Reduction of Process Cycle Time and Improvement of Mechanical Properties of Composite Parts Manufactured in Resin Transfer Molding by Application of Grilon MS Binder Yarn

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Abstract
GRILON MS is a phenoxy binder yarn developed by EMS-Chemie. Its use in the Resin Transfer Moulding (RTM) process was investigated in the context of a research project. In addition to examining how the yarn affects the preforming and infusion processes, its influence on the impact toughness, fire resistance and adhesion properties of the finished component were also studied. In the course of the work it became clear that using HUNTSMAN's newly developed epoxy resin LME10104 in combination with the phenoxy binder yarn offers a decisive process advantage. The new resin possesses extremely low viscosity, which makes it particularly suitable for the infusion process. It was shown that using it significantly reduced the process cycle time compared with that for other resins approved for use in the aircraft industry. The otherwise bothersome binder fibres are not washed out during injection but are dissolved in the resin, decisively improving the mechanical properties of the resin and the component. On the one hand undulations in the load-bearing carbon fibre filaments are reduced, and on the other the resin's impact toughness is significantly increased and hence its tendency to delaminate decisively reduced.

1. Introduction
At present the use of fibre-reinforcing technology in aircraft is expanding very rapidly. The aircraft constructor Airbus is using carbon fibre reinforced plastics (CFRP) in its latest models A380, A350 and A400M not only for the tail unit but also in the wings. Its competitor Boeing is launching with its B787 Dreamliner a large aircraft whose primary load-bearing structure is entirely made of CFRP materials. Similar trends are to be seen in the helicopter business. Besides its advantage of better mechanical

properties per unit weight, CFRP is more economical: the technology makes it possible to produce complex components with many functions built into them. Among other methods of making such components, resin infusion processes are being applied ever more often; and of these, Resin Transfer Moulding (RTM) and similar processes prove to be especially suitable for aircraft applications.

Various studies are unanimous in pointing out the growing importance of the RTM technology in the production of fibre-reinforced composite structural components. This holds for the replacement of metallic structural assemblies – as in the examples cited above – but also in substituting for the prepreg autoclave technology. The costly material logistics for prepregs and the high investment cost of autoclaves favour substituting the simpler RTM technology (with almost equal product quality) in an air transport industry that is coming under increasing pressure to cut costs.

Plastic structures reinforced with carbon fibres have two chief drawbacks. The first is brittleness, which manifests itself particularly in delamination under impact loading, and the second is a potential lack of uniformity because of local concentrations of resin and disturbance to the fibre layout, which can weaken the material. This article describes a technology for improving the mechanical properties of composite components, which also has advantages in the execution of the process itself.

2. Materials and processes

In Figure 1, a schematic description of the RTM process, it can be seen that the fabrication of the preform is a preliminary to the injection process itself [1]. The preform is produced, depending on the geometry and technical requirements of the end product, by weaving, braiding, sewing or by forming processes. The preform is then placed in the heated RTM mould for the actual infusion process, whereby a liquid thermosetting resin is injected into the dry preform. The mould cavity fills, the resin system undergoes chemical curing, and when the part is strong enough it is extracted from the mould and tempered.
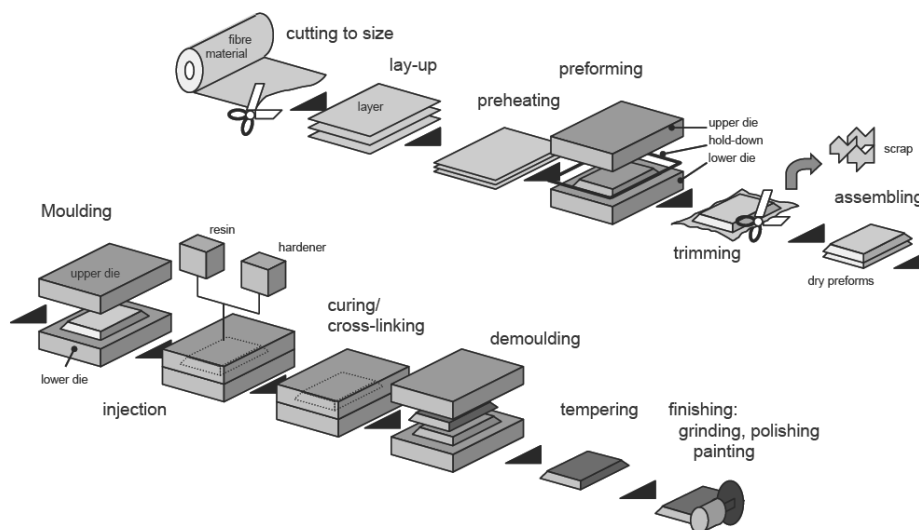

Figure 1: Resin Transfer Moulding (RTM).

The main advantages of resin transfer moulding are:
- A highly integrated and complex design which results in a lower number of parts and reduced assembly cost;
- Multi-material components may be produced by incorporating metallic parts in the form of inserts;
- Low-investment production facilities;
- Simple material handling (reinforcing fibres & resin systems).

In the last few years the "Vacuum Assisted Process" [2] – known as the VAP process – patented by EADS MAS Augsburg has found increasing application in aircraft construction (see Figure 2). Here too a prefabricated preform is laid in a single-chamber tool, impregnated and consolidated. The equipment is laid out such that the resin enters first a highly permeable space above the component and then in a second step impregnates the preform through its thickness, resulting in very short flow-paths. In order to ensure thorough soaking without air entrapment the preform is placed under vacuum using a special Gore-Tex® membrane which allows air to pass but is impervious to liquids.
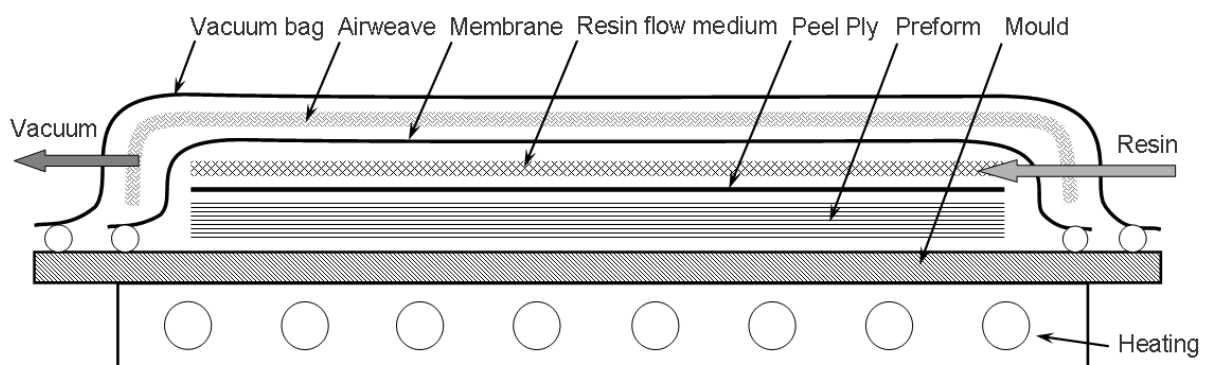

Figure 2: Vacuum Assisted Process VAP.

Both processes require a prefabricated dry fibre structure, the preform. This is often stabilised using binder material in powder form or as textile webs with sewn seams. Sometimes considerable amounts of thermoplastic binder may be used in making the preform. The binder can comprise up to 10% of the mass of the finished preform, which means that its effect on the mechanical properties of the matrix has to be considered, since these in turn will influence the performance of the finished component.

3. Raw material and preform manufacturing
GRILON MS is a phenoxy binder yarn developed by EMS-Chemie [3], which can be incorporated into a dry carbon fibre preform for various processes. It can be used in the first place as a yarn for stabilising the geometrical shape of the preform; moreover, MS can be "melted", thereby assuming the function of a thermal binder. Over the last few years EMS Chemie has developed the spinning process for producing phenoxy yarn and mat to make it suitable for mass production. The phenoxy fibres are of such good quality that they can be used in weaving and sewing. Phenoxy can be incorporated in the resin injection process in various ways:
- including it in woven or non-crimped fabric (NCF) textiles
- placing layers of pure phenoxy in the form of veil or woven fabric
- sewing up textile components using phenoxy yarn
- tailored fibre placement

Phenoxy's beneficial properties first become evident in the preforming process (Figure 3). Sheet material with embodied phenoxy is heated above the glass transition temperature of the phenoxy, at which the latter becomes soft and sticky, and is then formed into a three-dimensional shape and cooled down. On cooling the phenoxy hardens, keeping the three-dimensional shape stable for further processing.

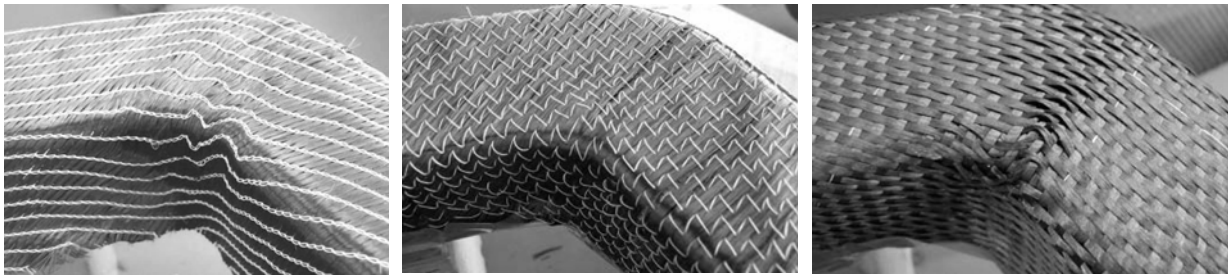| Saertex NCF | ECS 6090 3107 | G 0926 |

with Grilon MS

Figure 3: Preforming trials with NCF and Grilon MS (left picture),
NCF with polyester yarn (middle picture) and woven fabric (right picture)

The subsequent wetting with resin during injection also presents no problems. Care must be taken to ensure that the resin temperature during injection remains below the glass transition temperature of the phenoxy to prevent the latter from dissolving prematurely. The VAP process now widely used in the aircraft industry is especially suitable for impregnating the fibres because soaking through the thickness results in short flow-paths. Resin systems at present approved for use in aircraft construction are cured at high temperature, and this is a requirement for the complete dissolution of the phenoxy fibres, which in turn is a necessary condition for improving the impact resistance of the epoxy matrix (Figure 4).
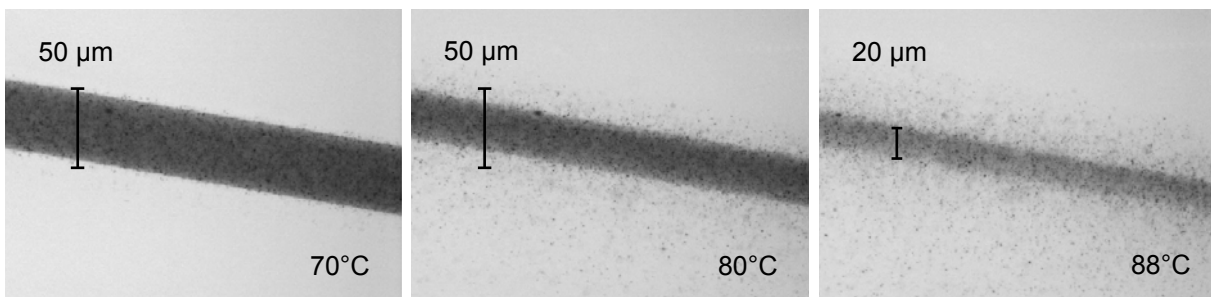

Figure 4: Dissolution of a MS-Grilon yarn in RTM6 epoxy resin.

It must be noted here that using phenoxy yarn in a preform increases the volume content of fibre; this reduces the permeability of the preform, which can lead to problems when the resin is injected. However, introducing the phenoxy into the resin-rich interlaminar layers makes it possible to alter the local properties of the matrix according to need, notably so as to reduce
the tendency to delamination. Other influences on the infusion process are described in the following section.

4. The effect of phenoxy on the resin infusion process

The RTM6 resin is injected at 80°C according to the guidelines set out by its supplier HEXCEL [4], the mould being preheated to 120°C. Since the phenoxy in the preform – yarn or powder – has a glass transition temperature of about 78°C, it is already molten before injection. As soon as the resin comes into contact with the premelted phenoxy, the latter dissolves in it, increasing the resin's viscosity. This higher viscosity prevents soaking the dry preform in the RTM process as soon as the resin in the preform contains more than 4% by weight of phenoxy. Figure 5 illustrates schematically the process of dissolution of the phenoxy fibre. The regions shown in beige are those in which the phenoxy diffuses by dissolution. Because of the increase in viscosity the phenoxy-enriched resin can no longer flow freely. Quite the reverse, it tends to stick to the fibres, increasing the flow resistance.
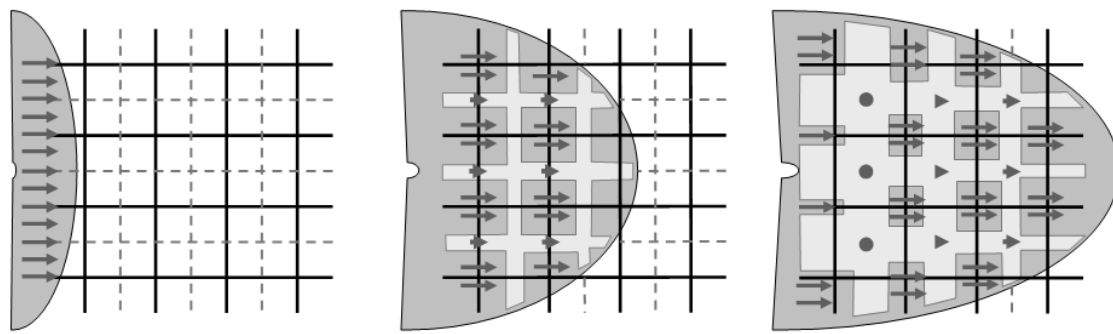
Legend:
— Carbon fibre   --- Grilon MS yarn   ▨ Resin front (RTM6)   ▢ Melted Grilon MS
→ Fast flow   ⇥ Slow flow   ● No flow

Figure 5: Increase in flow resistance due to higher viscosity.

Using HUNTSMAN's newly developed epoxy resin LME10104 in combination with the phenoxy binder yarn overcomes this disadvantage. The new resin possesses extremely low viscosity at temperatures below the glass transition temperature of phenoxy. Thus the mould temperature before injection can be below this glass transition temperature, so that the phenoxy is still solid when the resin impregnates the preform, does not melt and therefore does not increase the viscosity of the resin. Because there is no increase in flow resistance during impregnation less time is needed than with RTM6, and this, together with the lower mould temperature, significantly reduces the process cycle time compared with that for other resins approved for use in the aircraft industry. The binder fibres are not washed out during injection but are dissolved in the resin, improving the mechanical properties of the resin after curing and hence those of the component.

An extensive wash-out program was carried out in order to confirm these findings and to check whether the phenoxy distribution in the preform is altered during mould filling, i.e. whether it was partially washed out. Solubility investigations with the electron microscope showed that the lower-viscosity LME10104 dissolved the MS-Grilon threads faster than RTM6. A flow-channel was used to find out to what extent the MS-Grilon threads entered into solution and were washed out during injection; various experiments were carried out using RTM6 and LME10104 at different temperatures, samples of the liquid resin being taken from the channel for analysis. Uncured RTM6 and LME10104 resins can be analysed using gel permeation chromatography (GPC), eluting later than the phenoxy. By this means the proportion of phenoxy in the epoxy resin can be quantitatively evaluated. LME10104 has a lower molecular weight than RTM6, but the phenoxy can be separated out for both. The evaluation showed a washout effect at injection temperatures above 70°C. At lower temperatures and for typical RTM injection times of ten minutes a negligible amount of phenoxy dissolved, which argues in favour of the low-viscosity LME10104. The results confirmed quite generally that washout increases with higher temperature, longer injection (residence) time and lower viscosity. It follows that efforts must be made to ensure short flow-paths during injection, as is the case with the VAP process.

Once the preform is completely soaked, the mould is heated up. With RTM6 the already liquid phenoxy then dissolves in the resin as it heats up, whereas with

LTM10104 the solid phenoxy first melts and then dissolves. As the mould temperature increases to its steady level the resin with its dissolved phenoxy hardens and cures. This leads to the following mechanical advantages:
- The crimping up of the carbon fibres due to the sewing threads is undone
- There is no concentration of resin in the stitching holes
- There is no micro-cracking of the matrix due to the sewing threads
- The dissolved phenoxy thermoplastic gives the epoxy matrix better impact toughness

The following section describes the influence of the phenoxy on mechanical properties, fire-resistance and adhesiveness. Tests were carried out using RTM6 resin and also LME10104.

5. The effect of phenoxy on the properties of the composite

Tensile test samples were prepared according to EN ISO 527(-4) to check the effect of phenoxy on the stiffness and tensile strength of the resin. The plates are 2 mm thick and contain six layers of ECS 6090-3107 CF fabric (biaxial, 260 g/m^2), giving a fibre volume content of 50%. So as to be able to check the matrix properties a $[\pm45]_{3S}$ stacking sequence was chosen. The matrix was enriched with phenoxy in the proportions of 0, 5% and 10% by weight. Figure 7 shows the tensile test results.

[MPa]	0 % Grilon MS		5 % Grilon MS		10 % Grilon MS	
	$\overline{X}$	σ_x	$\overline{X}$	σ_x	$\overline{X}$	σ_x
RTM6	13'100	± 1'000	14'800	± 1'700	14'900	± 700
LME	12'800	± 1'700	12'000	± 1'300	12'200	± 400

Figure 7: Change in Young's modulus due to the phenoxy additions.

These results are inconclusive: there is no clear indication of the effect of the phenoxy on the strength of either the resin system or the composite material. Only slight improvements were to be seen, and because of the small number of samples even these could not be clearly attributed to the effect of the phenoxy. The wide spread in the results may also be partly due to variations in the quality of the test plates as produced.

The evaluation of the rate of energy release is documented in the following standards:
- ISO 15024:2001 E: Fibre-reinforced plastic composites – Determination of mode I interlaminar fracture toughness, GIC, for unidirectionally reinforced materials
- ASTM D5528-01(2007)e1: Standard Test Method for Mode I Interlaminar Fracture Toughness of Unidirectional Fiber-Reinforced Polymer Matrix Composites

For this test 3mm thick plates with eight layers of ECS 6090-3107 CF fabric were produced.   The stacking sequence was [0°, 90°, 0°, 90°,0°]$_S$, according to the standard. As in the tensile test, the matrix was enriched with 0, 5% and 10% of phenoxy by weight.
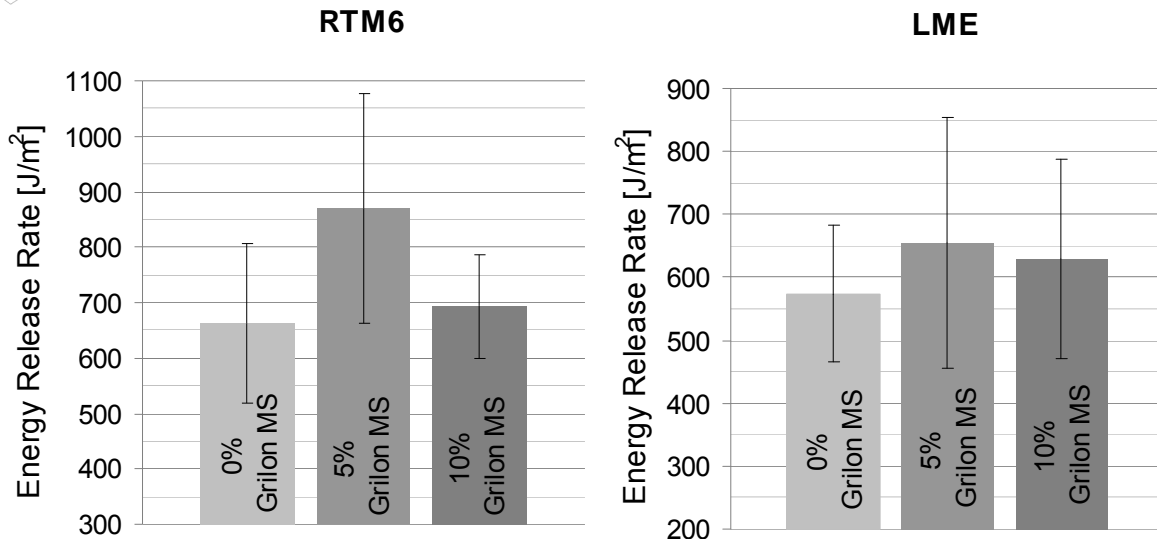
RTM6

LME

Figure 8: The effect of phenoxy on the rate of energy release G_{IC} for RTM6 and LME

The peel tests are also inconclusive. Various changes in properties took place for the resin systems used. Summing up, the results show little effect of the phenoxy on the impact toughness of the composite material; at least, it does not lessen it.

Composite components can in practice be exposed to impact loading. The resulting stresses can lead to failure, and can differ from those observed in quasi-static testing. An alternative to the quasi-static tensile and G_{IC} tests is the dynamic notched bar impact test, which can determine the effect of phenoxy on impact toughness. Experience indicates that the thermoplastic phenoxy has a bigger effect because of the higher strain rate.
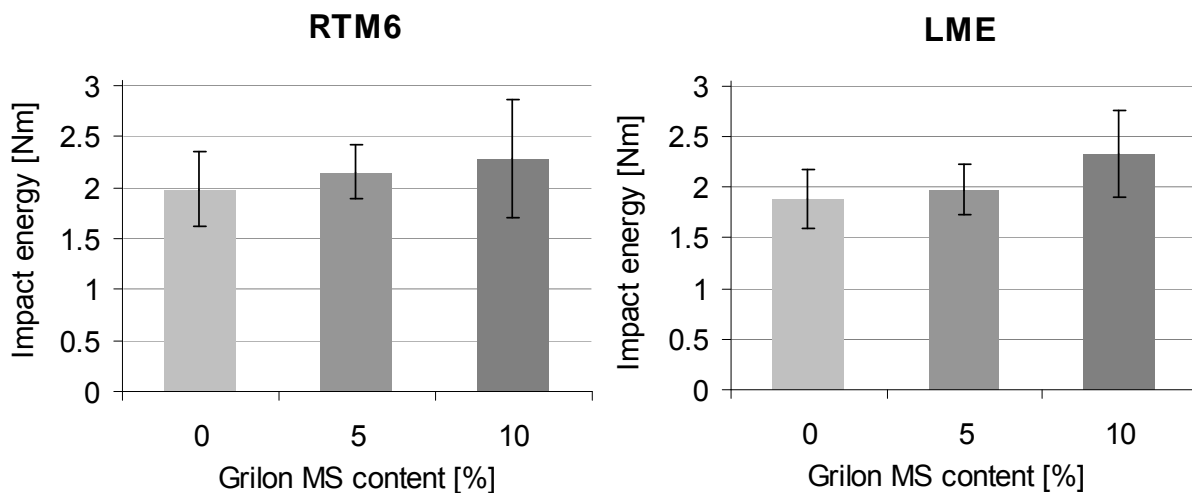
RTM6

LME

Figure 9: The effect of phenoxy on the notched-bar impact energy.

The effect of phenoxy on impact toughness as measured by the notched bar impact bending test tends to be more pronounced with the LME10104 samples than with those of RTM6.
It should be noted that because of the large variances the results are to be used for comparative purposes and not as an indication of absolute values. Despite this, it can be taken that for both resin systems a 10% phenoxy content tends to increase impact toughness by 10-25%.

To complete the program, Fire Smoke und Toxity (FST) investigations were carried out. As before, the phenoxy content was raised in steps 0 - 5% - 10%. Testing was done according to the following standards:
- Flammability test – F (Flammability test, FAR/CS 25.853 - Appendix F Part I),
- Smoke test – S (Smoke test, Airbus Directive ABD0031),
- Toxicity test – T (Toxicity test, Airbus Directive ABD0031),
- And as an addition the OSU Test - Heat Release Test (FAR/CS 25.853 -Appendix F Part IV/V)

The phenoxy had little effect on smoke development. Increasing the phenoxy content slightly increased smoke development. As regards flammability, toxicity and heat release, no effect of the phenoxy was noticed. In the flame test the time for which the material continued to burn after removing the heat source, and the time to extinction were slightly longer for LME than for RTM6. Apart from this, no significant difference between the various resin systems was noticed during fire testing.

Tests according to the DIN EN 2243-1 standard were performed to check how phenoxy affects adhesion behaviour. The results show that the share of cohesion fracture increases with increasing phenoxy content, and delamination decreases. There are two possible explanations for this: either the phenoxy increases the matrix toughness or else it reduces adhesion. Taking it that the adhesiveness and not the brittleness of the composite matrix is the cause of delamination, the following conclusion can be drawn from three out of the four stress diagrams: increasing phenoxy content from 0 to 10% results in a drop in adhesiveness of about 10 to 15%.

These predictions should be taken as indicative only, since for a proper statistical validation far more samples would be needed.

6. Conclusion
The following five points sum up the advantages of phenoxy:
- It is easy to integrate phenoxy into the various textile fabrication processes.
- It replaces binder materials in the production of preforms.
- Using phenoxy with very low viscosity resin systems reduces cycle time.
- Phenoxy improves impact toughness up to 20%.
- Micro-cracks due to sewing threads and resin-rich areas are avoided.

7. References
[1] Bürzle W, Henne M.: Resin Transfer Moulding – Massnahmen zur Reduktion der Formfüllzeit, Kunststoffe&Synthetics, 9 / 2006
[2] Patent: Method and device for producing fiber-reinforced components using an injection method, US2003011094, US6843953, DE10013409, EP1136238, EP1136238, EP1181149
[3] EMS Chemie AG, Business Unit EMS-GRILTECH, Technical Data Sheet: Grilon MS, Matrix Soluble Yarn
[4] HEXCEL Product Data HexFlow® RTM 6, 180°C epoxy system for Resin Transfer Moulding, Monocomponent System