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Performance Enhancements of Polymer-Matrix Composites by Changing of Residual Stresses

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Abstract

Manufacturing induced residual stresses of polymer-matrix composites (PMC) reduce the tensile load at which first ply failure occurs. Thermomechanical treatments offer the potential to change these residual strains, but their application is hindered because the shape stability of PMC components is limited at treatment temperatures, which must be above the glass transition temperature of matrix. This study describes successful localized treatments performed on a stress concentration induced by a circular hole in a laminate. Localization of the treatment allows significant property improvements at much lower treatments loads. Investigation of the influence of moisture pick up on treatment effectiveness revealed it reduces the benefits of treatment to a large extent. Calculations of local stresses between single fibres and predictions of laminate properties based on laminate plate theory using a quadratic failure criterion confirm the experimental results and provide confidence in the physical explanations offered for the measured effects.

Keywords: A. Polymer-matrix composites; B. Hygrothermal effect, Mechanical properties; C. Residual stress, Thermomechanical treatment

Introduction

Most of applied polymer-matrix composites (PMC) designs consist of many plies, which are dictated by the stiffness and strength requirements of the component or product. The single ply is characterized by anisotropic behaviour and very large property differences such as stiffness and thermal expansion between the fibre and the matrix. In high performance PMCs, these characteristics give rise to large internal residual stresses even immediately after manufacture, in the unloaded case at room temperature [1-5]. These stresses are fundamentally due to curing at elevated temperature. When injection technology is used instead of Prepreg technology, there is an additional source of residual stresses: matrix shrinkage [6]. During usage of a laminate, these internal stresses are changed by moisture pickup and the resulting volumetric expansion of the matrix. These effects depend

on environmental conditions, time of exposure, diffusion coefficient and geometric parameters [5,7]. Finally, the loading itself can induce additional inhomogeneities in the stress/strain distribution, particularly in those plies with reinforcement-oriented transverse to the primary loading direction [5]. The superposition of all of these spatially varying stresses results in a very inhomogeneous stress distribution and creates local stress concentrations in the matrix throughout the whole laminate. These stress concentrations in turn result in a much lower tensile load sustained at first ply failure stress/strain than the load sustained at final failure stress/strain [8-10]. This fact prevents a designer from fully exploiting the potential weight savings of PMCs, because in many applications, the components should be designed so as to preclude ply failure at any location. First ply failure makes the components more vulnerable to subsequent degradation, for example accelerating environmental effects (e.g. moisture pick up) as well as fatigue crack growth [11-16].

In the past this problem has been accepted, due to the lack of a simple solution. Approaches to change the internal stresses of PMC by applying thermomechanical treatment have been very successfully applied to laboratory scale specimens or simple components [17-26]. However, applications to large or complex components have been limited, primarily due to problems concerning components' shape stability during relatively high stress loading at temperatures above glass transition. This is a fundamental step in the application of thermomechanical treatments.

In this study, thermomechanical treatments were performed so as to localize the treatment to failure critical areas, thereby reducing the overall load on a component during treatment. Additionally, the influence of residual stress change by moisture pick up on untreated and differently treated specimens was investigated. The intent was to get a real view of potential property improvements under various service conditions by alteration of residual stresses. The results of this study should also provide insight into the potential property improvements which may result from future modification of matrix materials to contain nanoparticles [27-30]. Such matrix materials are thought to have less thermal expansion and/or less moisture pick up than conventional ones.

Experimental

Materials and specimens preparations

All investigations in this study were performed with a composite consisting of continuous carbon fibres T800 in a thermosetting matrix Cycom 5245C, former trade name NARMCO 5245C, (Resin type: Modified cyanate ester), because most characteristics of this PMC needed for predicting first ply failure and micromechanical calculation of local stresses and for achieving thermomechanical treatment were available from previous studies [21,24,25]. The fabricated laminates had a quasi-isotropic lay-up $[(+45^\circ/0^\circ/-45^\circ/90^\circ)_2]_s$. A fraction of them were completely cured (curing cycle to manufacturer's specification + post-curing), the remainder were produced using a shortened curing cycle (reduction of curing time = 30 %) without post-curing.

From these laminates, specimens of 36 mm by 280 mm were cut. A certain number of specimens were notched *before* thermomechanical treatment by drilling a central hole of a diameter of 6 mm (notched specimen) while being water-cooled. The remaining specimens were similarly notched *after* thermomechanical treatment. Before thermomechanical treatment and testing in dry condition or storage in defined climate, specimens were stored in a dry environment at 70 °C for three days and then at 90 °C until constant mass was reached. A certain number of untreated and treated specimens were moisturized by storage in a constant climate of 70 °C/95% relative humidity for 200 days. The moisture pickup was measured by weighing.

Thermomechanical treatment of specimens

A load frame designed for uniaxial creep testing at elevated temperatures up to 250 °C and tensile loads up to 100 kN was used for thermomechanical treatments. In general, these treatments were all based on the following steps, namely quick heating up to treatment temperature, uniaxial loading at this temperature, cooling down under load and finally releasing from the treatment load. Different treatments were applied to completely cured specimens (Treatment A) and to partially cured specimens (Treatment B). In the first case, the treatment loading was performed above the glass transition temperature for only a short period of time (details in Table 1). In the second case, the specimens were held under reduced load at curing or post-curing temperatures until complete cure occurred. The load

was then increased to a level higher than that applied in Treatment A (details in Table 1). The treatments were applied to both notched and unnotched specimens. Unnotched specimens were notched following treatment. The determination of proper treatment conditions was described in detail in [21,24,25].

Determination of properties before and after treatment

Uniaxial tensile tests were performed according to DIN 65559, in order to determine the number of transverse cracks as increasing load was applied to the specimens. During these tests, specimens were loaded stepwise in increments (500 N for untreated and 1000 N for treated specimens) and monitored via acoustic emission (AE) measurements until rupture occurred. After receiving the first AE signals, the specimens were removed from the load frame and prepared for radiographic examination. The specimens were contrasted by storage in a contrast fluid (zinc iodide dilution containing 1200 g zinc iodide, 160 ml H₂O, 200 ml wetting agent Agepon, 200 ml isopropanol) in a vacuum chamber for 4 hours. The contrasted specimens were then radiographed and the resulting images examined for indication of transverse cracks. The specimens were installed back into the load frame and loaded to the next load step, removed and radiographed again. This procedure was repeated until delamination occurred. After the onset of delamination the specimens were loaded up to final rupture and notch strength recorded.

Results

Moisture pick up of untreated and treated specimens

Fig. 1 illustrates the moisture pick up of untreated and different treated specimens versus storage time. It can be seen that treated specimens had less moisture pick up than the untreated ones, but there is essentially no influence between various types of treatment. The continuing moisture pick up over time is typical for the type of matrix used.

Tensile properties

Fig. 2 compares average laminate strains at first ply failure measured by AE on untreated and differently treated specimens in both dry and wet conditions. It can be seen that results depend on the measuring method applied. In dry and untreated wet specimens, approximately the same results were obtained by AE and radiography. However, a discrepancy is noted for wet treated specimens, particularly after Treatment B. It can be assumed this effect reflects the limited sensitivity

of the X-ray method, because cracks initiated at the notch do not extend through the whole specimen width. The rapid decay of stress with distance from the notch [33] implies that cracks should arrest. Especially at first ply failure, crack length and opening displacements should be small, thereby limiting the amount of contrast fluid to infiltrate the specimen. Because this assumption is supported by calculations discussed later in this paper, AE results were chosen for evaluation of influence of different treatment and moisture pick up on first ply failure strain. As Fig. 2 illustrates, the first ply failure of specimens in both wet and dry conditions is shifted to higher strains by all types of thermomechanical treatments. The relative increases vary from 100 to 179% in the dry condition and from 30 until 49% in the wet condition, as compared to untreated specimens. This shows that the improvement by thermomechanical treatment is fundamentally diminished by subsequent moisture pick up. Treatment B provides a larger shift of these strains, namely 169 to 179% in the dry condition and 44 to 49% after moisture pick up compared to Treatment A with 100 to 121% dry and 30 to 41% wet. In spite of the approximately 50 % lower treatment load applied, specimens notched before treatment tend on average to show more substantial strain shifts (121% to 179% dry and 41 to 49% wet) than specimens notched after treatment (100 to 169% dry and 30 to 44% wet). These results confirm that localization of treatment to areas of stress concentrations allows a fundamental reduction in treatment load.

Fig. 3 displays the transverse crack formation with increasing strain applied to dry specimens. As expected from the nature of such kinds of damage, there is a continuous increase in the number of transverse cracks with increasing strain. In the case of untreated specimens, there is a progressive increase of crack rate meaning that the rate of crack formation is low at low tensile strains and increases with increasing strain. A similar trend in crack rate can be seen for all specimens notched before treatment. Specimens notched after treatment reveal an approximately constant crack rate. The average crack rate (slope of the fitted crack number/tensile strain curve) of specimens notched before treatment is visibly larger than that of specimen notched after treatment. It is also significantly smaller in the case of Treatment B than in the case of Treatment A, despite much higher test strain level for Treatment B specimens.

The transverse crack formation of wet specimens is illustrated in Fig. 4. It can be seen that moisture pick up causes a fundamentally different trend in the crack

number vs tensile strain curves. Untreated and Treatment A specimens show a decreasing crack rate with tensile strain, meaning that rate of crack formation is high at low tensile strains and decreases with increasing strains. In contrast, Treatment B specimens show still a progressively increasing crack rate, but the average crack rate is clearly higher than that of comparable dry specimens. As a consequence of this different crack formation trend, wet Treatment B specimens notched after treatment reach higher numbers of cracks at high tensile strains than all Treatment A specimens.

In contrast to transverse crack formation however, no correlation was observed between final failure stress and the changes of residual stresses by thermomechanical treatment and moisture pick up.

Calculation of internal stresses/strains

The fundamentals of thermomechanical treatment, the procedures to calculate internal stresses and strains before, during and after this treatment and the characteristics of the laminates used have all been previously reported in detail [21,24,25]. The following overview should provide a short introduction, to these procedures and serve to address the specifics of the new results published in this paper. Because of the well-defined relationship between stresses and strains and for the sake of clarity, mainly only strains are considered in the following discussion.

Laminate ply strains

Laminate properties like modulus and ply strains caused by manufacture or external loading of a laminate were calculated according to Laminate Plate Theory (LPT) [5] using the properties of single plies. It has to be kept in mind from previous papers [21,24,25] that the permanent deformations which occur transverse to the reinforcement direction of single plies, govern the property improvement after treatment. These deformations can be realized by inducing strains at a temperature above the glass transition temperature of the matrix, and locking those strains in during cool down to a temperature below the glass transition temperature. In addition to the mechanical loading itself, temperature changes are a fundamental source of induced strains during treatment. They result also in strains mainly perpendicular to the ply reinforcement due to anisotropy of the thermal expansion and stiffness of the single ply.

The simplest condition from which to calculate the internal strains during and after thermomechanical treatment is the completely cured laminate at curing temperature, because it can be assumed to be stress free. In this case the first change of internal strains is caused during heating up to treatment temperature. A second change of ply strains is given by the mechanical loading while at treatment temperature. During the subsequent cooling down back to curing temperature, the first changes of internal strains are reversed. This means that heating up from curing temperature to treatment temperature and the reverse process have no influence on internal strains. The subsequent cooling down to test temperature causes further changes of ply strains. To enhance the accuracy of the calculation for this treatment step, the temperature range should be divided into two parts, from cure temperature to glass transition temperature and from glass transition temperature to test temperature, because permanent deformations can only be produced above the glass transition temperature. The dependence of glass transition temperature on loading condition [31,32] as well as the above mentioned reduced stiffness contribution of plies and its effect on single ply strain during loading above the glass transition temperature must also be considered. Additionally, moisture pick up of a PMC in a humid environment causes swelling of the matrix and contributes to its internal strains. The cumulative resulting residual strain components of a ply “i” can be calculated by

$$\{\varepsilon\}^{(i)r} = \{ (\varepsilon^{(i)\text{Th-Mech}} + \varepsilon^{(i)\text{Tg-Shift}}) * F_r + \varepsilon^{(i)\text{Thermal}} + \varepsilon^{(i)\text{Moisture}} \} \quad (1)$$

where $\{\varepsilon^{(i)\text{Th-Mech}}\}$ are the strain components by loading at treatment temperature, $\{\varepsilon^{(i)\text{Tg-Shift}}\}$ are thermal induced strain components during cooling down from curing temperature to shifted glass transition temperature, $\{\varepsilon^{(i)\text{Thermal}}\}$ are residual thermal induced strain components during cooling down from curing temperature to property test temperature, $\{\varepsilon^{(i)\text{Moisture}}\}$ are residual strain components caused by moisture pick up and F_r is the quotient of applied strain and permanent deformation of a ply.

All of these strain components can be calculated on the basis of LPT [5]. For calculation of stresses/strains at the notch during treatment and property testing, a stress concentration factor of 2.57 was applied, which was calculated as described for isotropic materials in [33] using the dimensions of the specimens researched in this study.

The accuracy of the ply strain/stress predictions depends on the selecting the proper ply characteristics, which in turn depend on load/strain level, temperature and moisture content. In Table 2 the best possible choice of ply characteristics used for prediction of laminate properties and the alteration of residual strains/stresses due to thermomechanical treatment and moisture pick up are listed.

The predicted transverse and shear strain components in untreated and different treated laminates in dry and wet conditions are compared in Fig. 5 and 6. Because the first ply failure is expected to occur between fibres in 90° - and 45° - plies, only the transverse strains (in ply axis 2) and shear strains (in ply axis 6) are considered. Due to the laminate lay-up used (quasi-isotropic), shear strains are induced by treatment loading only. It can be seen that production initiated transverse strains are positive, while those induced by moisture and treatment are negative. That means moisture pick up or thermomechanical treatment tend to offset the production induced residual strains, depending on the amount of water picked up and the effectiveness of treatment (Fig. 5 to 7). A thermomechanical treatment and subsequent moisture pick up of the magnitude studied here result in an inversion of residual strains induced during production. One consequence of this inversion, especially in unloaded wet specimens, is that the compressive ply strains/stresses limit the infiltration of contrast fluid, thereby hindering the detection of cracks by radiography. These compressive stresses explain the discrepancy in first ply failure measurements between AE and radiography, and provide a rationale for using only the AE measurements for evaluation of property changes.

These residual stresses can be added to the mechanically applied strains previously described [5] using the following equation:

$$\{\epsilon\}^{(i)res} = \{\epsilon^{(i)r} + \epsilon^{(i)m}\} \quad (2)$$

where $\{\epsilon\}^{(i)res}$ are the resulting ply strain components and $\epsilon^{(i)m}$ the ply strain components caused by mechanical loading both given during property testing.

For the prediction of failure strain in this study a quadratic failure criterion [5] was applied using a normalized interaction term of -0.5 (bounded by the generalized von Mises criterion). Fig.8 to 10 show examples of failure envelopes for an artificial laminate in the absence of residual strains and for untreated and treated laminates in dry and wet conditions tested. The comparison of the envelope of a lami-

nate without residual strains to that of a dry untreated laminate (Fig.8) illustrates that production induced residual strains cause a reduction of the strain space/area without first ply failure, which takes place mainly in the tensile strain space. Thermomechanical treatment reduces or inverts this effect (Fig.9). It causes an enlargement of first ply failure free strain space to higher tensile strains in laminate axis 1 compared to untreated laminates (Fig.8), due to the reduction or inversion of residual strains in this direction mentioned above. Treatment B effects a greater enlargement of this failure free strain space than Treatment A because of higher permanent transverse ply deformation (Fig 5 to 7) due to the higher final treatment load (Table 1) and the higher degree of permanent retention of treatment strain following this treatment (ratio "permanent deformation"/"treatment strain", Table 2) (Fig.9). In laminates without residual strains and in all dry laminates (untreated and treated), first ply failure is expected to occur in 90°-plies under uniaxial tensile load in laminate axis 1 (Fig.8 and 9) as applied during property testing in this study. Considering only the swelling effect, moisture pick up should also lead to an enlargement of first ply failure free strain space, due to the reduction or inversion of residual strains. But the large decrease of tensile strength in ply axis 2 limits this effect in the case of untreated laminates, and negates this effect in the case of treated laminates in the tensile strain space (Fig. 10). In the first case, the line of strain path for uniaxial tensile loading intersects the failure envelope of 90°- and 45°-ply at very similar strain values, which predicts a simultaneous ply failure initiation and development in both type of plies. This effect could be one reason for the much higher rate of transverse crack formation compared to untreated dry laminates (Fig. 3 and 4). The predicted first ply failure of all treated laminates shifted from 90°-plies to 45°-plies by moisture pick up. The reason is that in the case of a poor transverse tensile loading, a reduction or inversion of residual tensile strains should contribute directly to the loading capacity to first ply failure, because the given internal material change and loading have approximately the same direction of effectiveness. This is not the case however in 45°-plies, because an inversion of residual strain transverse to fibre direction does not improve the shear loading capacity of 45°-plies. The reason for lower crack formation rates for specimen notched before treatment compared with specimens notched after treatment cannot be derived from the calculations done in this study, because the influences of stress gradients around the notch were not investi-

gated. But it can be assumed this effect is based in similar loading conditions during treatment and property testing, which cause a reduction of internal stresses similar to cases considered above.

In Fig.11, predicted and experimental first ply failures are compared. For all considered cases a nearly perfect correlation of predicted and measured first ply failure was observed. That means in the dry condition the change of strain at first ply failure by thermomechanical treatment goes along with the amount of introduced permanent deformation depending on condition of the treatment applied (Treatment A or B, notched before or after treatment). The influence of moisture pick up has been already discussed. Essential additional effects on the improvements obtained by thermomechanical treatment cannot be expected from these results.

Local micromechanical strains between fibres

A square fibre arrangement model was used to calculate local stresses/strains of matrix between single fibres. The smallest single element of volume/area of this arrangement, containing quarter segments of 2 fibres in cross section and the matrix filling the space between, was divided in subelements (slices) with very small thickness. This model allows an easy illustration and understanding of the cause of variation of local strain between two fibres. In principal, the dominant effects depend on the length fraction of fibre and matrix within the various subelements. For instance, the slices closest to a line joining to fibres' axes will include most of each fibres' radii, but only a relatively small length of matrix. Those slices further from this line would have a correspondingly higher matrix/fibre ratio. By considering the differences in matrix/fibre ratio between subelements, the magnitude of the various factors affecting residual local stress can be determined. These factors include the different expansion of matrix and fibre by temperature change, permanent deformation of matrix caused by thermomechanical treatment, expansion by swelling due to moisture pick up and strains induced by mechanical loading. Calculations were performed for two cases while respecting the statistical distribution of fibres in the matrix. In the first case, all fibres were assumed to have an average separation. In the second case, single fibres with approximately contact (fibre distance/fibre diameter=1.019) were assumed to be surrounded by fibres with average separation. A detailed description of this model including these extreme cases, as well as a simplification used to calculate micromechanical stresses and strains are given in [24,25].

The following examples were selected to illustrate the variation of influences on residual stresses. Fig.12 and 13 show local stresses transverse to fibre and parallel to the loading direction in unidirectional 90°- laminates (UDL) and 90°-plies of quasi-isotropic laminates (QIL), in dry and wet condition calculated with properties given in [25] or back calculated from UDL values (e.g. moisture expansion coefficient = 0.5/%). As already stated in [21,24,25], production of UDL forms fundamentally compressive stresses in areas where the fibre surfaces are relatively close together (small matrix/fibre ratio), balanced by fundamentally tensile stresses areas where the fibre surfaces are further apart (large matrix/fibre ratio) (Fig.12). Loading transverse to the fibre direction itself creates an inverted stress distribution compared to the production induced one. The superposition of local stresses from production and loading up to failure results in approximately uniform local stresses between fibres, so that the transverse strength of dry UDLs is very close to that of the neat resin.

In a QIL, production induced stresses are positive and raise the average value of local residual stresses, thereby diminishing the load at which first ply failure of the laminate occurs (Fig.12). Thermomechanical treatment shifts the local stress curves to lower values due to permanent deformation of 90°-plies transverse to fibre direction. The magnitude of this effect depends on the intensity of treatment. In the most intensive treatments applied (Type B on specimens notched before treatment) predominantly compressive stresses occur, which fundamentally increase the loading capacity of the laminate. It should be noted that the contact of single fibres does not influence the maximum local stress. In [24,25], it was already shown that no significant change of local stress distribution is caused by thermomechanical treatment beyond that of the previously described permanent deformation.

Moisture pick up reduces or inverts the production induced local stresses (Fig 13). The extent of moisture pick up measured in this study is sufficient to induce tensile stresses in areas where the fibre surface are closer together (fibre centre). The contact of single fibres amplifies this effect. Loading transverse to fibre direction creates a similar change of stress distribution as moisture pick up, which further increases the local stress magnification near the fibre centres. These combined effects lower the loading capacity of an UDL and are reflected in a low transverse strength of this type of laminate in the wet condition. In an unloaded

QIL, the average swelling transverse to fibre direction reduces or inverts average production-induced residual stresses. It reduces the stress magnification in areas where the fibre surfaces are closer together (above the fibre centre). Subsequent loading would cause an increase of stress magnification as before, but compared to the situation in a wet UDL, the stresses are reduced somewhat by the previously mentioned swelling effect. The effect of thermomechanical treatment was already shown for dry QIL. In the case of subsequently moisturized specimens it produces a relatively high level of compressive stresses transverse to fibre direction. Assuming no compressive failure occurs, it should elevate the tensile load capacity up to first ply failure of the laminate partly compensated by moisture reduced transverse ply strength. This prediction was confirmed experimentally.

Summary and Conclusions

In this paper, different thermomechanical treatments and/or storage in humid environment were applied to illustrate the potential for property improvements in polymer-matrix composites by alteration of residual stresses. Notched specimens were researched, because such stress concentrations are often responsible for damage initiation in system components. Additionally, they offer local limited changes of residual stresses by thermomechanical treatment.

The results demonstrate that application of thermomechanical treatments increases the tensile strain at first ply failure at a circular notch in a quasi-isotropic laminate by 30% to 179%, depending on treatment type and moisture content. Treatments on notched specimens lead on average to noticeably higher increase of strain at first ply failure than treatment on unnotched specimens. That means a localized treatment is possible and may be more effective than a treatment of a whole structure. This knowledge facilitates application of thermomechanical treatments to real structures, because the level of load required for treatment is a critical parameter and is often limited by the reduced shape stability of composite structures at treatment temperature.

In dry laminates (untreated and treated), first ply failure at a notch in quasi-isotropic laminates occurs exclusively in 90° plies. Moisture pick up and its related matrix swelling reduce or invert residual stresses, but also reduce the transverse ply strength by magnifying the stresses between fibres as well as by weakening of fibre/matrix interface strength. The elongation effect transverse to fibre di-

rection produces, especially in treated laminates, compressive stresses in 45°-plies, which reduce the loading capacity of these plies. This in turn results in a shift of first ply failure from 90°-plies to 45°-plies. Moisture pick up therefore reduces the potential for property improvement by thermomechanical treatment.

It can be concluded that moisture pick up in realistic service environment neutralizes the property improvement achieved by thermomechanical treatments and demonstrated in dry laminates. New developments in polymer matrix materials are aimed at reducing moisture pick up, such as by matrix modification with nanoparticles. In addition to a general property improvement from reducing local strain magnifications, they should allow the designer to more fully exploit potential property improvements by altering residual stresses e.g. by thermomechanical treatment of laminates used in wet environments.

References

- [1] Pagano N J, Hahn H T. Evaluation of Composite Curing Stresses. In: Composite Materials: Testing and Design, ASTM STP 617, 1977, p. 317-329.
- [2] Hashin Z. Analysis of Properties of Fiber Composites With Anisotropic Constituents, Journal of Applied Mechanics 1979; 46 (9):543-550.
- [3] Collings T A, Stone D E. Hygrothermal Effects in CFRP Laminates: Strains Induced by Temperature and moisture, Composites 1985;6 (4):307-316.
- [4] Bailey J E, Curtis P T, Parvizi A. On transverse cracking and longitudinal splitting behaviour of glass and carbon fibre reinforced epoxy cross ply laminates and the effect of Poisson and thermally generated strain, Proc.R.Soc.Lond.A. 1979; 366:599-623.
- [5] Tsai S W, Introduction to Composite Materials, Technomic Publishing Co., Inc., 1980.
- [6] Rudd C D, Long A C, Kendall K N, Mangin C G E. Liquid Moulding Technologies, Woodhead Publishing Limited, Cambridge, England, 1998.
- [7] Springer G S. Environmental effects on composite materials, Technomic Publishing Co., Inc., Westport, 1981.
- [8] Kies J A, Maximum Strains in the Resins of Fibre Glass Composites, U.S. Naval Research Lab. Report No. 5752, 1962.
- [9] Masters J E, Basic Failure Modes of Continuous Fiber Composites. In: Engineered Materials Handbook, vol.1, Composites, ASM International, 1987, p. 781-785.
- [10] Van Daele R, Verpoest P, Meester P de, Matrix Cracking in Cross Plyed Thermosetting and Thermoplastic Composites During Monotonic Tensile Loading, In: Developments in the Science and Technology of Composite Materials, ECCM3, Bordeaux, 1989, p. 493-498.
- [11] O'Brien T K, Characterization of Delamination Onset and Growth in a Composite Laminate. In: Damage in Composites, ASTM STP 775, 1982. p. 140-167.
- [12] Jamison R D, Schulte K, Reifsnider K L, Stinchcomb W W, Characterization and Analysis of Damage Mechanisms in Tension-Tension Fatigue of Graphite/Epoxy Laminates. In: Effects of Defects in Composite Materials, ASTM STP 836, 1984, p. 21-55 .
- [13] Maier G, Ott H, Protzner A, Protz B, Damage Development in Carbon Fibre-Reinforced Polyimides in Fatigue Loading as a Function of Stress Ratio, Composites 1986;17:111-120.
- [14] Maier G, Ott H, Protzner A, Protz B. Notch Sensitivity of Carbon Fibre-Reinforced Polyimides in Fatigue Loading as a Function of Stress Ratio, Composites 1987;18:375-380.

- [15] Baron Ch, Schulte K. Fatigue Damage Response of CFRP With Toughened Matrices and Improved fibres, ICCM6 + ECCM2, London: Elsevier, vol. 4, 1987, p. 4.65-4.75.
- [16] Konur O, Matthews. Effect of the Properties of Constituents on the Fatigue Performance of Composites, *Composites* 1989;20:317-328.
- [17] Schürmann H. Gezielt eingebrachte Eigenspannungen erhöhen die Belastbarkeit von Bauteilen aus Faser-Kunststoff-Verbunden, *Kunststoffe (German Plastics)* 1984;74:520-526.
- [18] Schürmann H, Zur Erhöhung der Belastbarkeit von Bauteilen aus Faser-Kunststoff-Verbunden durch gezielt eingebrachte Eigenspannungen, Reihe 1: Konstruktionstechnik/ Maschinenelemente Nr. 170, VDI-Verlag GmbH, Düsseldorf, 1989.
- [19] Maier G, Verfahren zur Herstellung eines festigkeitsgesteigerten Produkts aus Duroplast, Deutsches Patent Nr. 3942046, applied on 20.12.1989, approval on 27.2.1992.
- [20] Maier G, Friedrich K. Performance Increase of Polymer Composites by Thermal Treatment Under Load. In: *Advanced Composites in Emerging Technologies, Third International Symposium*, University of Patras, Greece, 1990.
- [21] Maier G, Friedrich K. Property Improvements After Loading at High Temperature. In: *High Temperature and Environmental Effects on Polymeric Composites*, ASTM STP 1174, American Society for Testing and Materials, Philadelphia, 1992, p. 147-160.
- [22] Schulte K, Marissen R. Influence of artificial prestressing during curing of CFRP laminates on interfibre transverse cracking, *Composites Science and Technology* 1992; 44:361-367.
- [23] Cuntze R G, Heibel R. Increasing the limit of usability of CFRP tubes by built-in-stresses, *Composite Structures* 1993; 24:251-264.
- [24] Maier G. Festigkeitssteigerung von ebenen Hochleistungsfaserverbund-Laminaten mit polymerer Matrix durch thermomechanische Behandlung, *Deutsche Hochschulschriften* 535, Verlag Hansel-Hohenhausen, 1994, ISBN -Nr. 3-89349-535-5.
- [25] Maier G, Friedrich K. Mechanisms of Property Improvements of Polymer Composites by Thermomechanical Treatment. In: *High Temperature & Environmental Effects On Polymeric Composites*; ASTM STP 1302, 1997, p. 18-34.
- [26] Bartosch H. Verbesserung des Zwischenfaserbruchverhaltens von CFK-Laminaten bei praxisrelevanten Belastungen durch thermomechanische Behandlung, *Fortschritt-Berichte VDI, Reihe 18; Mechanik/Bruchmechanik*, VDI Verlag, Band 226, 1998.
- [27] Schadler L S. Polymer-based and polymer-filled nanocomposites. In: *Nanocomposites Science and Technology*, ed. Ajayan PM, Schadler LS, Braun PV, Wiley-VCH, 2003.
- [28] Adebahr T, Roscher C, Adam J. Reinforcing Nanoparticles in Reactive Resins. *European Coatings Journal* 2001;4:144-149.
- [29] Preghenella M, Pegoretti A, Migliaresi C. Thermo-mechanical characterization of fumed silica-epoxy nanocomposites. *Polymer* 2005;46:12065-12072.
- [30] Zhang H, Zhang Z, Friedrich K, Eger C. Property improvements of in situ epoxy nanocomposites with reduced interparticle distance at high nanosilica content. *Acta Materialia* 2006;54:1833-1842.
- [31] Maier G. Bestimmen des Glasübergangs von Faserverbundwerkstoffen im statischen Zugversuch, *Kunststoffe (German Plastics)* 1988; 78(4):330-333.
- [32] Maier G. Zur Lastabhängigkeit der Glasübergangstemperatur von Faserverbundwerkstoffen, *Kunststoffe (German Plastics)* 1990;80(8):906-908.
- [33] Young W C, Budynas R G. *Roark's Formulas for Stress and Strain*, Seventh Edition, McGraw-Hill, 2002, ISBN 0-07-072542-X, p. 785.

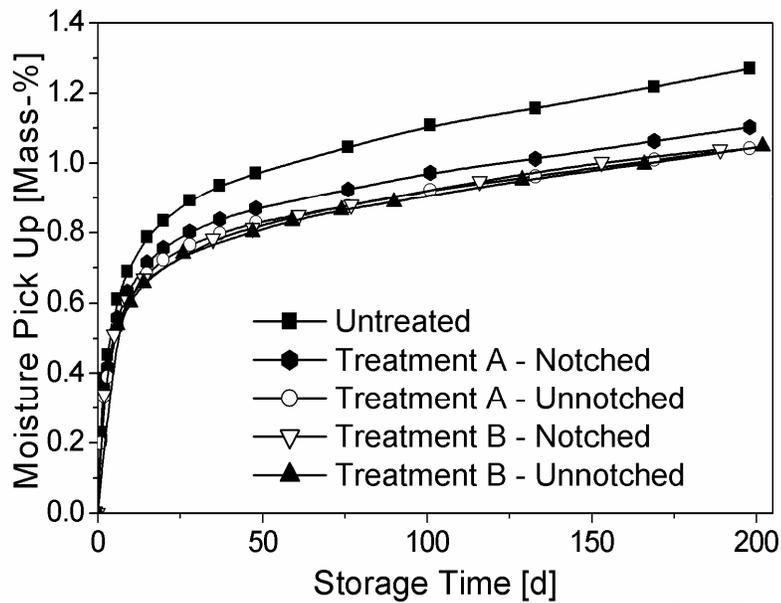


Fig.1: Influence of thermal treatment on water pick up

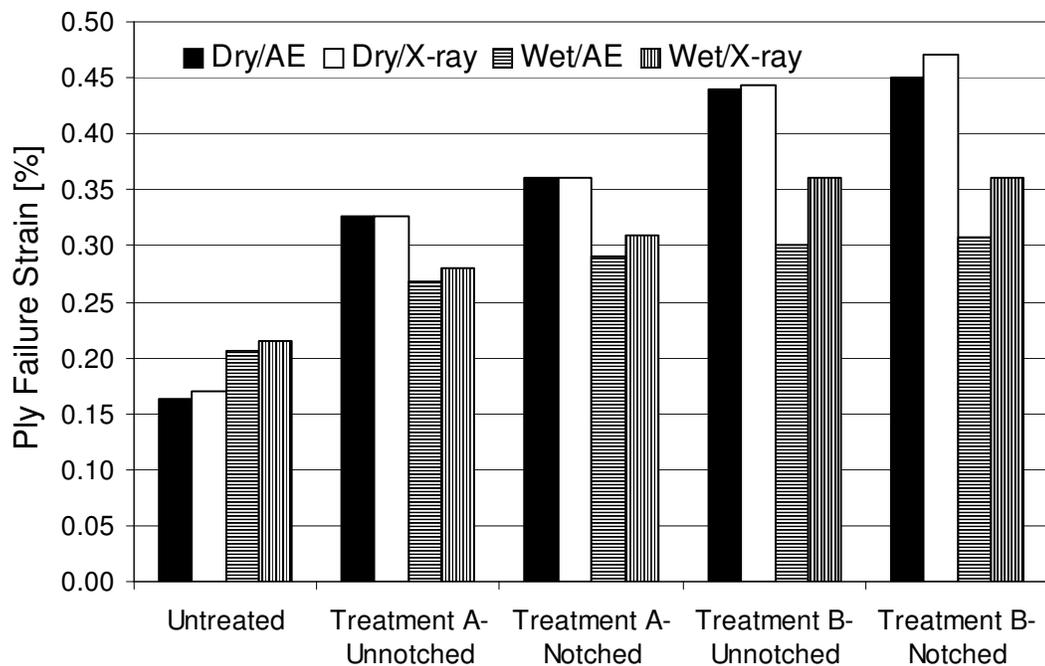


Fig. 2: Average laminate strain of smallest cross section at first ply failure of untreated and treated specimens measured by acoustic emission (AE) and radiography (X-ray)

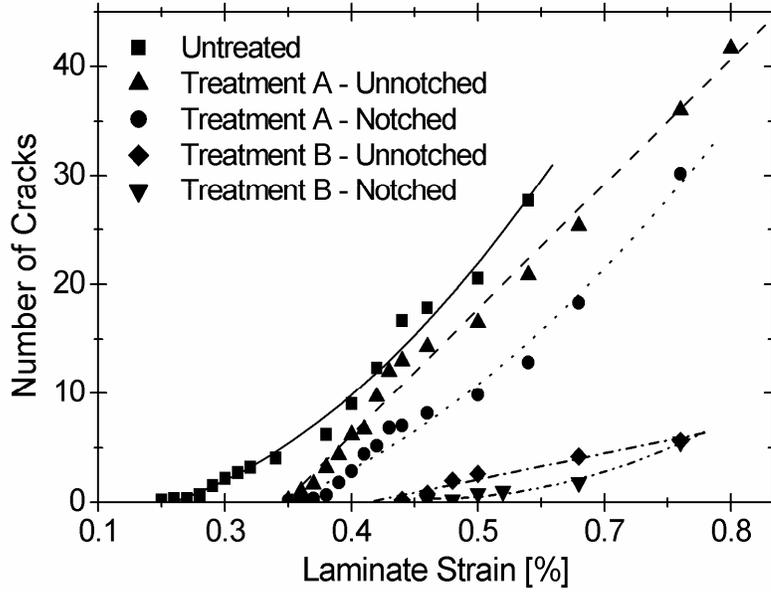


Fig.3: Transverse crack formation versus average strain at smallest cross section of dry specimens

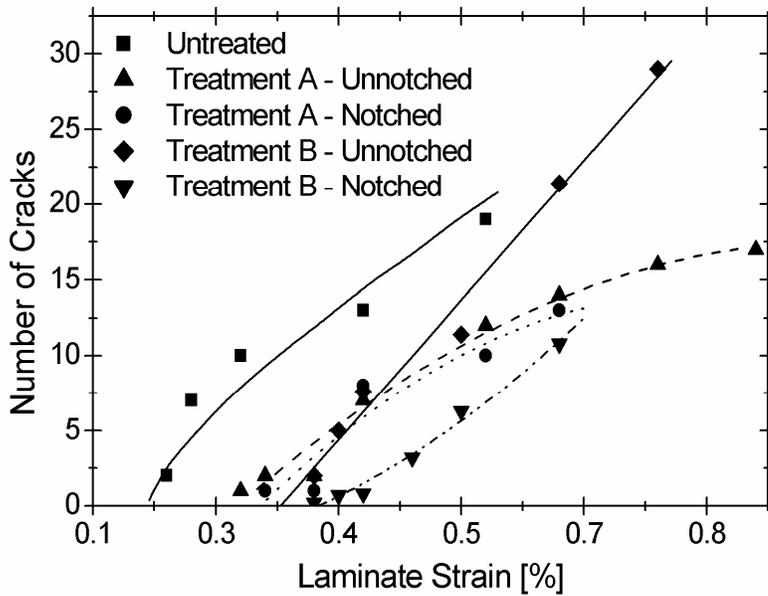


Fig.4: Transverse crack formation versus average strain at smallest cross section of wet specimens

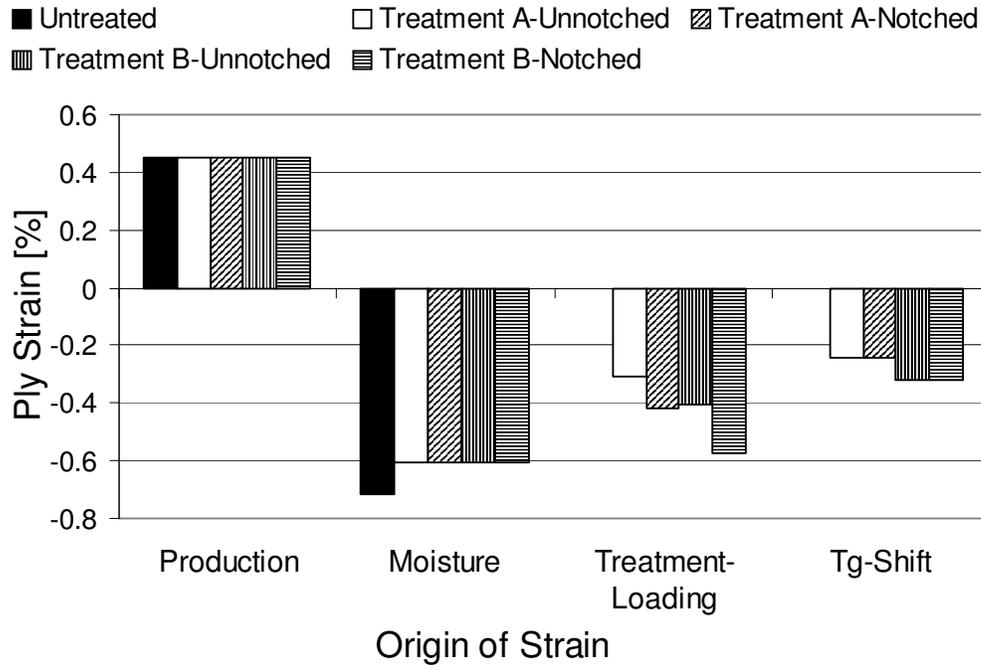


Fig.5: Predicted residual transverse strain components of 90°-plies at the specimen notch

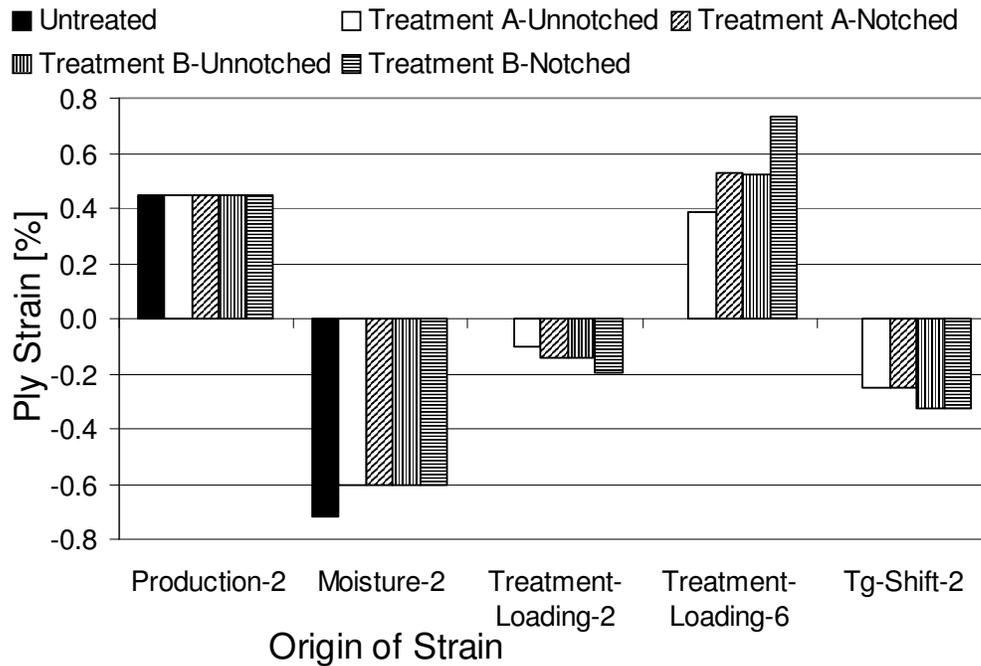


Fig.6: Predicted transverse (2) and shear (6) strain components of 45°-plies at the specimen notch

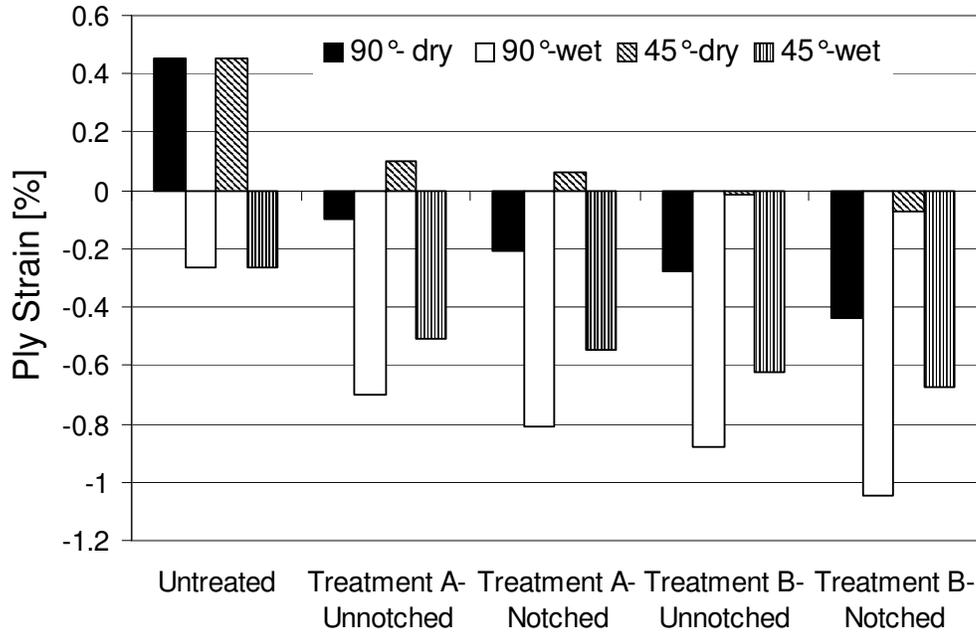


Fig.7 Predicted total residual transverse strains of 90° and 45°-plies in untreated and treated laminates in dry and wet condition at the specimen notch

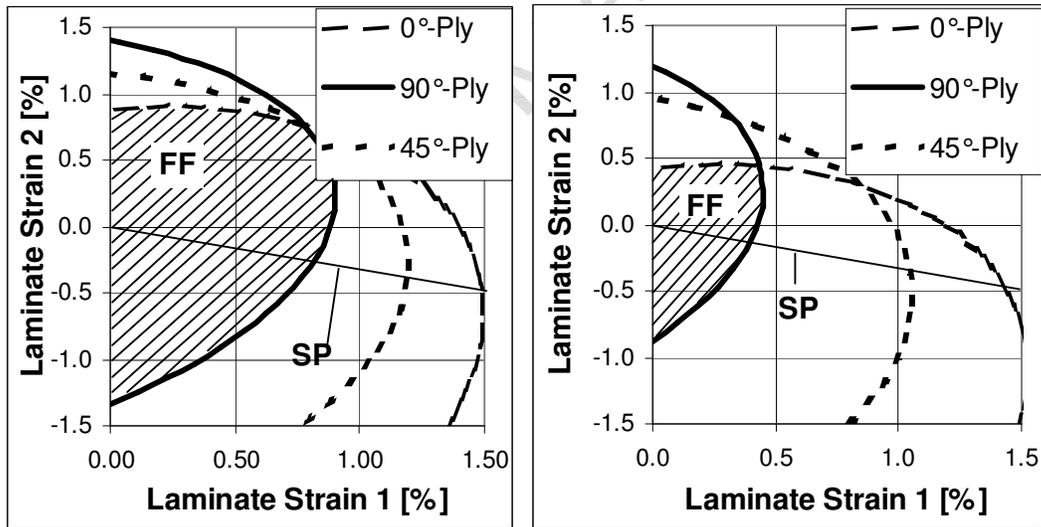


Fig.8: First ply failure envelopes of a laminate without (left) and with production induced residual strains (right) in dry condition, FF = failure free area/space, SP = strain path of uniaxial loading

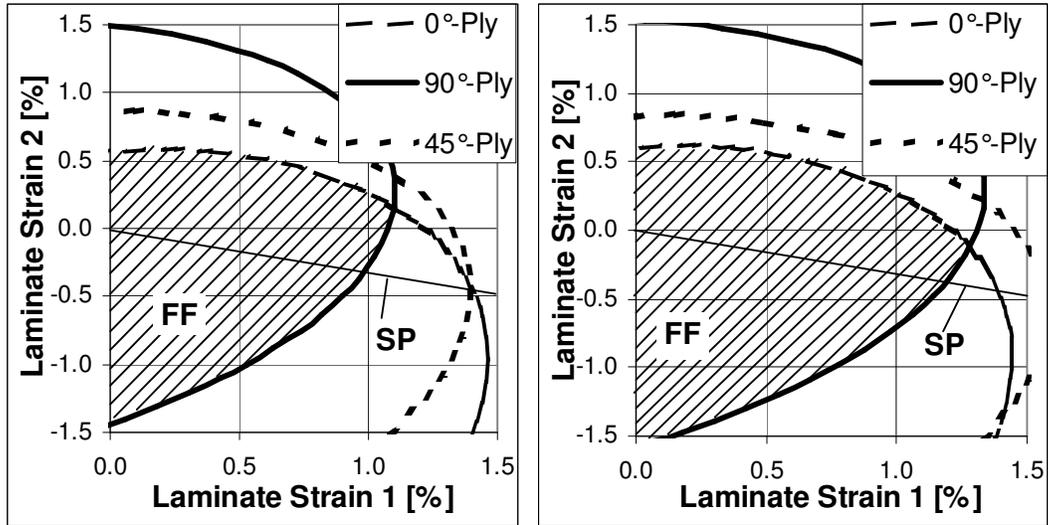


Fig.9: First ply failure envelopes of specimens after treatment A (left) and Treatment B (right) with notch in dry condition; FF = failure free area/space, SP = strain path of uniaxial loading

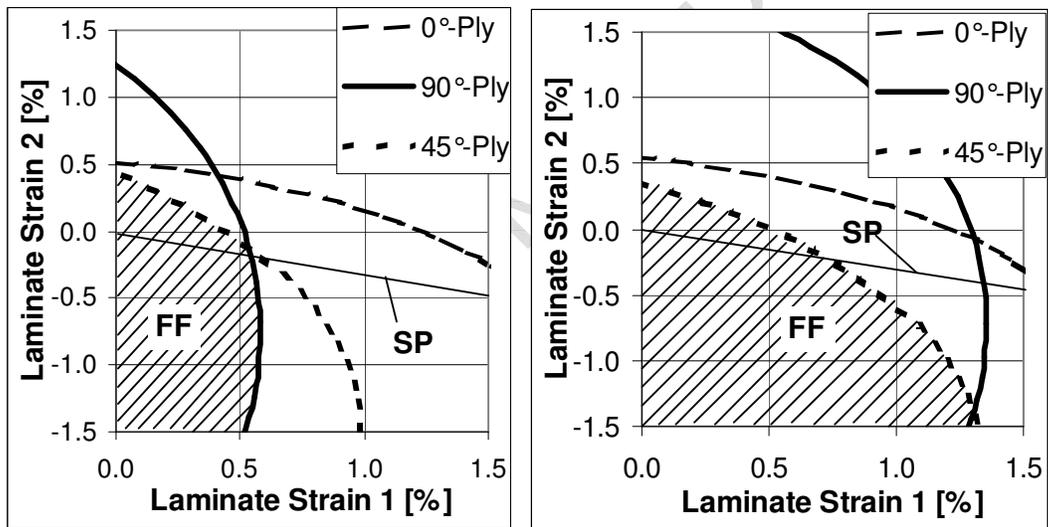


Fig.10: First ply failure envelopes of untreated specimens (left) and specimen after Treatment B with notch (right) in wet condition, FF = failure free area/space, SP = strain path of uniaxial loading

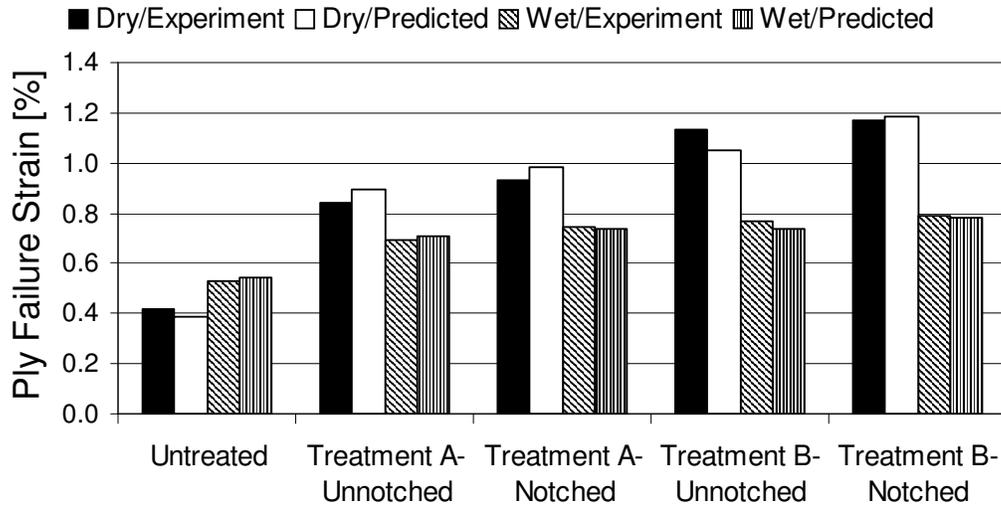


Fig.11: Comparison of predicted and measured strains at first ply failure at the specimen notch

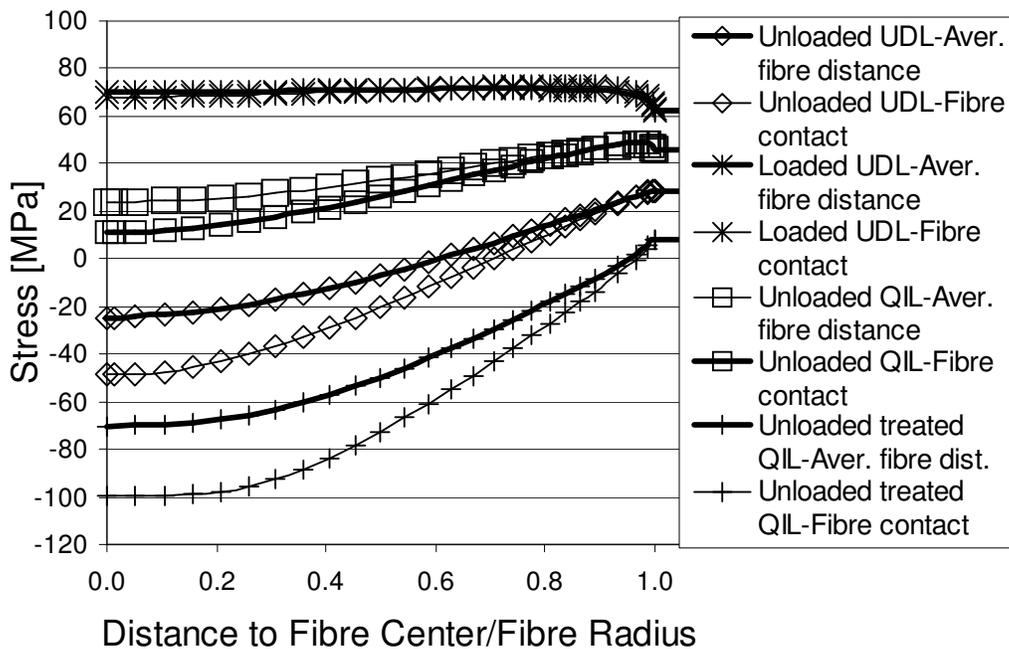


Fig.12: Micromechanical stresses transverse to fibre and parallel to loading direction in dry unidirectional 90° -laminates (UDL) and 90° -ply of quasi-isotropic laminates (QIL) in untreated, treated, unloaded and up to failure loaded condition for average fibre distance and fibre contact

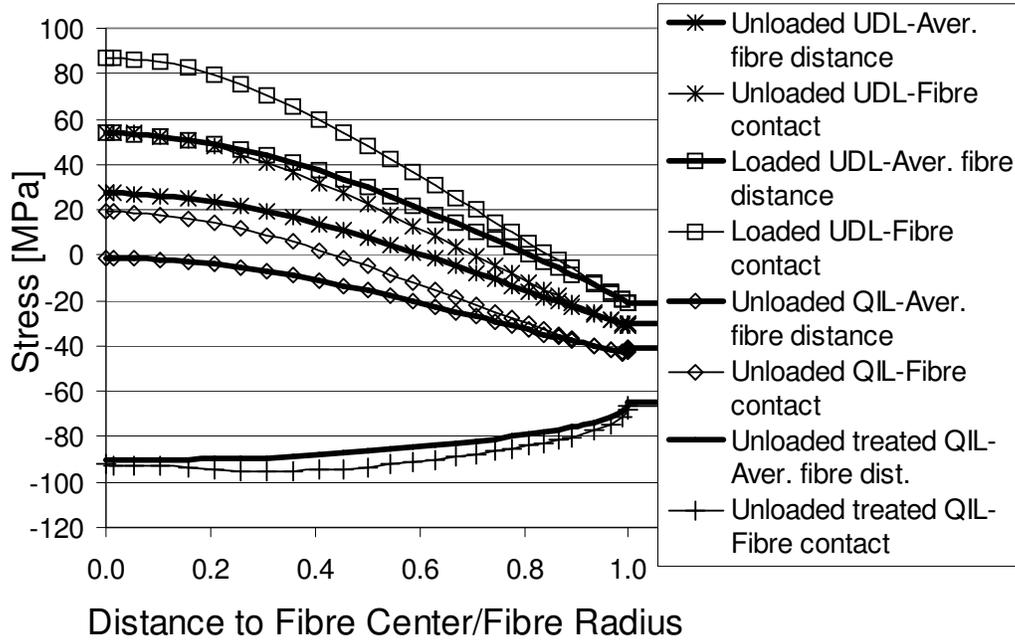


Fig.13: Micromechanical stresses transverse to fibre and parallel to loading direction in wet unidirectional 90° -laminates (UDL) and 90° -ply of quasi-isotropic laminates (QIL) in untreated, treated, unloaded and up to failure loaded condition for average fibre distance and fibre contact

Table 1: Conditions of thermomechanical treatments

Type of Treatment/Step		Unnotched specimen			Notched specimen		
		Temperature [°C]	Stress [MPa]	Duration [min]	Temperature [°C]	Stress ¹⁾ [MPa]	Duration [min]
A	Heating up	23 to 210	0	15	23 to 210	0	15
	Loading	210	250	5	210	133	5
	Cooling down	210 to 23	250	15	210 to 23	133	15
	Unloading	23	250 to 0	1	23	133 to 0	1
B	Heating up	23 to 180	0	15	23 to 180	0	15
	Loading	180	222	115	180	117	115
	Heating up	23 to 190	222	5	23 to 190	117	5
	Loading	190	222	115	190	117	120
	Heating up	190 to 200	222	5	190 to 200	117	5
	Loading	200	222	120	200	117	120
	Heating up	200 to 210	222	5	200 to 210	117	5
	Loading	210	222	235	210	117	235
	Loading	210	306	5	210	167	5
	Cooling down	210 to 23	306	15	210 to 23	167	15
	Unloading	23	306 to 0	1	23	167 to 0	1

1) Average stress at the smallest cross section.

Table 2: Characteristics of Cycom 5245C/T800 UDL used for calculations

No.	Property	Condition	Value	Source/Remarks
1	Young Modulus 1, GPa	23 °C, dry, wet	167.5	[24], at 0.5% strain
3		Treatment A	169	[24]
4		Treatment B	172	[24]
5	Young Modulus 2, GPa	23 °C, dry	7.897	at 80% failure load
6		23 °C, wet	7.792	at 0.4% strain
7		Treatment A	0.315	[24]
8		Treatment B	0.070	[24]
9	Poisson Ratio	23 °C, dry, wet	0.3256	[24]
8	Shear Modulus 12, GPa	23 °C, dry	4.373	at 80% failure load
9		23 °C, wet	4.315	at 40% failure load
10		Treatment A	0.105	[24]
11		Treatment B	0.023	[24]
12	Tensile Strength 1, MPa	23 °C, dry, wet	2500	[24]
13	Tensile Strength 2, MPa	23 °C, dry	69.5	[24]
14		23 °C, wet	19.5	measured
15	Compr. Strength 1, MPa	23 °C, dry	1730	[24]
16		23 °C, wet	1590	measured
17	Compr. Strength 2, MPa	23 °C, dry	246	[24]
18		23 °C, wet	218	measured
19	Shear Strength, MPa	23 °C, dry	90.3	[24]
20		23 °C, wet	74	measured
21	Thermal Exp. Coef. 1, 1/°C	23 °C to 180 °C	0.02E-6	[24,25]
22	Thermal Exp. Coef. 2, 1/°C	23 °C to Tg	30.5E-6	[24,25]
23		Tg to 180 °C	75.0E-6	[24]
24	Moisture Exp. Coeff. 1, 1/%	23 °C	0	[5]
25	Moisture Exp. Coeff. 2, 1/%	23 °C	0.6	[5]
26	Permanent Deformation/Treatment Strain	Treatment A	0.75	[24]
27		Treatment B	0.83	[24]
28	Tg, °C		180 °C	= Tcuring
29	Tg-Shift, °C	Treatment A	-47	[31,32]
30		Treatment B	-56	[31,32]