NEW HIGH-PERFORMANCE FIBRE REINFORCED MATERIALS WITH NANOCOMPOSITES

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Abstract: Injection techniques are well established for production of high-performance fibre composites due to their cost advantages in comparison to the Prepreg method. However, the properties of high performance composites produced using the injection technique have not yet reached the level of the Prepreg composites. Among other factors this is due to matrix shrinkage, which leads to intrinsic tension within the part and thereby reduces the material performance. At the DLR Institute for Structural Mechanics, a new innovative method was selected for compensating the previous material disadvantages of the injection technique. With the single line injection method (SLI), developed at this institute, the composite qualities are optimised by using nanocomposites. It has been shown on the basis of selected nanoparticle systems, that the thermal and mechanical performance parameters of tested epoxy resins can be improved specifically even at very low particle content. Considered in detail, a high-performance epoxy resin is modified with nanoscaled barium sulphate. This is distinguished by a significantly higher impact strength and strain at break in comparison to unmodified resin without reducing any other composite parameters. Transfer of the high ductility of the polymeric matrix to fibre reinforced composites might compensate the material disadvantages from matrix shrinkage, normally resulting for fibre composites produced using the injection technique. Accordingly, the material disadvantages of the injection technique compared to the Prepreg technique can be compensated and the problems of the injection technique appear to be solved. Moreover, initial results with fibre-reinforced composites (GFRP) are introduced, which are filled with nanoscaled silicon dioxide particles and produced using the SLI technique. Particularly the significant increase of the Young's modulus and its high linearity in the stress-strain diagram leads to reduction of the inter-fibre fractures and improvement of the material performance in comparison to unfilled fibre composite. The larger damage-free range for the new type of fibre composites opens new fields of application and increases the application potential for SLI technique.

Key words: Nanoparticles, Nanocomposites, Liquid Resin Infusion Technique (LRI), Fibre Reinforced Polymers (FRP)

1. INTRODUCTION

High performance fibre reinforced polymers (FRP's) have successfully proven their qualities in the aerospace and automobile industries. The lightweight construction and excellent mechanical properties as well as the possibility of tailor-made material design are their most important advantages in comparison to conventional construction materials. FRP's consist primarily of glass or carbon fibres embedded in thermoset resins.

At present, the prepreg technique is the most widely used technique for the production of advanced high-performance composites for the aerospace industry. Although this technique has reached a high quality level, a drastic reduction of costs cannot be realised due to expensive raw materials, complex logistics and time-consuming preparations. Additionally, in the case of prepregs, the possibilities of optimising semi-finished fibre materials are highly limited. Currently, massive efforts have been taken to replace the prepreg technique with other processes in order to achieve the goals set by the industry. Injection techniques such as RTM, VARI, SCRIMP, DP-RTM and SLI are well established as technical process alternatives. In comparison to the prepreg technique, particularly the low production costs resulting from the use of economical resins and raw fibre materials are decisive. Future lightweight structures will allow cost savings of 40 % and weight reductions of 30 % favouring the use of the injection technique.

However, the properties of high performance composites produced using the injection technique have not yet reached the level of the Prepreg composites. Among other factors this is due to the polymer system. Its matrix shrinkage leads to intrinsic tension within the part and thereby reduce the material performance.

However, at this point, the design of new monomers for the resin is subject to close limits, because it is always necessary to ensure that the resins are capable of injection. Admixture of microscaled particles is also a problem, because the viscosity is increased considerably resulting in technical processing problems in production. In addition to significant increases in the viscosity, particularly with the injection techniques, filtration effects also occur, which lead to insufficient impregnation of the semi-finished fibre product.

At the DLR (Deutsches Zentrum für Luft- und Raumfahrt e.V.) Institute of Structural Mechanics a new innovative course was selected by the application of nanotechnology. Instead of microparticles, nanoparticles (1-100 nm) were used as fillers for thermoset resins, which have proven themselves in aircraft applications. In comparison to conventional resins these so-called nanocomposites show remarkable improvements in the mechanical and thermal properties, which are already achieved at very low degrees of filling (< 5 wt.%).

The objective is to eliminate the previous disadvantages of the injection technique in the production of high performance composites by using nanoparticles and simultaneously increasing the material composite qualities. It is particularly important to increase the strength, stiffness, impact strength, heat distortion temperature, glass transition temperature and flame resistance as central parameters for fibre composites. On the other hand, it is necessary to reduce the matrix shrinkage and the thermal expansion of the polymer matrix as well as to keep the resin viscosity low. The *S*ingle *L*ine *I*njection method (SLI) developed at the Institute is used as the injection technique.

2. STATE OF THE ART

2.1 *PRODUCTION OF COMPOSITES*

A variety of different techniques has been established for the production of continuous fibre reinforced composites. Of these the most important production techniques are the Hand Lay-up Procedure, the Filament Winding Process, the Prepreg-Technique and the RTM-Technique. With the exception of filament winding structures, high-quality, continuous fibre-reinforced components are currently being produced industrially using the prepreg method. However, due to rising production costs, research on the so-called liquid resin infusion method (LRI) has been intensified lately, since this method promises a significant reduction in production costs.

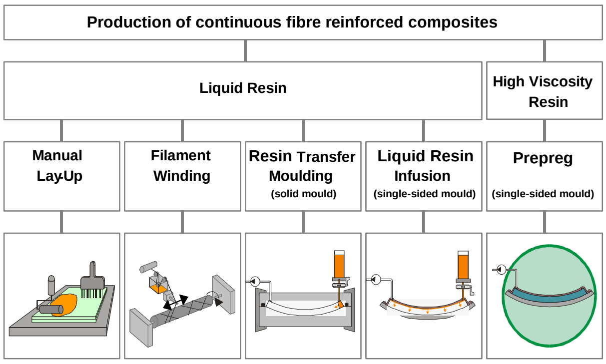


Figure 1: Production techniques for fibre reinforced composites.

2.2 *PREPREG AUTOCLAVE TECHNIQUE [1, 2]*

At present, the prepreg autoclave method is used primarily for production of high-quality composite components because it provides a very high and reproducible component quality while requiring only moderate investments for tools. The high component quality is attained by compacting the prepregs (resin impregnated, continuous fibre products), in the autoclave. Simple tools are required because only single-sided supporting tools with a flexible vacuum cover are required. However, prepregs are costly due to their specialised production process. In addition the lay-up process with prepreg is more complicated than with dry fibre material.

2.3 *RESIN-TRANSFER-MOULDING TECHNIQUE [1, 2]*

The *R*esin-*T*ransfer-*M*oulding (RTM) method has been established in the past few years as an alternative to the Prepreg Autoclave technique. With this method, a cost-effective, non-impregnated fibre preform is placed in a solid mould into which a low viscosity resin mixture is injected under pressure. The significantly lower costs of the semi-finished products are advantageous here when the production quantity warrants the enormous investment costs for the vacuum-tight, temperature-adjustable, pressure-stressed, and frequently very complex and heavy moulds. Since compacting of the composite, which is even and expandable in all directions, is not possible in solid RTM moulds, a reduction in the quality of the composite and fibre content must be expected.

2.4 *LRI / SCRIMP Technique*

A promising subtype of the LRI (*L*iquid *R*esin *I*nfusion) technique is the SCRIMP method. With SCRIMP (*S*eeman *C*omposite *R*esin *I*nfusion *M*oulding *P*rocess) a flow aid is applied to the dry fibre preform enabling rapid distribution of the resin over the surface of the parts during infiltration. As opposed to RTM methods, the infusion and curing process take place at ambient pressure.

In contrast to conventional LRI methods, infiltration of the resin take place perpendicular to the flat fibre reinforcement. Normally, a single-sided mould sealed with a vacuum bag is also used here. Because of the low fibre compacting as well as uncontrolled resin distribution, the quality of the composite is usually considerably lower than with the Prepreg Autoclave method.

2.5 *Single Line Injection (SLI) Technique [3]*

Since the quality and economical production of fibre composite components are decisive for successful introduction on the market, a production process was developed at the Institute of Structural Mechanics with the goal of producing high-quality fibre composite components with the best possible composite and surface quality using a cost-optimised production process.

The process was optimised for the production of small lots and prototype components with a quantity of up to 500 parts per year since a great market potential is developing in the areas of aircraft, railway, and vehicle prototype construction.

2.5.1 *Principle of the SLI Technique*

The approach to development of the SLI method is essentially to combine the advantages of the raw material used for the liquid resin technique with the composite quality of the Prepreg Autoclave technique. The advantage of this method in comparison to the LRI method is that the resin is injected under pressure and that the composite can be compacted by the autoclave pressure. The name of the method is an indication that the evacuation of the fibre preform as well as the injection of the resin system is accomplished by the same resin transfer line. This resin transfer line can be located on the fibre preform in any arrangement to shorten the flow path and, thereby the injection time.

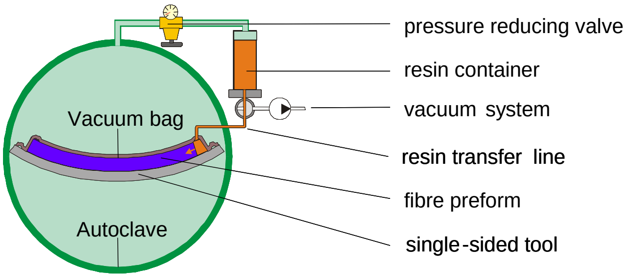
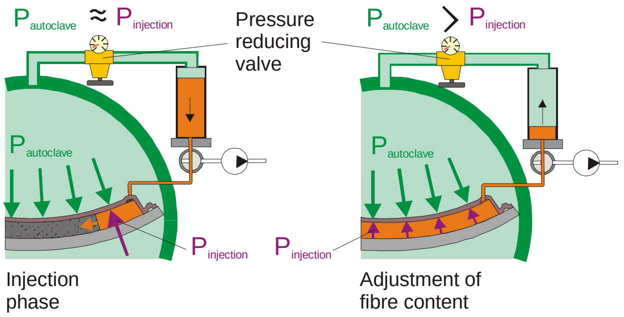


Figure 2: Depiction of SLI Method

Using the SLI method, it is possible to combine cost-effective and dry semi-finished fibre products such as fabrics, weaves, and warp-knitted fabrics with the optimal matrix resin for each application. In addition to the standard epoxy resins, vinyl ester resins, polyisocyanurates (Blendur), heat-resistant resins such as bismalimide, cyanate ester and even phenolic resins can be processed. The excellent, void-free composite quality achieved by the Autoclave Process leads to a high component quality which almost achieves the status of a Class A surface.

2.5.2 *Variation of the Fibre Volume Content*

An additional characteristic of the SLI method is the possibility of directly influencing the fibre content with the process parameters. This is possible because the flexible side of the mould enables the autoclave pressure to be in equilibrium with the inner resin pressure of the component and the restoring force of the fibre material. If the autoclave pressure is adjusted to the same value as the inner resin pressure, the fibre material can relax in the thickness direction and can support the impregnation due to greater permeability. If the fibre preform is completely impregnated, the autoclave pressure on the fibre material can be selectively increased by reducing the injection pressure until the desired fibre volume content of typically 60 % is reached.



Injection phase

Adjustment of fibre content

Figure 3: Pressure distribution during injection and adjustment phase

3. MATERIAL AND METHOD

Barium sulphate ($BaSO_4$) and spherical silicon dioxide (SiO_2) have been studied in detail as interesting and commercially available nanoparticle systems. Barium sulphate is produced in large-scale commercial production and used with heterogeneous particle distribution (∅ < 200 nm). Spherical silicon dioxide is produced using the sol-gel process. The particles grow directly in the polymer matrix [4]. Their size can be adjusted with quenching processes (∅ = 8–50 nm). Nanoscaled barium sulphate and spherical silicon dioxide are predispersed mixtures which are easy to handle. Established epoxy resins approved for aeronautical applications are used as the polymer matrix.

4. PREPARATION AND CHARACTERIZATION OF COMPOSITES

4.1 NANOCOMPOSITES: PURE RESIN WITH NANOPARTICLES

In series tests, the influence of the various nanoparticle systems ($BaSO_4$; SiO_2), which differ in terms of their inherent characteristics (hardness, chemical composition, habits, specific surface area), were tested for the characteristic spectrum of pure resin systems.

The final dispersions of barium sulphate and spherical silicon dioxide were stirred directly into the resin/hardener system. Afterwards the resin mixtures were cured in plate-shaped moulds. A wide performance range of the nanocomposites could be adjusted by systematic variation of the degree of filling. The filled and unfilled polymer matrices were characterised comprehensively in terms of their thermal and mechanical characteristics. The stiffness, impact strength, tensile strength, shearing strength and flexural strength were determined as static properties. Rheological studies and DSC tests were also performed.

In addition to macroscopic analyses, the microscopic architecture of the nanophase was also of interest. The efficiency of the dispersions (particle size distribution) of the nanoparticles in the composite was determined by means of electron microscope procedures (REM, TEM). The degree of dispersion is particularly important, because only an extremely homogeneous particle distribution leads to efficient reinforcement of the polymer matrix.

4.2 GFRP WITH SILICON DIOXIDE NANOPARTICLES

The silicon dioxide nanocomposite was used as a new matrix system for glass-fibre reinforced composite materials. The composites were produced using the new and rational SLI technique. Bidirectional glass-fibre fabric with ± 45° orientation was used as the reinforcement material (matrix dominated composite).

The new nanofilled fibre composite materials were subjected to comprehensive thermal and mechanical testing (see Chapter 4.1). Corresponding unfilled conventional glass-fibre composites were produced as references materials for examination the improvement of the properties.

5. RESULTS AND DISCUSSION

Of the previously tested nanoparticle systems, the results of commercially available barium sulphate and silicon dioxide are introduced as examples. With an optimised shearing technique, these predispersed nanoparticle systems were mixed well into the epoxy resin. REM and TEM photographs prove the homogeneous distribution in the pure resin (*Figures 4 and 5*).

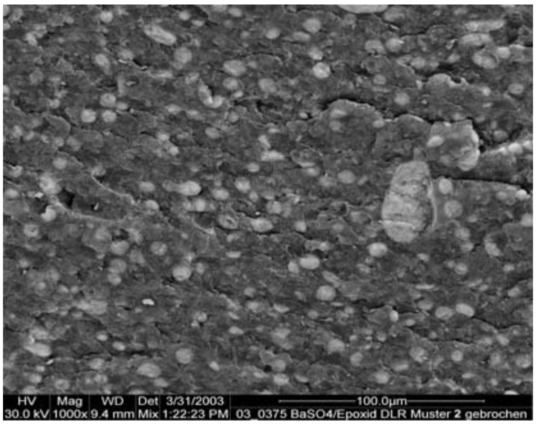


Figure 4: REM photograph of a nanocomposite based on barium sulphate and epoxy resin.

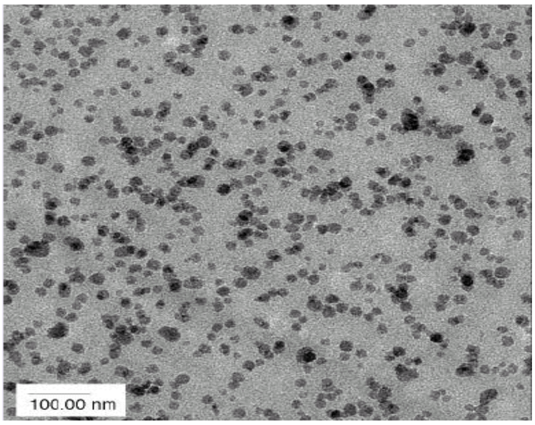


Figure 5: TEM photograph of a nanocomposite based on silicon dioxide and epoxy resin.

5.1 *BARIUM SULPHATE NANOCOMPOSITES*

The effect of the barium sulphate content on the thermal and mechanical properties of the epoxy polymer matrix were studied. For this purpose, nanocomposites were produced containing varying amounts of nanoparticles and compared with the characteristic profile of the unfilled epoxy resin. The results are presented in *Figure 6*.

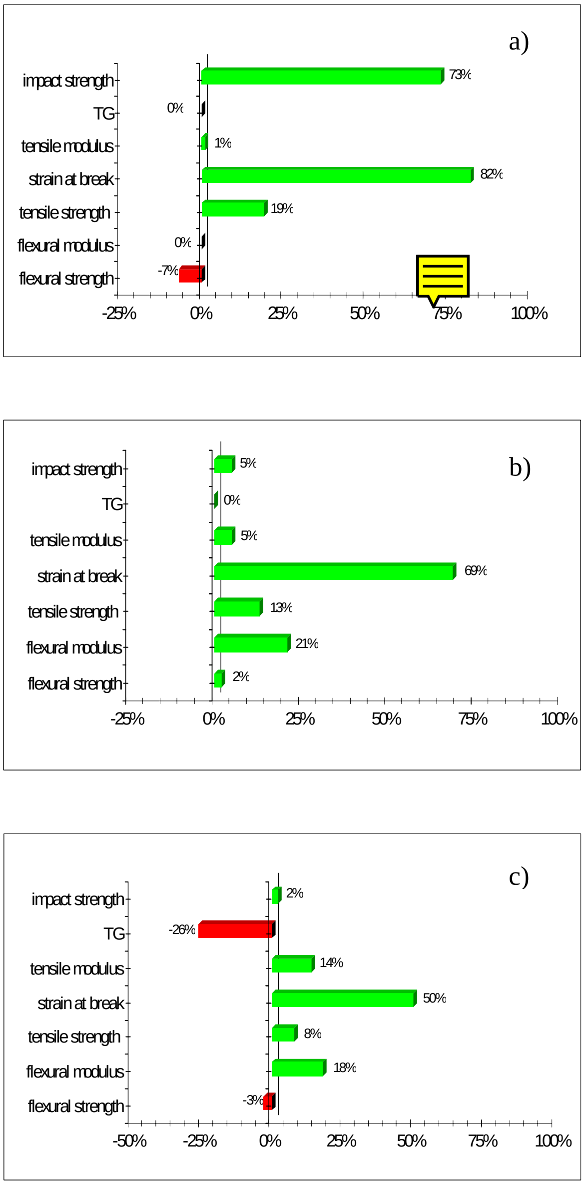


Figure 6: Mechanical and thermal values for barium sulphate nanocomposite in comparison to the unfilled epoxy resin on a relative scale (zero value corresponds to the reference; barium sulphate content: a) 2.5 %; b) 10 %; c) 20 %.

The nanoscaled barium sulphate represents a modifier, which allows resins to be provided with particular impact strength and strain at break.

The optimum is achieved with a particle content of 2.5 %. Compared to unfilled resin, an essential increase of impact strength and strain at break is achieved (strain at break: +82 %; impact strength: +73 %) without any decrease in other composite parameters.

Consequently, an improved high performance resin was obtained with an inexpensive filler and even at a low degree of filling. Furthermore, these values show that the modified resin is not brittle, but rather behaves in a ductile manner. Transfer of the high ductility of the polymer matrix to fibre reinforced composites might compensate the material disadvantages from matrix shrinkage normally resulting for fibre composites produced using injection technique. Accordingly, the material disadvantages of the injection technique compared to the Prepreg technique can be compensated and the problems of the injection technique appear to be solved.

This results also in higher damage tolerances for the composite materials which might reduce the production cycle times, for example, because the greater damage tolerance allows more rapid thermal processing.

The injection capability of the favoured nanocomposite with 2.5 % barium sulphate was proven by means of rheological tests (*Figure 7*). Obviously, the initial viscosity of the differently filled resins is influenced only slightly at a typical injection temperature of 80 °C. However, an improved heat conductivity or catalytic effects appear to accelerate the curing reaction, because the time during which injection is possible is reduced. Under practical aspects, however, the filled resins are well suited for the injection process, particularly the resin system with 2.5 % barium sulphate.

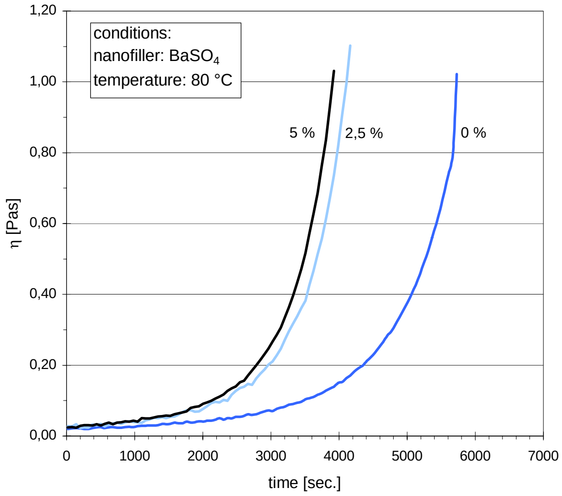


Figure 7: Rheological tests of barium sulphate nanocomposites; epoxy resin with varying barium sulphate content (x = 0–5 wt.%).

5.2 SILICON DIOXIDE-GFRP-COMPOSITES

Furthermore, preliminary results were obtained with a glass-fibre composite filled with 20 % silicon dioxide nanoparticles. The matrix-dominated, glass-fibre composite was prepared using the injection technique (SLI). The results for the matrix-dominated tensile-shear experiment are presented in *Table 1*.

Table 1: Filled and unfilled GFRP composites; Filler: nanoscaled spherical silicon dioxide; GFRP: 60 % fibre content; GF ± 45°; epoxy resin.

Parameter		Unfilled Reference	With 20 % Nanopar.	Difference
Tensile modulus	[MPa]	9,900	16,191	+64 %
Shear modulus	[MPa]	2,874	5,016	+75 %
Max. Tensile strength	[MPa]	115	144	+25 %

Very interesting is the significant increase of strength and stiffness of the filled glass-fibre composite compared to the unfilled reference composite. In particular, the essential enlargement of the tensile modulus (+64 %) and its great linearity compared to the unfilled glass-fibre composite leads to a 30 % higher damage-free range (*Figure 8*).

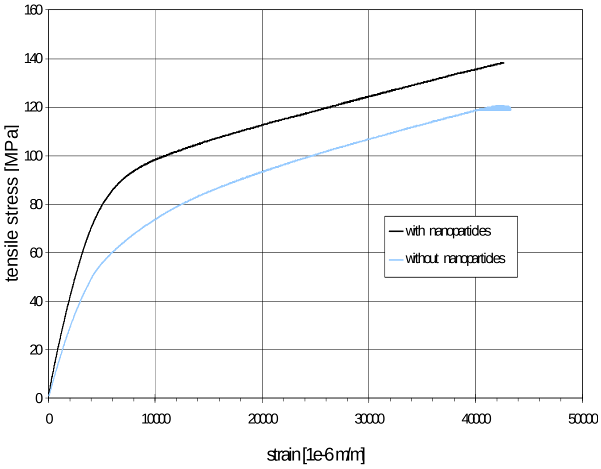


Figure 8: Stress-strain diagram of filled and unfilled GFRP composites; Filler: spherical silicon dioxide; GFRP: 60 % fibre content; GF ± 45°; epoxy resin.

Therefore, the performance of the modified GFRP composite and the field of potential applications are essentially improved. Obviously, nanoscaled silicon dioxide is an interesting and promising reinforcing filler for fibre composites.

Moreover, it was possible to show that fibre composite materials filled with nanoparticles can also be produced using the injection method as a matter of principle, i.e. the injection capability of the filled polymer matrix (nanocomposite) was proven without recognizable filtration effects or inhomogeneities.

6. CONCLUSION

Barium sulphate nanoparticles essentially increase the impact strength and strain at break in comparison to the unfilled reference and that without any decrease in other technical constants and even at very low nanofiller concentrations. This leads to ductile behaviour of the matrix. The transfer of the high ductility of the polymer matrix to fibre reinforced composites might compensate the material disadvantages from matrix shrinkage, normally resulting for fibre composites produced using the injection technique. Accordingly, the material disadvantages of the injection technique compared to Prepreg technique can be compensated and the problems of the injection technique appear to be solved.

In correspondence with the very small nanoparticle concentration required, the viscosity of epoxy resin is nearly unchanged compared to the reference, so that the resin is still suitable for injection. Also, due to the small nanoparticle concentration the density of the nanocomposites is only increased slightly so that the principles of the lightweight construction remain unaffected.

The silicon dioxide nanoparticles used as fillers for GFRP, increase the stiffness essentially (+64 % E-modulus; +75 % G-modulus). This results in an increase of the damage-free range for the GFRP, which generally improves the fibre composite performance and enables the development of new fields of application for the SLI technique. Obviously, nanoscaled silicon dioxide is an interesting and promising reinforcing filler for fibre composites.

7. PROSPECTS

The goal is to develop tailor-made, high performance resins using suitable nanoparticle systems for the injection technique. Furthermore, it is necessary to transfer the new resin characteristics to high-performance fibre composites, i.e. from GFRP to CFRP.

Additionally, the material performance should not only correspond to Prepreg quality but should be even better. The transfer of these results to structural elements, i.e. production of complex and integral high performance composite structures using the injection technique, requires further examination.

Finally, the production costs for the injection technique must be further reduced and, at the same time, potential application fields analysed.

8. REFERENCES

[1] M. Flemming, G. Ziegmann, S. Roth, Faserverbundbauweisen – Fertigungsverfahren mit duroplastischer Matrix, *Springer-Verlag Berlin Heidelberg* (1999).

[2] G. W. Ehrenstein, Faserverbundkunststoffe, *Carl Hanser Verlag, München Wien* (1992).

[3] M. Kleineberg, J. Nickel, A. Pabsch, C. Sigle, C. Schöppinger, Vorrichtung und Verfahren zur Herstellung von faserverstärkten Kunststoffen bzw. Kunststoffbauteilen nach einem modifiziertem RTM-Verfahren. *DE 198 53 709 C1* (2000).

[4] T. Adebahr, C. Roscher, J. Adam, Reinforcing Nanoparticles in Reactive Resins, *European Coatings Journal* **4** (2001) 144-149.