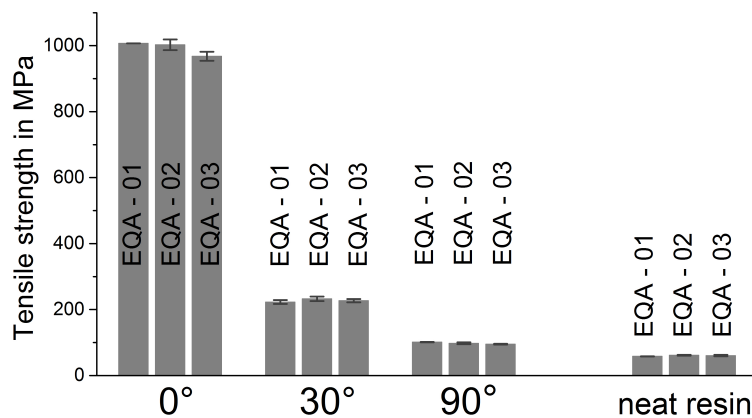


Figure 8. Tensile strength of composite and neat resin material.

Table 3. Young's modulus for composite specimen in GPa

ID	0°			30°			90°		
	EQA-01	EQA-02	EQA-03	EQA-01	EQA-02	EQA-03	EQA-01	EQA-02	EQA-03
mean value	37.6	37.9	36.5	23.0	23.3	22.4	15.7	15.5	14.5
deviation	0.08	0.03	0.41	0.29	0.30	0.39	0.07	0.18	0.06

Table 4. Tensile strength for composite specimen in MPa

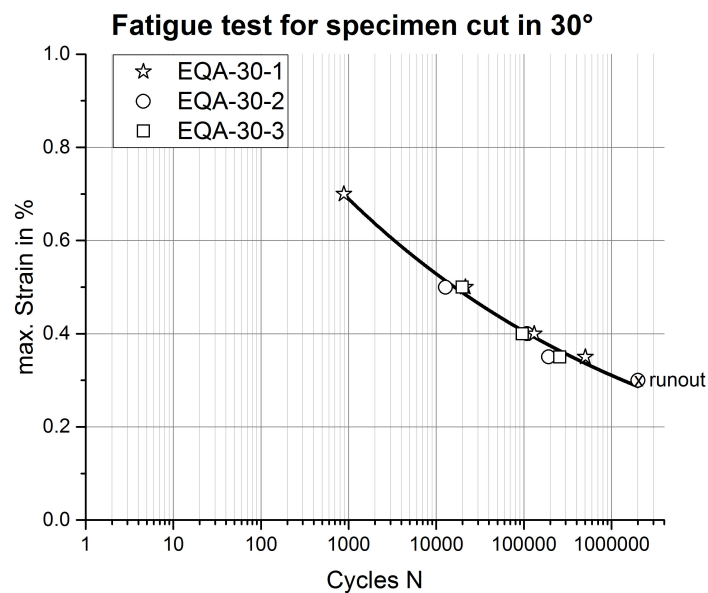
ID	0°			30°			90°		
	EQA-01	EQA-02	EQA-03	EQA-01	EQA-02	EQA-03	EQA-01	EQA-02	EQA-03
mean value	1007	1003	968	223	233	227	101	98	98
deviation	0.0	16.1	13.7	6.0	6.8	5.0	0.8	2.8	1.5

Table 5. Quasi-static tensile properties for neat resin samples

ID	Young's modulus in GPa	Tensile strenght in MPa
EQA-01	2.8 ± 0.11	58 ± 0.5
EQA-02	2.7 ± 0.07	61 ± 1.2
EQA-03	2.8 ± 0.09	61 ± 0.4

3.4. Fatigue Test Results

Results for fatigue performance in 0° , 30° and 90° are given in figures 9 to 11. For the specimens in 30° - and 90° -direction, the individual measurements are consolidated in one S-N-curve a time. For the series in 0° -direction (figure 11), three separate S-N-curves have to be distinguished. The fits are calculated using a standard method involving a linear regression with a Basquin-function of type $N = C \times S^m$, with the number of cycles N , the input load S and the constants C and m .

**Figure 9.** S-N-curve for specimen cut in 30° .

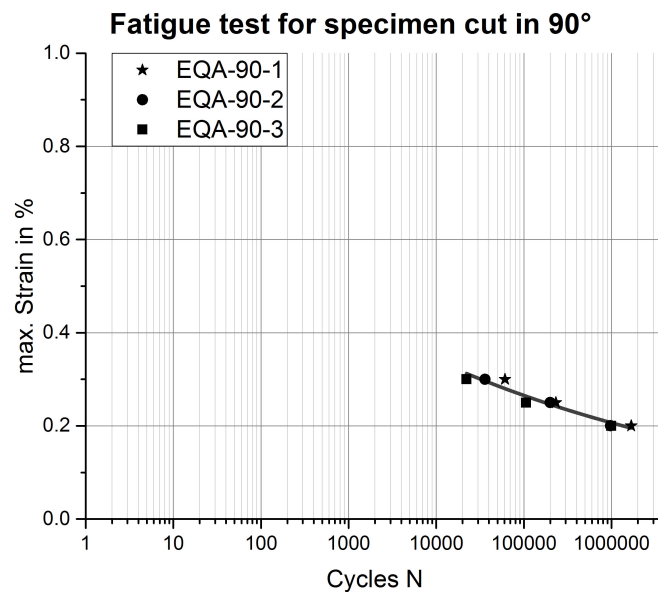


Figure 10. S-N-curve for specimen cut in 90° .

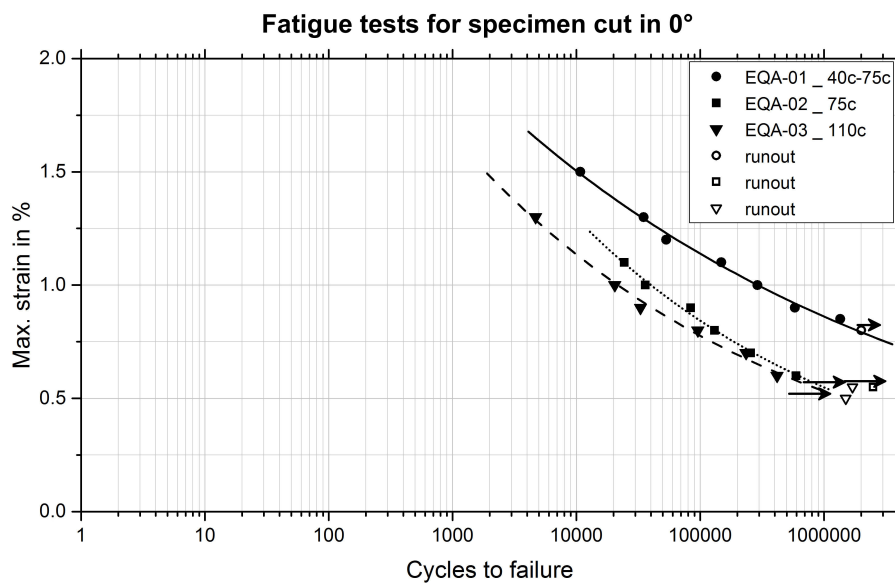


Figure 11. S-N-curve for specimen cut in 0° .

4. Discussion

Variation in the fiber volume contents are low and this is only reflected in a minor differences found in the measured Young's modulus. As the architectures are identical, the major changes in the materials mechanical properties can directly be related to the different curing cycles.

The quasi-static tension tests of the cured resin (the matrix material) clearly show that the mechanical properties of the polymer are not influenced by the curing cycles. The test material has not been constrained and no internal stresses are build up. Also the tensile strengths of the three panels measured in the 0° , 30° , and 90° directions respectively, are not influenced by the internal stresses and the curing cycles. This demonstrates that static properties of fiber reinforced composites are not heavily influenced by the matrix properties, but are only a result

of the architecture and the fiber-matrix interface strength. As an interesting and valuable observation, apparently the latter (the interface strength) is not expected to be influenced by the curing temperatures as especially the 90° static strength is the same for all three panels.

The fatigue behavior in the fiber direction is strongly influenced by the internal stresses. The reason is explained and observed by Zangenberg et al. [3] and is due to the fact the fatigue damage is initiated in the transverse backing fibers. The shrinkage stresses in the resin builds up tensile strain in the matrix along the UD fibers as the fibers prevent the resin to shrink freely. This leads to cracks in the backing fibers and these cracks further initiate cracks in the UD fiber bundles. This is demonstrated in figure 12 [3] and further validated in by using CT scanning by Jespersen et al. [14]. Hence the drop in fatigue resistance in the UD fiber direction is directly related to the shrinkage stresses.

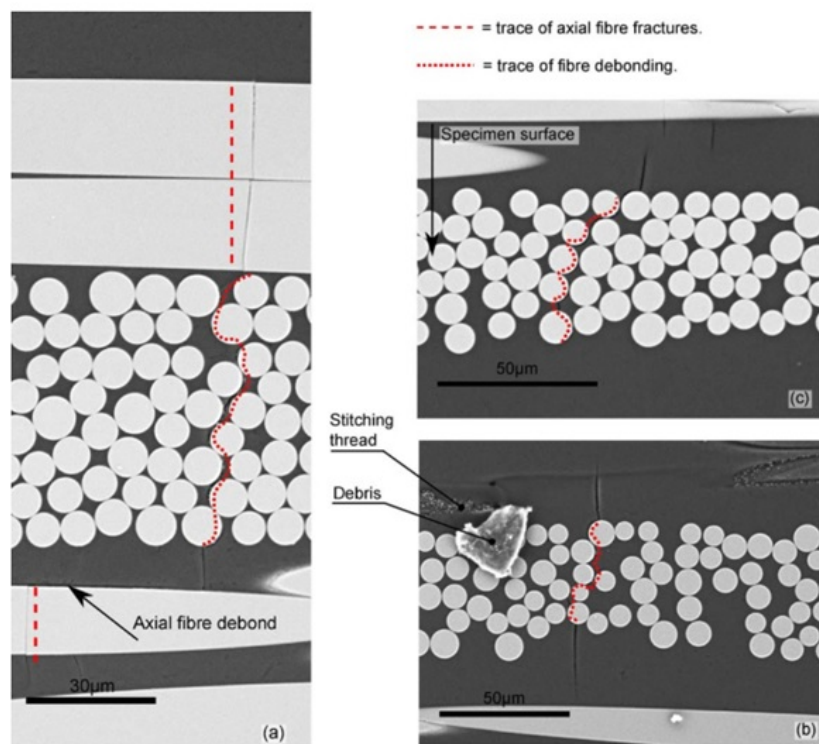


Figure 12. Cracks in UD fiber bundles caused by cracks in the backing fibers [3].

For the off axis fatigue loading in 30° direction we found no influence from the residual stresses. The expected damage mechanism in this loading case is dominated by the shear properties of the laminate and on a micro structural level dominated by the matrix toughness and partly the fiber-matrix interface strength. Hence, apparently similar to the conclusion drawn from the static transverse strength the interfaces are not significantly influenced by the shrinkage stresses.

The damage mechanism expected in the case of 90° loading direction is transverse debonding in the fiber matrix interface. As the UD fibers are constrained in the length directions but free to move and pack in the transverse directions, stresses are not build up in these directions. The only degradation that can be expected might be explained by the assumption that the strength contribution is lower from the backing layers because they are loaded in tension. This can explain the non significant observation, that the fatigue life time might seem to be lower in the panels having undergone a one stage cure.

5. Conclusion

Elevated temperatures during the curing lead to higher residual stresses in unidirectional glass fiber reinforced composites as the resin cannot shrink freely. Neither quasi-static mechanical properties nor the mechanical properties of the pure resin are influenced by the curing cycle.

However, higher residual stresses are related to a decrease in fatigue performance when the direction of loading and reinforcement are the same. Here, cracks in the transversal backing layer initiate cracks in the load carrying UD fibers. For tests with reinforcements not aligned with the load direction (off axes) as demonstrated in this work, no significant influence on the fatigue performance is found.

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