Neue Garnmaterialien zur Herstellung von Hochleistungs-Faserverbundwerkstoffen aus vernähten Preformen


New yarn materials for high-performance fibre-reinforced composites made of stitched preforms

The cost-reduced manufacturing of complex textile preforms used for liquid composite moulding of high-performance fibre-reinforced polymer composites is of significant importance for today’s aerospace industry. In order to not outweigh the anticipated improvement of the out-of-plane performance achieved through modern stitching technologies by reduced in-plane mechanical composites properties, innovative stitching yarns were used. As compared to a standard polyester stitching yarn, low melting-temperature polyamide as well as soluble phenoxy yarns are shown to significantly reduce the maximum fibre undulations in the final epoxy composites; effectively allowing a further pre-stabilisation of the dry performs by thermobonding as well as leading to an optimised composite performance.
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1 INTRODUCTION

Modern stitching technologies are considered to be one of the key approaches for the cost-reduced manufacturing of complex textile preforms subsequently used for liquid composite moulding (LCM) of high-performance fibre-reinforced polymer composites [1]. However, depending on various experimental parameters including the type of composite, the used yarn materials, the stitching parameters as well as the particular composite loading conditions, stitching has been shown to improve, seriously degrade or leave unchanged the in-plane and out-of-plane composite performance [2-11] – a situation presently hampering the wide-spread utilisation of stitching technologies in advanced applications of fibre-reinforced composites.

A key parameter influencing the overall in-plane mechanical performance of composites based on stitched preforms has been identified as the induced undulations of the reinforcement fibres [8]. Such fibre undulations are severely influenced by the yarn thickness and the yarn tension among other factors and in combination with other detrimental factors including a weak matrix-yarn interphase, broken in-plane fibres, resin cracks, an increased porosity and resin-rich regions – commonly lead to the reduced composite properties. However, there is, as yet, no consensus regarding the direct correlation of the final composite properties with the underlying stitching parameters and materials used. These unresolved challenges as such still pose serious implications for the application of stitched composites in the aircraft industry, as the potential reduction of the in-plane properties may outweigh the cost-savings and any possible benefits to several other mechanical properties. Although some predictive models have been proposed in the literature [12-15], it still appears to be rather difficult to predict the overall mechanical properties by simple model descriptions considering all relevant parameters.

A novel approach might help to resolve these challenges by evading the main origin of the performance reduction, namely the disturbing and undulating presence of a solid, tension-loaded stitching yarn. This approach can be realised using yarns that melt or soften during the LCM process or even dissolve in the matrix completely. To accomplish the melting or softening event, a low-melting temperature thermoplastic yarn (replacing the common carbon, aramid, glass, polyester etc. yarns) is required. For dissolving the yarn
completely, a good miscibility of the yarn material under the used LCM-parameters in the given matrix is necessary. Once the thermoplastic yarn dissolves or builds up a more or less connected second phase in the matrix, additional toughening effects can be anticipated as a result of different possible toughening mechanisms including crack pinning, micro-cracking, localised shear yielding or banding, particle-bridging, crack path deflection etc. [16]. The benefits of incorporating thermoplastics as toughening agents into epoxy resins have already been demonstrated [6, 17-26].

Such low melting-temperature thermoplastic yarns can also be chosen for the additional pre-stabilisation of the dry preforms by thermobonding. Exploiting this potential, the handability of preforms should be significantly enhanced while minimising the negative effects on the resulting mechanical properties and the preforming time due to high stitch densities; a critical issue for the desired use of automated manufacturing approaches. Compared to state-of-the-art binder-based preforming, stitching of non-crimped carbon fibre fabrics (NCF) material leads to a superior drapeability and the possibility to tailor the amount of binder material to the local demand.

Here, a comparative assessment of different yarn materials with different linear densities, namely a (prewashed) polyester (2*53 dtex), polyamide (3*23 dtex) and phenoxy (150 dtex) yarn, on the resulting mechanical performance of stitched NCF composites is presented. Variations in the local composite microstructure due to different the stitching yarns are used to explain the observed mechanical properties.

2 MATERIALS AND EXPERIMENTAL DETAILS

2.1 Materials

The fibre reinforcement of the epoxy laminates was built up of layers of commercial non-crimped carbon fibre fabrics (NCF). This particular NCF is based on either (0°/90°), (90°/0°) or (-45°/+ 45°), (+45°/-45°) biaxial layers of carbon fibres (Tenax HTS 12k) with a polyester 48 dtex sewing thread used as a binding yarn (approximately 3 mm stitch pitch and 5 mm stitch row spacing), manufactured by Saertex; with a carbon fibre weight per unit area of approximately 250 g/m² per biaxial layer.

For stitching of the non-crimped fabric, a prewashed polyester yarn (Serafil 200/2) by Amann, Germany, twined from two yarns with a fineness of 53 dtex, a polyamide yarn (Grilon K 140) by EMS-Griltech, Switzerland, twined from three yarns with 23 dtex, or a phenoxy-yarn (Grilon MS150) with a fineness of 150 dtex, respectively, was employed. The chemical structure of the phenoxy yarn is shown in fig 1. The polyamide and the phenoxy yarns were not washed separately and were used as-delivered.
The epoxy matrix used for all composites was HEXFLOW RTM6 aerospace grade, supplied by Hexcel, and was used as-received. This one-component resin system is commonly used in aerospace applications and is characterised by a generally good processability in liquid composite moulding technologies.

2.2 Specimen manufacturing

The preforms for the intended compression and interlaminar shear strength (ILSS) tests of the composites were stitched at $\pm 45^\circ$ ($\alpha = \pm 45^\circ$) with a modified lock-stitch arranged in the geometry as schematically shown in fig. 2, using a 2D-CNC sewing machine by KSL, Germany. The stitch row spacing $s$ was set as 20 mm. To ensure a good handling of the dry preforms and in order to obtain a high dimensional (bending) stability in either direction (parallel and perpendicular to the preform outline), two crossing seams were employed. The layer stacking sequence for both the compression and ILSS tests was $[(0/90)]_{4s}$.

The specimens intended for the hot-wet ILSS measurement were conditioned in water (70 °C) until saturation was achieved, as verified by continuous weight measurements.

In contrast, the layer sequence for the preforms intended for the compression after impact (CAI) tests was $[(+45/-45)/(90/0)]_{4s}$ (quasi-isotropic). In this case, the preforms were also stitched with a modified lock-stitch with a nominal stitch pitch of 3 mm and a stitch row spacing of 20 mm, but the orientation of the seams was set as $\alpha = \pm 22.5^\circ$. In contrast to the overall stitch density of about 3 stitches/cm² for the preforms for the compression and ILSS tests, 3.2 stitches/cm² are present in the preforms for the CAI specimens.

All composites were fabricated using vacuum-assisted resin transfer moulding (VARTM). The square mould was preconditioned with release agent (Loctite 770-NC Frekote), was evacuated and heated up to 120 °C prior to impregnation of the dry preforms with the epoxy resin at 120 °C, applying a pressure of 0.1 MPa. The mould has one injection point in each of the four corners and one central vent. After complete impregnation, which took about 5 minutes, a dwell pressure of 0.15 MPa was applied for 10 minutes. The final curing temperature of 180 °C was reached after approximately 2 hours and was kept constant for 2 hours, followed by a slow cooling to room temperature.
The final RTM panels were 420 x 420 mm\(^2\) in size, with a nominal thickness of 2.0 ± 0.1 mm for the \([(0/90)]_{4s}\) lay-up and of 3.9 ± 0.1 mm for the CAI laminates, respectively.

2.3 Panel quality assessment

The quality of all manufactured composite panels with regard to the general homogeneity, possible delaminations, and porosity was verified by detailed impulse echo ultrasonic scans in water (using a Hilgus HFUS 2400 Air Tech) as well as by light microscopy (using either a Polyvar MET by Reichert-Jung or a Keyence VHX 100 microscope, respectively) of polished cross-sections. In addition, the misalignment of the reinforcing carbon fibres due to stitching was further analysed in detail using micro-computer tomography (µ-CT). Here, a Skyscan X-Ray Microtomograph 1072 µ-CT with a maximum spot resolution of 5 µm operating at a voltage of 79 kV and a current of 94 µA was used. Specimens of 5 x 5 x 2 mm\(^3\) were examined with the cone-beam technology, 2-dimensional (2D) cross-sectional images were taken in steps of 0.23° up to a complete rotation of 360°. 3-dimensional (3D) volumetric images were digitally reconstructed from the set of 1600 2D X-ray images by using a proprietary software "NRecon" from Skyscan.

2.4 Mechanical testing

The composite plates for the compression tests were equipped with 1mm thick, +45° glass-fibre reinforced epoxy (G10) end taps following the VARTM process. Specimens with the required dimensions for the various tests were prepared by cutting the panels with a water-cooled diamond saw (Mutronic DIADISC 6200) in such a way that the direction of the stitching seam was ±45° to the loading direction; which is identical to the 0° fibre orientation. All specimen edges were subsequently polished in order to eliminate surface defects.

In-plane compression tests were performed according to the DIN EN 2850 (Celanese) specification. The composite specimens with the \([(0/90)]_{4s}\) lay-up had a thickness of approximately 2.0 mm, and a width of 15 mm. This specific width is larger than the one defined by the standard (standard width of 6.35 mm or 10 mm) but was selected in order to ensure an improved quality of the test data. The overall specimen length was set as 110 mm, with a gauge length of 10 mm. The seam geometry with respect to the specimen geometry is highlighted in fig. 2. All specimens were tested using a Zwick Z050 at a constant cross-head displacement speed of 1 mm/min at room temperature. For each composite type, at least seven specimens were tested.
Interlaminar shear strength (ILSS) tests (short beam) were performed according to the DIN EN 2563 specification, using composite specimens again with the [(0/90)]_{4s} lay-up. Rectangular specimens of 10 mm in width and 20 mm in length were tested using a Zwick Z050 operating at room temperature. The seam geometry with respect to the specimen geometry is outlined in Fig. 2. The span between the support cylinders was 10 mm, resulting in a span-to-thickness ratio of about 5. The loading cylinder was forced against the specimen at a constant cross-head displacement speed of 1 mm/min. The maximum apparent shear strength, \( \tau \), in the mid-plane of the composite was approximated by the Euler-Bernoulli beam theory

\[
\tau = \frac{3P}{4wt},
\]

where \( P \) is the force at failure, \( w \) is the specimen width, and \( t \) is the specimen thickness. The hot-wet specimens were tested at ambient temperature approximately one minute after removal from the hot water.

Fig. 2: Schematic representation of the assembly seam stitching pattern within the tested compression specimens, ILSS and CAI specimens, respectively.
In order to obtain specimens for the compression after impact tests, impacted specimens with a \([(+45/-45)/(90/0)]_s\) lay-up were prepared by clamping a specimen on a plate according to AITM 1.0010. The spherical impactor had a weight of 3 kg and a diameter of 16 mm. The impact energy was fixed at 25 J for all composite types under investigation. An anti-rebound device controlled the impactor.

Subsequently, the determination of the size of the delaminated area generated by the impact as well as the CAI tests at room temperature were carried out according to AITM 1.0010. The specimens had a thickness of 3.9 mm, a width of 100 mm, and a length of 150 mm. For the compression tests, a Zwick Z1485 was used at a constant cross-head displacement speed of 1 mm/min at room temperature. The CAI measurements were repeated six times for each composite type.

3 RESULTS AND DISCUSSION

The overall aim of using this specific seam geometry and the selected polyester, polyamide and phenoxy yarns as assembly seams to ensure a good initial handling of the dry NCF preforms was achieved. In addition, the resulting assembly seams manufactured with all yarn types appeared to be of good quality. Following initial thermo-bonding trials, the polyamide- and the phenoxy-stitched preforms especially showed an enhanced stiffness and handability; an effect that could be exploited to a greater extent in the future.

All manufactured composites appeared to be of a homogeneous good quality (verified using the ultrasonic technique) and revealed a good surface finish; the assembly seams did not lead to any detrimental effects on either processability or general product appearance.

In order to evaluate the resulting undulation of the carbon fibres in the stitched NCF composites in more detail, both micro-computer tomography as well as light microscopy was utilised. The representative µ-CT images of cross-sections of the stitched NCF composites in fig. 3 (A) to (C) show 3D- and 2D-image planes of the polyester-, the polyamide- and the phenoxy-stitched composites, respectively.

These micrographs clearly indicate that the reinforcement fibres are displaced from their original alignment in the vicinity of the stitching yarn to some extent. Surprisingly, the fibre undulations appear to be similar for all yarn types although the phenoxy-yarn has about twice the fineness as the polyamide yarn.

In fig. 3 (B), gas inclusions within the polyamide-stitch holes can clearly be detected. In these specific areas, the x-ray absorption is very low, a telltale sign for gas-inclusions.
As highlighted by the cross-sectional light microscopy image of the polyester-stitched composite in fig. 4 (A), the individual filaments are still clearly visible following the RTM process. In contrast, in the polyamide-stitched composites, fig. 4 (B), no individual filaments of the yarn are visible as the yarn melts during the VARTM-processing. Consequently, a single thick strand remains and the interface between the strand and the matrix seems to be of good quality. The representative image shown in fig. 4 (C) clearly demonstrates the absence of the phenoxy yarn in the vicinity of a stitch hole. This observation can be explained by either the yarn dissolving homogeneously in the epoxy during processing and a subsequent phase-separation below the resolution limit of the light microscope or by simply being washed away from the stitch-hole by the injected resin.

Neither scanning electron nor transmission electron microscopy (TEM) investigations could provide clear evidence for the presence of small phase-separated particles in the vicinity of the stitches. However, a detailed TEM analysis of neat RTM6 resin plates containing 10 wt% of phenoxy prepared as a reference clearly verified a phase-separation of the phenoxy on the nanoscale (fig. 5) following similar thermal treatments; an effect that could also be detected using dynamic mechanical analysis.

Fig. 3: Representative 3D and cross-sectional computer micro-tomography images of the stitched NCF composites showing the stitching yarn penetrating the laminate.
Fig. 4: Representative light microscopy micrographs showing the stitching yarn penetrating the laminate. (A) polyester yarn, (B) polyamide yarn, and (D) phenoxy yarn.

top row: overview; bottom row: close up

Fig. 5: TEM picture from RTM6 + 10 wt% of phenoxy.
3.1 Compression performance

The carbon fibre content of all composites investigated was between 53 and 56 vol\%. It must be noted that all the compression stiffness and strength values reported in this study are normalised to a fibre volume content of 60 vol\%. This normalisation procedure ensures better comparability of all results for the different laminates; a detailed description of the normalisation approach is given in the literature \[27\]. In addition, the increased specimen width used in this study as compared to the standard 6.35 mm width led to a reduced standard deviation and a more consistent fracture behaviour. In addition, the overall compression properties of the complete panel are reflected in a more accurate and representative way in the test specimens.

Fig. 6 shows a comparative plot of the normalised in-plane compression modulus of all composite systems under investigation. The error bars in this and all following graphs represent the standard deviation of the presented data. As can be seen, none of the assembly seams did significantly affect the modulus of the non-crimped fabric composites.

![Fig. 6: Comparative plot of the compression modulus of the various composites](image-url)
In contrast, the use of the washed polyester yarn induced a reduction of the compression strength of the laminates by 13% as compared to the non-stitched NCF reference, as shown in fig. 7. While the polyamide 3*23 dtex yarn also slightly reduced the compression strength by 7%, the phenoxy yarn (150 dtex) only led to a reduction of the normalised compression strength by 4%. This limited degradation of the compression strength for the phenoxy-stitched laminates appears especially surprising, taking into account the initial yarn thickness.

This mechanical performance data can be explained considering the undulations of the carbon fibres in the vicinity of the stitches (figs. 3 and 4) in more detail. There are severe local fibre undulations as well as corresponding resin-rich regions in the immediate vicinity of the stitches for all yarn types. However, the average fibre undulation appears low for all types. It is therefore not surprising that the compression modulus of the NCF composites is hardly influenced by these assembly seams, as this parameter depends on the average fibre undulation [8].

The variations in maximum fibre undulation however can be used to explain the observed reductions in compression strength for the various yarn types [8]. As compared to the thicker polyester yarn, the polyamide 3*23 dtex yarn induced a reduced maximum fibre undulation: however, the air inclusions might have acted as crack initiation sites and might have offset an even better compression
strength performance. In a similar manner, the dissolution of the phenoxy yarn during processing and following rearrangement of the carbon fibres might be responsible for the good performance of these composites. In addition, it is likely that phase-separation of the phenoxy and subsequent toughening of the epoxy matrix has contributed to the suppression of cracks starting at the undulated regions around the stitches in these composites.

In general, these experimental observations regarding the effect of assembly seams on the compression behaviour of carbon fibre-epoxy VARTM laminates are in good agreement with previously published data [2, 7, 11] where strength reductions up to 19% were reported whereas the compression modulus was not affected by stitching. It is interesting to note that the use of a washed polyester yarn in this study as compared to previous attempts using the unwashed yarn clearly reduces the overall degradation of the composite compression strength, maybe indicating problems with the particular sizing of the polyester.

Stitching with a comparably thin 2*23 dtex polyamide yarn [7, 11] showed a reduction of the normalised compression strength for similar composite laminates of 7%, whereas the use of a 2*75 dtex polyamide yarn led to a reduction of 16%. Comparison of these results to the data shown in this study clearly indicates that the initial thickness of the meltable but insoluble polyamide yarn plays an important role. However, the effect of the initial yarn thickness cannot only be compensated by using a softening yarn material but also by employing a yarn that can be dissolved completely during the resin injection. As demonstrated here, the 150 dtex phenoxy yarn leads to a minimised loss in compression strength; the use of a thicker (300 dtex) phenoxy yarn however has been shown to induce a more pronounced loss (10%) in compression strength [7].

3.2 Apparent interlaminar shear strength

The apparent interlaminar shear strength of the various composites measured using the short beam test method is summarised in fig. 8. As can be seen, stitching did not influence the ILSS properties of the dry and the conditioned composites significantly, independent of yarn type. Again, the values reported here are in good agreement with previously published data [7], where neither a thin (2*23 dtex) nor a thick polyamide (2*75 dtex) yarn affected the ILSS values for similar laminates. Similarly, the use of a thicker (300 dtex) phenoxy yarn also led to comparable ILSS properties, indicating that this composite property is rather insensitive towards the incorporation of these particular assembly seams, although other stitching geometries and yarn types have been shown to degrade the ILSS performance [2].

Regarding the hot-wet ILSS properties, all composites, the stitched as well as the non-stitched reference, showed about the same residual interlaminar shear strength. This observation is consistent with the measured water absorption of
approximately 0.9 wt% for all composites, reflecting the very low overall yarn content.

![Image of shear strength comparison](image)

**Fig. 8:** Comparative plot of the apparent interlaminar shear strength of the various composites

### 3.3 Compression after impact

The ultrasonic C-scan images shown in fig. 9 verify that the general appearance and size of the delaminated area induced by the 25 J impact was quite similar for the stitched composites as compared to the NCF reference. In agreement with this optical evaluation, the delaminated areas were determined as $10 \pm 2$ cm$^2$ for the non-stitched NCF, the polyester-stitched and the polyamide-stitched laminates, and $12 \pm 1$ cm$^2$ for the phenoxy-stitched composites respectively. Although there appears to be an improvement in compression after impact strength properties for the stitched composites, the increase is 9% for the polyester-stitched composites only (fig. 10). However this compares well with data obtained for stitched composites based on the unwashed polyester-yarn [11]. The residual strength of the polyamide- and the phenoxy-stitched composites is not affected significantly.
Fig. 9: Representative ultrasonic C-scan images showing the damage area of the various composites following a 25 J impact

Fig. 10: Comparative plot of the CAI strength of the various composites following an impact at 25 J
4 CONCLUSIONS

The use of thermoplastic yarns that melt or even dissolve during preforming and/or the subsequent RTM process is a promising route towards the enhanced utilisation of stitching technologies for the automated manufacture of advanced textile performs for liquid composite moulding of high-performance polymer composites. The experimental results shown in this study clearly demonstrate a generally high mechanical property level for such composites as compared to non-stitched NCF reference composites. With regard to the generally critical compression strength especially, it becomes apparent that yarn parameters such as linear density and base thermoplastic material determine both the microstructure of the composite as well as the resulting overall properties. Depending on the specific yarn material type, there exists an optimum linear density that allows efficient stitching while leading to reduced maximum undulations of the reinforcement fibres; an effect that minimises the loss in strength properties.

Soluble yarns especially appear to be quite promising as the data presented here clearly indicate that such yarn materials induce the lowest degradation of composite performance. Future attempts are directed towards tailoring the yarn material (and RTM process parameters) even further in order to ensure an effective phase separation of the thermoplastic material in the cured epoxy matrix. Improvements in composite performance due to additional toughening mechanisms can be anticipated.

Another approach currently under investigation is the combination of stitching and interleaving technologies using non-woven mats of thermoplastic material based on i.e. polyamide or phenoxy. The achievement of the locally required amount of thermoplastic might lead to the desired superior mechanical performance of stitched composites.

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