

FIBRE-REINFORCED NANOCOMPOSITES FOR SPACECRAFT STRUCTURES

Manufacturing, Characterisation and Application

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ABSTRACT

The DLR Institute of Composite Structures and Adaptive Systems has found a new and innovative way to compensate the deficits of the well-established injection technique compared to the prepreg technique with regard to material and procedure. The improvement of the composite quality by using nanocomposites was tested with the Single Line Injection technique (SLI), which was developed at the institute.

Using a selected nanoparticle system, it was possible to show that the mechanical and thermophysical parameters of a established and aviation-approved, high-performance epoxy resin could be improved. A closer look was taken at an epoxy resin filled with nanosized silicon dioxide that could be provided with high stiffness and strength compared to pure resin. In addition, the resin shrinkage could be considerably reduced and thermal conductivity increased. The nanocomposite remained injectable so that there were no disadvantages in the composite manufacturing procedure with the preferred injection method. Compared to the unfilled reference resin, the density of the nanocomposites was maintained at an almost constant level (the lightweight construction aspect remained valid).

These results could be transferred to fibre composite structures (GF/SiO₂/epoxy matrix) that were made with the SLI technique. Particularly the significant increase of the Young's modulus and its high linearity in the stress-strain diagram led to reduction of the inter-fibre fractures and improvement of the overall material performance in comparison to unfilled fibre composite (greater damage tolerance).

The improved material properties of the fibre-reinforced nanocomposites (higher load-carrying capacity of the laminate, decrease in safety factors, reduction of the structural weight) as well as the cost-efficient manufacture of composites using the LRI technique make this new class of materials particularly interesting for use in space travel described by some examples in this paper.

1. INTRODUCTION

Future fibre composite materials for use in space travel must have a very high degree of capability, reliability

and safety and must be cost-efficient. These goals can only be realized with the targeted optimization of the fibre composite material and its manufacturing process. Nanoparticles can particularly help to meet these central requirements.

The prepreg technique is presently the most common manufacturing technology for the manufacture of high-performance composites in aerospace. However, despite the good composite quality, the extreme production costs are a great disadvantage (costly semi-finished fibre products, sophisticated logistics, a time-consuming manufacturing process). Injection techniques (e.g. RTM, VARI, DP-RTM and SLI) have proven to be good alternatives over the past few years. Compared to the prepreg technique, the decisive factors of the injection method are the lower manufacturing costs as the result of using cost-efficient resins and semi-finished fibre products. However, the property level of high-performance composites manufactured with the injection method still does not compare with that of the prepreg composites. The main reason is the volume shrinkage of the polymer systems which leads to shrinkage stress in the composite. This, in turn, decreases the material performance.

The DLR Institute of Composite Structures and Adaptive Systems has found a new and innovative way of avoiding this problem by using nanotechnology. Nanoparticles (1–100nm) are used instead of microparticles as a filler material for high-performance matrices. These so-called nanocomposites show a remarkable improvement in the mechanical and thermophysical properties compared to conventional resins at relatively low degree of filling.

The goal of applying nanoparticles is to eliminate the disadvantages of the injection technique during the manufacture of high-performance fibre composites and simultaneously improve the composite material qualities. It is particularly important to increase the strength, stiffness, impact strength, heat distortion temperature and glass transition temperature. 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 Single-Line-Injection technique (SLI) that was developed and patented at the institute is used in this process [3]. This paper provides an overview of the goals that have been reached in this

new research field so far and presents the potential areas of application in space travel.

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.

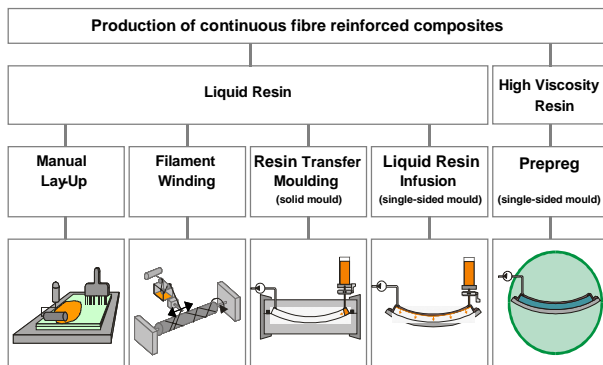


Figure 1: Production techniques for fibre-reinforced composites.

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 *Resin-Transfer-Moulding* (RTM) method has been established in the past few years as an alternative to the

Prepreg Autoclave technique. With this method, a cost-efficient, 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 (*Liquid Resin Infusion*) technique is the SCRIMP method. With SCRIMP (*Seeman Composite Resin Infusion Moulding Process*) 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 Composite Structures and Adaptive Systems 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 aerospace, 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.

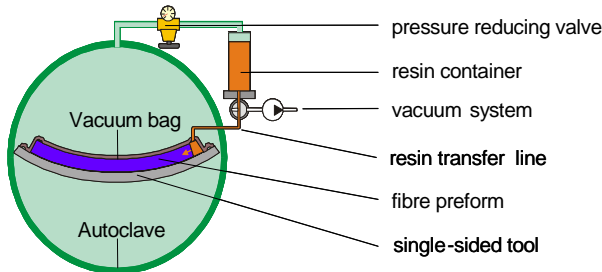


Figure 2: Depiction of SLI Method

Using the SLI method, it is possible to combine cost-efficient 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

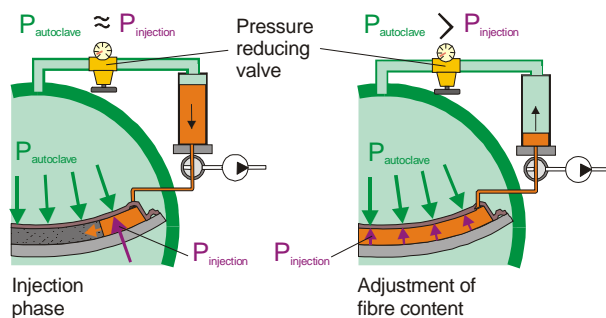


Figure 3: Pressure distribution during injection and adjustment phase

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.

3. MATERIALS AND METHODS

A system based on silicon dioxide (SiO_2) was studied as an interesting and commercially available nanoparticle formulation. The epoxy resin matrix modified with spherical silicon dioxide particles (Araldite LY type) was obtained as a master batch from Hanse-Chemie (Geesthacht, Germany). These particles are manufactured by means of a sol-gel technique and grow directly in the polymer matrix [4]. Their size can be adjusted through quenching processes ($\varnothing = 8\text{--}50\text{ nm}$).

Surface modification allows for polymerisation directly into the resin matrix and prevents agglomeration. An established and aviation-approved anhydride-curing epoxy resin (Araldite LY type) was used as the polymer matrix and cured in a standard cycle (4 h at $80\text{ }^\circ\text{C}$ and 4 h at $120\text{ }^\circ\text{C}$).

A bidirectional GF fabric made by Interglas (type 92140; 0/90°; twill-weave; no binder; sized; G.S.M.: 390 g/m^2) was used to manufacture GFRPs. The composites were manufactured by the SLI procedure described above. The curing cycle was identical to the one used for the pure resins.

4. PREPARATION AND CHARACTERIZATION OF COMPOSITES

4.1 Resin with Nanoparticles: Nanocomposites

The influence of the concentration of the nanoscale silicon dioxide on the range of properties of the reaction resin (Araldite LY type) was investigated in a series of tests in order to determine the optimal concentration range for the production of fibre composites. For this purpose, portions of the pre-conditioned master dispersion of silicon dioxide (50 wt.%) were stirred directly into the resin-hardening agent system in order to produce various nanoparticle concentrations. Subsequently, the resin formulations were cured in plate-shaped casting moulds. Through systematic variation of the filler content (0–25 wt.%), it was possible to produce a wide performance range for comparison to the pure resin.

The filled and unfilled matrix systems were characterised extensively in terms of their thermophysical and mechanical properties. Tensile and flexion measurements in accordance with the German industry standard DIN were performed in order to determine essential parameters of the materials (tensile: DIN EN ISO 527-3;

flexion: DIN EN ISO 14125). In addition, the viscosities, resin shrinkage (DIN EN ISO 3521), thermal conductivity, and glass transition temperatures (DSC) were determined. In addition to the macroscopic tests, the microscopic architecture of the nanophase was also of great interest. By combining the methods of electron microscopy (TEM) and small-angle neutron scattering (SANS) we managed to obtain a detailed view of the particle size distribution and the type and shape of the nanoparticles.

4.2 Glass Fibre-Reinforced Nanocomposites

The nanocomposite formulations were then used as novel matrix systems for GFRP composite materials. The composites were manufactured according to a new, resource-efficient resin injection technique (SLI). A bidirectional GF fabric was selected as the reinforcement material (see Chapter 3). The fibre volume fraction of the GFRP composite was 60 vol.% in all cases. A symmetrical 0/90° laminate structure with 9 plies of fabric was selected. The novel fibre-reinforced nanocomposites were subjected to extensive mechanical testing. Matrix-focussed tests, e.g. shear tests in the $\pm 45^\circ$ tensile test, were performed to detect at high sensitivity the influence of the nanoparticles on the properties of the composites. In order to determine the shear properties (G_{12} ; τ_{12}), $\pm 45^\circ$ sample bodies were sawed from the GFRP composites and tested by a procedure similar to DIN EN 6031. For quantification of the improvement of the properties, conventional GFRP composites, also without filler, were manufactured to serve as reference materials.

5. RESULTS AND DISCUSSION

5.1 Nanocomposites

With an optimised shearing technique we managed to successfully incorporate the pre-dispersed nanoparticulate SiO_2 formulation into the epoxy resin (EP resin). TEM images document the homogeneous distribution of the spherical SiO_2 particles in the reaction resin as well as the absence of any major agglomeration of particles (see Figure 4). Small angle neutron scattering (SANS) was used to demonstrate the very narrow particle size distribution in the range of 5–40 nm in the resin system (see Figure 5).

This is evidence that the dispersion quality is retained in the nanocomposite from the liquid to the fully cured state (homogeneous distribution, high degree of dispersion). The nanocomposites with varying filler contents were subsequently subjected to extensive thermophysical and mechanical analysis.

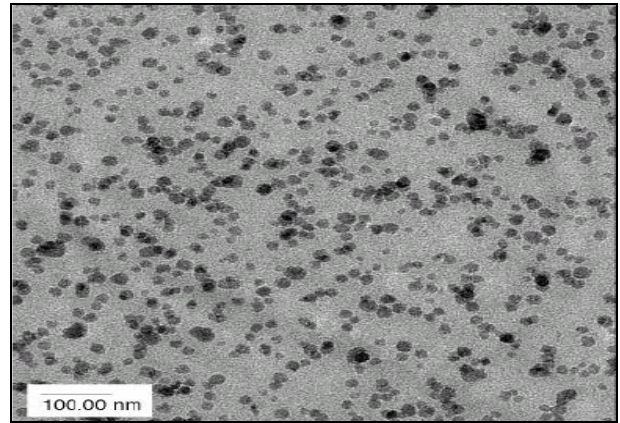


Figure 4: TEM image of a nanocomposite based on SiO_2 and epoxy resin (5 wt.% SiO_2). Source: Hanse-Chemie (Germany).

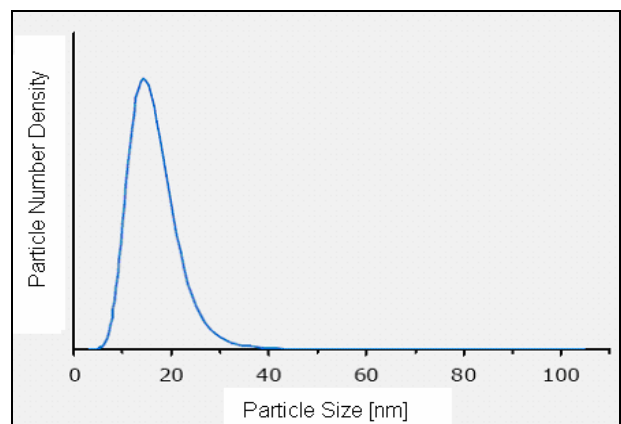


Figure 5: Differential particle size distribution of SiO_2 nanoparticles in an epoxy resin as determined by SANS. Source: Hanse-Chemie (Germany).

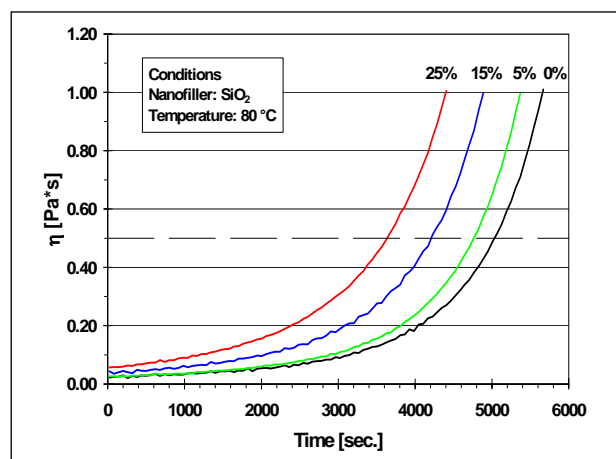


Figure 6: Isothermal viscosity-time curves of SiO_2 /epoxy resin nanocomposites with varying SiO_2 contents (0–25 wt.%) at 80 °C. Limiting viscosity number line for SLI method shown dashed.

➤ Rheology

Isothermal viscosimetry was used to investigate the injectability of the nanocomposites. Increasing the filler content up to 25 wt.% SiO₂ at a typical injection temperature of 80 °C leads to a reduction in pot life (see Figure 6). However, with regard to the filler contents studied herein, the reduction in pot life as well as the small increase in initial viscosity are acceptable and are no problem for production purposes (s. Figure 6: Limiting viscosity line at 500 mPas; applies to SLI technique). This shows that the injectability is retained in the modified resins.

➤ Reaction Enthalpy

The reaction behaviour of the various nanocomposites was investigated by means of DSC (see Figure 7). The experiments revealed that the exothermic character of the hardening reaction decreases strongly with increasing filler content ($\Delta H \approx -27\%$). The reaction process being less severe prevents overheating in the composites. This means that the curing process proceeds more homogeneously and the occurrence of internal mechanical stress is reduced. This effect is of great interest especially for the manufacture of thick-walled composites.

➤ Resin Shrinkage

Measurements of the density showed resin shrinkage to be reduced by approx. 50 % depending on the nanoparticle content (see Figure 8). Both the reduced resin shrinkage and the less exothermic character (see above) cause the internal mechanical stress (shrinkage stress) in the composite to be reduced which improves the applicability of the material (higher tolerance to damage).

➤ Thermal Conductivity

The thermal conductivity of the various nanocomposites was determined using the flash method, in which the thermal diffusivity (a), specific heat capacity (C_p), and density (ρ) of the resins determined are used to calculate the thermal conductivity (λ) according to the following equation:

$$\lambda(T) = \rho \cdot C_p(T) \cdot a(T) \quad (1)$$

Interestingly, the thermal conductivity of the nanocomposites was increased by approx. 15 % as compared to the reference (see Figure 9). Any improvement of the thermal conductivity leads to a more homogeneous transport of heat into the composite and thus prevents

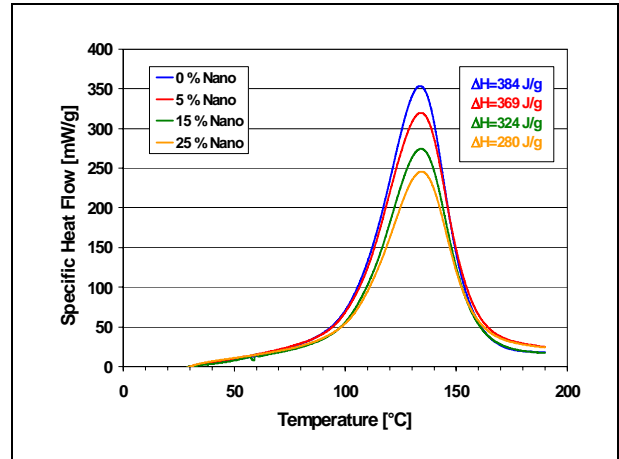


Figure 7: Dynamic DSC curves at a heating rate of 2°C/min. for SiO₂/epoxy resin nanocomposites (SiO₂ content: 0–25 wt.%).

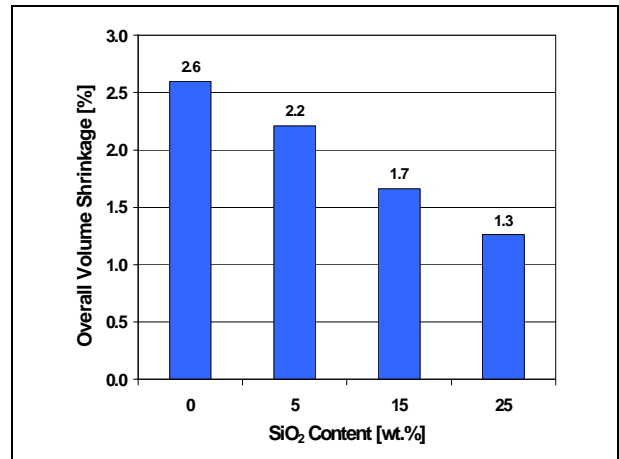


Figure 8: Overall volume shrinkage of SiO₂/epoxy resin nanocomposites at RT as a function of SiO₂ content.

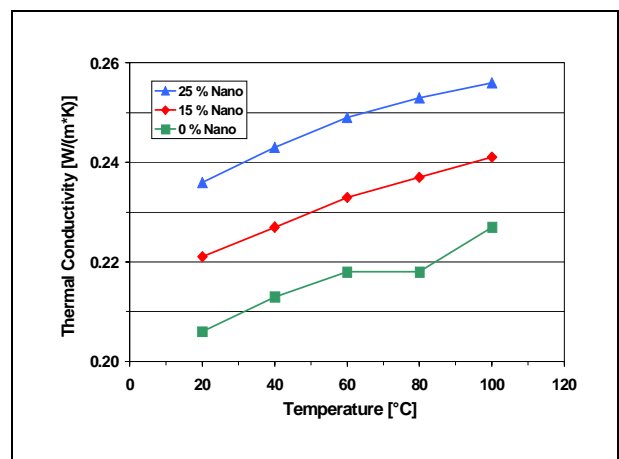


Figure 9: Thermal conductivity of SiO₂/epoxy resin nanocomposites as a function of temperature.

local overheating (lesser shrinkage stress). Moreover, the formation of thermal stress in the composite is reduced such that the large temperature variations in outer space, for example, have a less detrimental effect on the composite materials (reduction of thermal aging).

➤ Mechanical Characterisation

The results of the mechanical tests versus pure resin are shown in *Figure 10*. The increase in the stiffness and strength of the nanocomposites with increasing silicon dioxide content is clearly evident. The filler content of up to 25 wt.% SiO₂ investigated in this study improved the tensile modulus by up to 34 % and the flexural modulus by up to 35 % (G₁₂ calculated: +37 %). The tensile strength (ultimate) can be increased by up to 17 %. Other mechanical parameters are either unchanged as compared to the pure resin or adversely affected to a minor extent only. Especially the fact that the strain at break decreases only slightly from 2.7 % to 2.4 % as compared to the reference is evidence that the nano-modified polymer matrix possesses insignificant brittleness with this effect becoming noticeable only at nanoparticle contents in excess of 20 wt.% (see *Figure 11b*). Consequently, improved stiffness and strength can be implemented without any loss of essential material properties.

As a thermal parameter, the glass transition temperature (T_g) was determined by DSC. Interestingly, the T_g can be increased with nanoparticles, but decreases again with increasing filler content though none of the values was lower than the reference resin value of 123 °C. This demonstrates that an important parameter for the design or dimensioning of materials is either unchanged or even improved.

Both the strength and the stiffness values show a continuous linear increase over the range of filler contents investigated (see *Figure 11a*). However, the mechanical parameters investigated here show no peaks, which means that the peak for this material has not been reached yet and the possibilities of the material may not have been exhausted yet. In contrast, considering the strain at break, there is evidence that the matrix begins to become somewhat brittle above 20 wt.% SiO₂ (see *Figure 11b*). However, this negative effect is more than compensated by the significant increase in the stiffness and strength of the polymer matrix such that the current optimum for the material was limited to a filler content of up to 25 wt.% SiO₂. This optimum needs to be confirmed in further experiments.

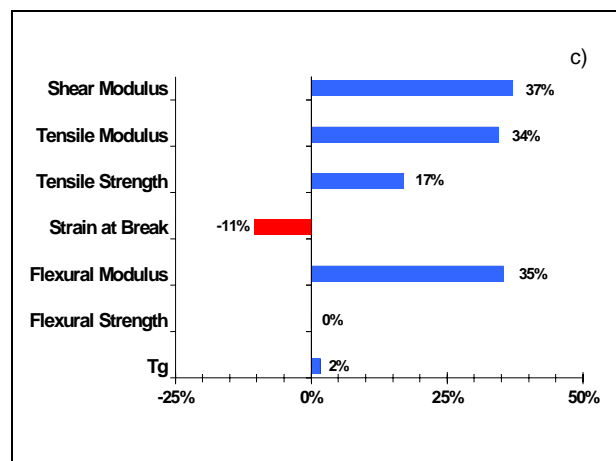
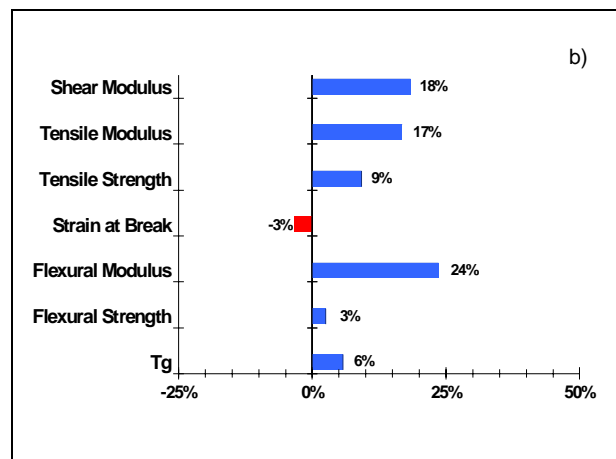
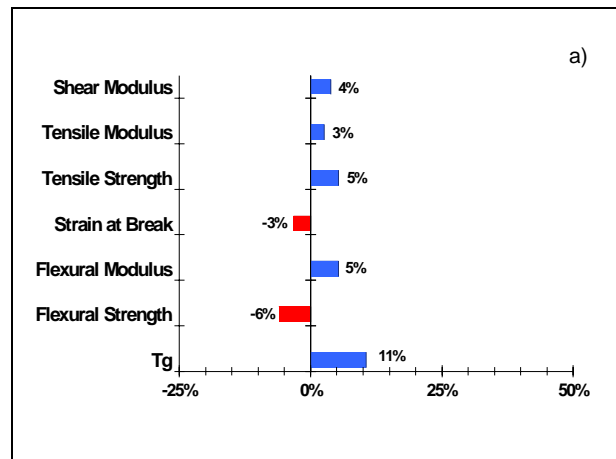


Figure 10: Mechanical and thermal values of SiO₂/epoxy resin nanocomposites in comparison to the unfilled reference resin on a relative scale (zero corresponds to the reference). SiO₂ content: a) 5 wt.%; b) 15 wt.%; c) 25 wt.%. Reference values absolute: shear modulus: 1202 MPa, tensile modulus: 3345 MPa, tensile strength (ultimate): 76 MPa, strain at break: 2.7 %, flexural modulus: 3576 MPa, flexural strength: 164 MPa, T_g (DSC): 123 °C.

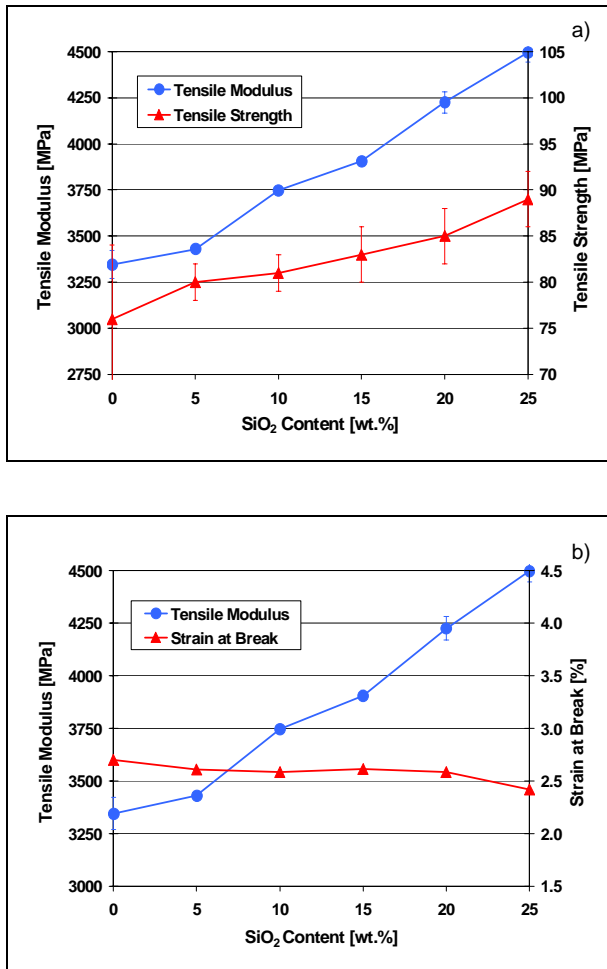


Figure 11: Tensile characteristics vs. SiO₂ content of SiO₂/epoxy resin nanocomposites.

In summary, the structural-mechanical and thermophysical properties of a high performance epoxy resin were improved significantly through the use of a reasonably-priced nanoparticle system. The limit of optimal usage range of the EP resin tested in the present study is at a nanofiller content of 25 wt.% SiO₂. A further increase of the filler fraction is expected to cause problems related to process technique (reduced pot life) and induce effects that are detrimental to the structure of the material (increasing brittleness of the matrix). The slight increase in the density of the matrix¹ can be disregarded in this context and does not contradict the aspect of lightweight design nor the overall consideration of the GFRP composite in Chapter 5.2.

¹ Matrix density measurements: EP reference: 1.21 g/cm³; EP nanocomposite (25 wt.% SiO₂): 1.34 g/cm³.

5.2 GFR Nanocomposite Results

Subsequently the SiO₂ nanocomposites were used as a new matrix system for GFRP composites. On the basis of the preliminary results obtained with the SiO₂-modified nanocomposites (see Chapter 5.1), the nanoparticle content was varied up to 25 wt.% (relative to the EP resin) in order to cover a large performance range of GFRP composites. The GFRP plates were manufactured using resource-efficient resin injection technique (SLI). The structural-mechanical results obtained with the GFRP plates are shown in Table 1 and Figures 12 and 13.

In the matrix-focussed shear-tensile test, the significant increase in the stiffness (E_{11} : +44 %; G_{12} : +53 %) and strength (τ_{12} : +16 %) of the SiO₂ nanoparticle-filled GFRP plates as compared to the unfilled reference is evident (see Table 1 and Figure 12ab). The over-proportional increase of the shear modulus values as compared to the tensile modulus values is explained according to the equation, $G_{12} = E_{11}/(2+2\mu)$, as a result of the decrease in Poisson's ratio μ with increasing SiO₂ content (see Figure 12b and Table 1).

Similar to the non-reinforced nanocomposites described above, there is no peak over the investigated range of filler contents and the mechanical parameters increase continuously and linearly. Therefore, the possibilities of the material should not have been exhausted yet (see Figure 12ab).

The small difference in density between the unfilled GFRP reference ($\rho = 2.05 \text{ g/cm}^3$) and the GFRP composite with 25 wt.% SiO₂ ($\rho = 2.10 \text{ g/cm}^3$) is consistent with lightweight design. However, a further increase of the SiO₂ fraction may be reason for concern due to the aspects of process technique and a detrimental effect on the structure as mentioned in Chapter 5.1 above. For this reason, the optimum of the material so far is being limited to a nanofiller content of up to 25 wt.% SiO₂ (relative to the EP resin matrix). This confirms the trends observed with the non-reinforced nanocomposites with regard to the optimal filler content also for fibre-reinforced composites.

Table 1: Filled and unfilled GFRP composites. Nanoparticle content: 0–25 wt.% SiO₂ relative to epoxy resin. GF content: 60 vol.% fabric ($\pm 45^\circ$); matrix: epoxy resin.

Parameter		0 wt.% SiO ₂	10 wt.% SiO ₂	25 wt.% SiO ₂
Tensile Modulus	[MPa]	14.664	16.518	21.062
Shear Modulus	[MPa]	4.683	5.574	7.165
Shear Strength (ultimate)	[MPa]	61	71	71
Poisson's Ratio	--	0.5656	0.4818	0.4698

The very good reproducibility of the parameters in the case of the fibre-reinforced nanocomposites can be interpreted to evidence the very homogeneous particle distribution within the composite (fibre-reinforced nanocomposites: σ_{n-1} : $\pm 2\%$; unfilled reference: σ_{n-1} : $\pm 11\%$). As a result, local inhomogeneities due to filtering effects (permeation issues) can be excluded. This demonstrates that we successfully achieved the targeted manufacture of fibre-reinforced nanocomposites by means of an injection technique.

Compared to the reference material, the GFRP composite with 25 wt.% SiO₂ (relative to EP resin) is notable for the significant increase in the tensile modulus and the extensive linearity of the tensile modulus in the stress-strain diagram (see Figure 13). Whereas the reference material shows a broad transition from the damage-free (linear-elastic) to the damaged area, the nano-filled composite shows a pronounced linear-elastic material behaviour with a sharp bend at the transition to the damaged area. In the reference material, the initial damage (visible turbidity) occurs at a strain of $\epsilon > \text{approx. } 0.4\%$, whereas this is observed with the nanomaterial only from $\epsilon > \text{approx. } 0.6\%$. Consequently, the elasticity limit, and therefore the usable damage-free range, was increased by approx. 50%. Similarly, the critical tensile stress (first damages) of approx. 50 MPa of the reference material was successfully increased to approx. 100 MPa in the nano-filled GFRP composite, i.e. by approx. 100%.

Consequently, the higher stiffness and strength of the nano-modified resin system were transferred to the fibre composite to a large degree. The increased support effect of the resin on the semi-finished fibre product is fully reflected in the enlargement of the damage-free strain range in the case of the $\pm 45^\circ$ laminates. Accordingly, inter-fibre fractures and delaminations are reduced and the general performance of the composite as compared to the unfilled fibre composite is significantly improved (producing a laminate with higher load-carrying capacity, reduced safety issues, and reduced structural weight).

Moreover, it can be presumed that especially the optimisation of the shear parameters of the nanocomposites also improves the transverse tensile strength and therefore the compression strength of the fibre composites too. The expansion of the damage-free range – measured under static conditions – can be expected also to improve the properties of the composite under dynamically changing loads. Knowledge of this behaviour is crucial for the strength of a material in practical use. These considerations need to be confirmed in further studies.

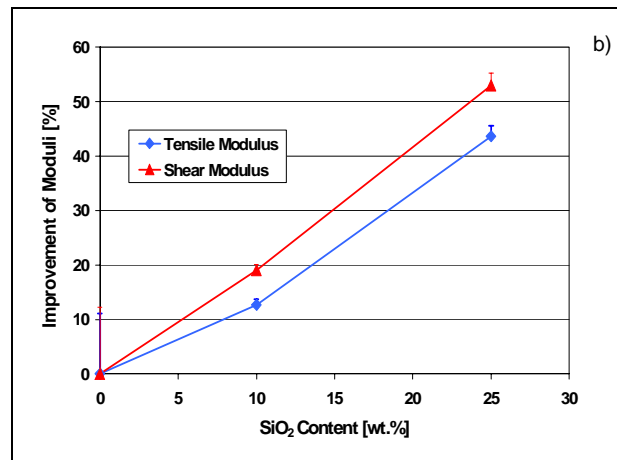
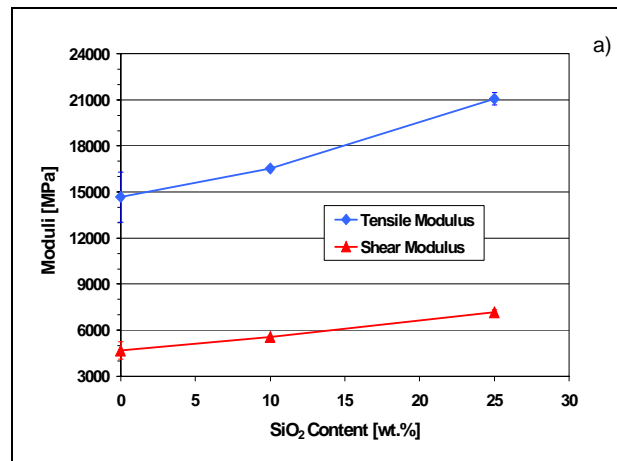


Figure 12: Moduli of GFRP composites with varying nanoparticle content absolute (a) and relative (b). Nanoparticle content: 0–25 wt.% SiO₂ relative to epoxy resin. GF content: 60 vol.% fabric ($\pm 45^\circ$); matrix: epoxy resin.

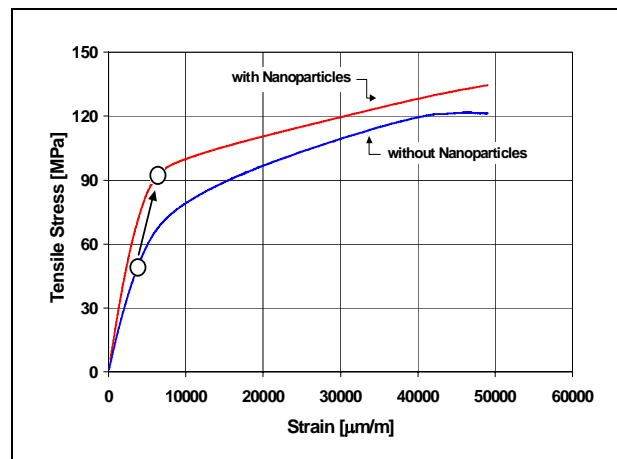


Figure 13: Stress-strain diagram from tensile tests of filled and unfilled GRFP composites. Nanoparticle content: 25 wt.% SiO₂ relative to epoxy resin. GF content: 60 vol.% fabric ($\pm 45^\circ$); matrix: epoxy resin.

6. FIBRE-REINFORCED NANOCOMPOSITES FOR SPACECRAFT STRUCTURES – POTENTIAL FIELDS OF APPLICATIONS

Today, space transportation systems are still primarily made out of metallic components. For example, only metallic fuel tanks are used in European space missions. However, since future materials must be lighter and more operationally efficient, CFRP composites and hybrid materials will have to be used to a greater degree. In particular nanocomposites will provide a considerable contribution to the improvement of the material properties. As previously mentioned, the range of applications of nanocomposites lies in the construction of spacecrafts and space structures due their improved mechanical characteristics (higher firmness and stability and a concurrently lower density) compared with conventional materials. Nanocomposites could in particular contribute to the reduction of the lift-off masses of spacecrafts which would lead to substantial cost savings and also ensure safer and more flexible space missions. Spherical and layered silicates, POSS (Polyhedral Oligomeric Silesquioxanes) and carbon nanotubes (CNT) are currently undergoing intensive research as interesting nanoparticle classes for space structures [5]. Depending on these nanoparticles, the following improvements for composites can be expected:

- ◆ Better mechanical performance (higher stiffness and strength, better impact and damage tolerance)
- ◆ Reduction of structure weight (higher material usage, lower safety factors, lower matrix density)
- ◆ Good thermal properties (high temperature resistance, thermal shielding)
- ◆ Improved thermal conductivity (no or little thermal aging by thermal stress)
- ◆ Resistance to atomic oxygen (ATOX) and ultraviolet and charged particle radiation
- ◆ Barrier layer effects (no or low outgasing rate)
- ◆ electric and magnetic effects (EMI shielding)

Below are some examples from the institute that demonstrate possible application potentials for nanocomposites in the area of fibre-reinforced composites in space structures:

➤ ARIANE 5 Booster [6, 7]

MAN Technology AG (Germany) prefers the manufacture of CFRP booster segments for ARIANE 5 manufactured with the filament winding technique [6]. A booster segment (CFRP) made with the dry winding technique and then injected with the “one-shot” VARI method (see Figure 14) has already been manufactured as a demonstrator. Its wall thickness is 18–40 mm.

One problem is that thick-walled laminates tend to have local overheating due to an extreme exothermal reaction during curing. The result is a heterogeneous and uncontrolled curing process that leads to a greater shrinkage of the resin. More shrinkage stress is produced which leads to the formation of inter-fibre fractures and delaminations between the individual layers.

The application of nanoparticles can reduce the risk of crack formation and delamination since it reduces resin shrinkage and improves the thermal conductivity of the matrix (isothermal curing, no overheating). As a result, the performance of the material is significantly improved so that safety factors can be reduced. That allows the reduction of structural weight as well as transportation costs and enables the increase of the payload.

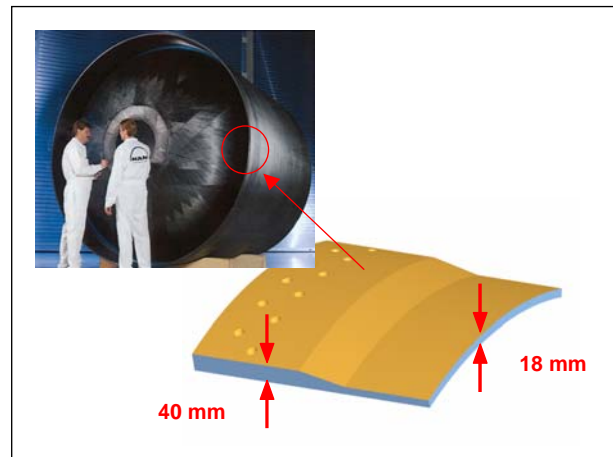


Figure 14: Demonstrator of a CFRP booster segment for ARIANE 5 manufactured by a combination of dry winding technique and VARI process (designed reference structure shows the coupling area and illustrates the problems of thick-walled laminates; $\varnothing = 18\text{--}40\text{ mm}$).

➤ Pressure Vessels

Gas tanks for application in space were developed in cooperation with the OHB company (Germany) (see Figure 15). A CFRP structure was manufactured with the winding technique instead of using the classical metal construction. The gas tank is made of a thin-walled aluminium cylinder (liner) that guarantees gas impermeability overwrapped by a isotensoid CFRP structure that contributes to the strength of the tanks. The structural weight was reduced with the CFRP construction to such an extent that, e.g., the fuel level could be increased (a high pressure loading is possible at a lower structural weight compared to conventional metal constructions).

The application of nanocomposites enables a better performance of the fibre-reinforced composite material since the resin shrinkage is reduced and as a further point the transversal tensile properties are increased. As

a result less matrix fractures and delaminations occur. Less formation of cracks also results in a reduction of the outgasing rate of the fuel and nanoparticles that have a barrier layer effect (layered silicates) help to improve the sealing of the tank. Nanocomposites probably also generate a greater impact resistance so that the gas tank is better protected against micrometeorite impact.



Figure 15: Isotoisoid CFRP pressure vessel produced by wet filament winding technique (OHB demonstrator).

7. SUMMARY

Future fibre composite materials for use in space travel must have a very high degree of capability, reliability and safety and must be cost-efficient. These goals can only be realized with the targeted optimization of the fibre composite material and its manufacturing process. Nanoparticles can particularly help to meet these central requirements.

The example of a SiO_2 nanocomposite shows that it is possible to directly improve the performance parameters of the polymer matrix (improvement of the mechanical and thermophysical parameters, reduction of resin shrinkage, increase in thermal conductivity). The nanocomposite remained injectable so that there were no disadvantages in the composite manufacturing procedure with the preferred injection method. Compared to the unfilled reference resin, the density of the nanocomposites was maintained at an almost constant level (the lightweight design aspect remained valid).

These results could be easily transferred to fibre composite structures (GF/ SiO_2 /epoxy matrix) that were made with the SLI technique. Particularly the significant increase of the Young's modulus and its high linearity in the stress-strain diagram led to reduction of the inter-fibre fractures and improvement of the overall material performance in comparison to unfilled fibre composites. The greater damage tolerance – measured under static conditions – should also lead to an improved composite behaviour under dynamically chang-

ing loads. The improved material properties of the fibre-reinforced nanocomposites (higher load-carrying capacity of the laminate, decrease in safety factors, reduction of the structural weight) as well as the cost-efficient manufacture of composites using the LRI technique make this new class of materials particularly interesting for use in space travel.

8. PROSPECTS

A long-term goal is to develop tailor-made, high performance resins using suitable nanoparticle systems for the injection technique. There is an enormous research potential in the selection of an appropriate nanoparticle system to optimize the material of a spacecraft structure, the development of an efficient dispersing technology as well as the optimization of the nanocomposites. Particularly the transferability of each of the new resin characteristics to high performance composites (CFRP) needs to be researched. The focal point is the cost-efficient manufacture of complex and highly integral fibre composite structures (demonstrators) that show the advantages of the injection method.

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