

NANOTECHNOLOGY FOR NOVEL HIGH-PERFORMANCE COMPOSITES

MANUFACTURING, CHARACTERIZATION AND APPLICATION

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Abstract

An innovative way to compensate the deficits of composites (FRP) produced by the well-established injection technique (LRI) compared to the prepreg technique was found at the DLR Institute for Composite Structures and Adaptive Systems. The improvement of the composite quality by using nanocomposites was tested with the Single Line Injection technique (SLI). A closer look was taken at an epoxy resin filled with nanosized silicon dioxide (SiO_2). With SiO_2 the stiffness and strength could be improved significantly compared to the neat resin. In addition, the resin shrinkage could be considerably reduced and thermal conductivity increased. The nanocomposites remained still injectable and the density of the nanocomposites was maintained at an almost constant level (lightweight aspect). The results could be transferred to fibre-reinforced composites 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 and opens therefore new fields for aerospace applications.

1 Introduction

Future fibre composite materials for use in aerospace applications 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. A

variety of different techniques has been established for the production of continuous fibre-reinforced composites (Fig. 1).

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. Injection techniques (e.g. RTM, VARI, DP-RTM, SLI etc.) have proven to be good alternatives over the past few years [1-3]. 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.

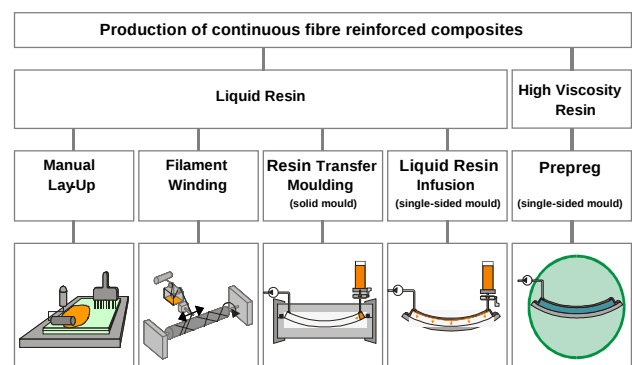


Fig. 1: Production techniques for fibre-reinforced composites.

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 thermo-physical 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 [3] is used in this process (*Fig. 2*). This paper gives an overview of the goals that have been reached in this new research field so far.

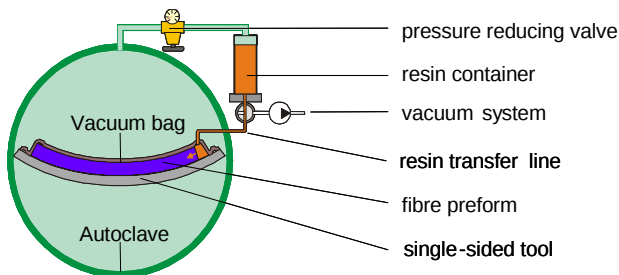


Fig. 2: Depiction of SLI technique [3].

2 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 the 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; $0/90^\circ$; 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 resin.

3 Preparation and Characterization of Composites

3.1 Nanocomposites

The influence of the concentration of the nano-scaled 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 batch of silicon dioxide (50 wt.%) were introduced directly into the resin-curing 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 thermo-physical and mechanical properties. Tensile and flexural tests 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 Scanning Electron Microscopy (SEM) and Photon Cross Correlation Spectroscopy (PCCS) [5, 6] we managed to obtain a detailed view of the particle size distribution and the type and shape of the nanoparticles.

3.2 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 2). 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.

4 Results and Discussion

4.1 Nanocomposites

With an optimised shearing technique we managed to successfully incorporate the pre-dispersed nanoparticulate SiO₂ formulation into the epoxy resin (EP resin). SEM images document the homogeneous distribution of the spherical SiO₂ particles in the reaction resin as well as the absence of any major agglomeration of particles (see Fig. 3). Photon Cross Correlation Spectroscopy (PCCS) was used to demonstrate the very

narrow particle size distribution in the range of 2–50 nm in the resin system (see Fig. 4).

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 thermo-physical and mechanical analysis.

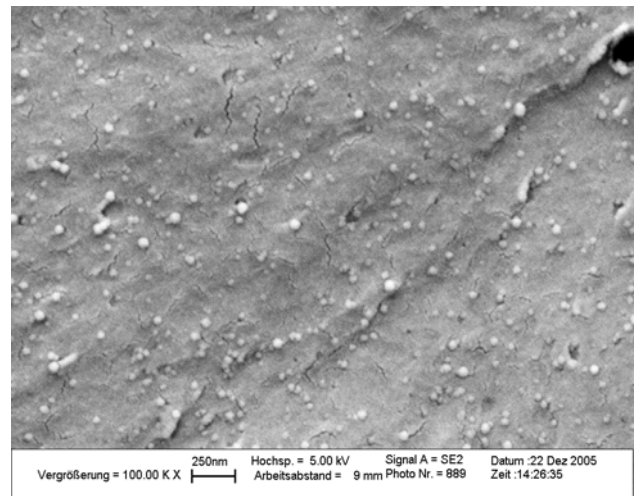


Fig. 3: SEM image of a nanocomposite based on SiO₂ and epoxy resin (5 wt.% SiO₂). Surface prepared by cryoscopic fracture.

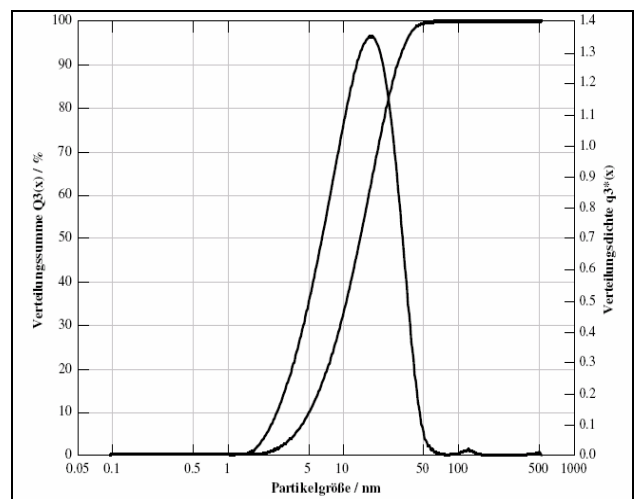


Fig. 4: Differential and integral particle size distribution of 5 wt.% SiO₂ nanoparticles in an epoxy resin determined by PCCS.

➤ 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 (Fig. 5). 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 (Fig. 5: Limiting viscosity number 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 (Fig. 6). 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 (Fig. 7). Both the reduced resin shrinkage and the less exothermic character (see above) cause the reduced internal mechanical stress (shrinkage stress) in the composite 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:

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

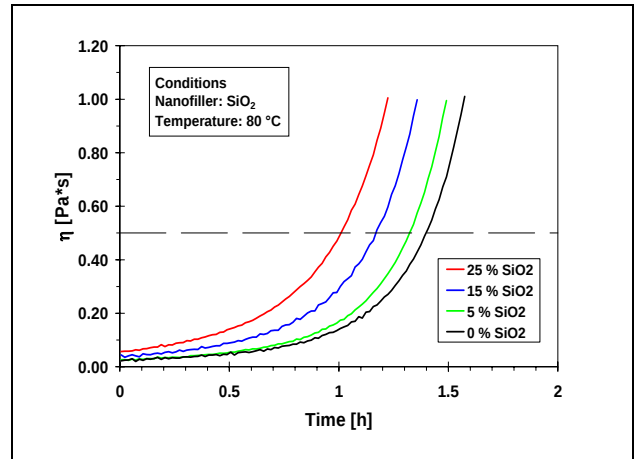


Fig. 5: Isothermal viscosity-time curves of SiO₂/epoxy resin nanocomposites with varying SiO₂ contents (0–25 wt.%) at 80 °C. Limiting viscosity number line for SLI method shown dashed.

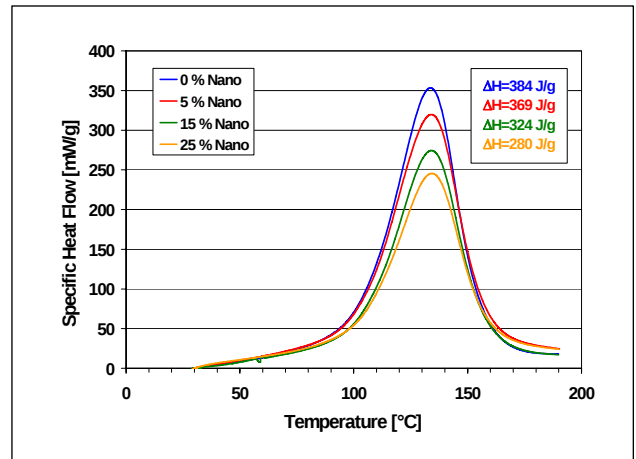


Fig. 6: Dynamic DSC curves at a heating rate of 2°C/min. for SiO₂/epoxy resin nanocomposites (SiO₂ content: 0–25 wt.%).

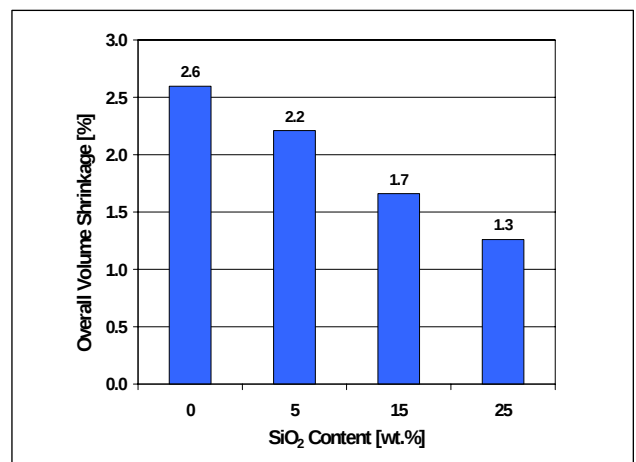


Fig. 7: Overall volume shrinkage of SiO₂/epoxy resin nanocomposites at RT as a function of SiO₂ content.

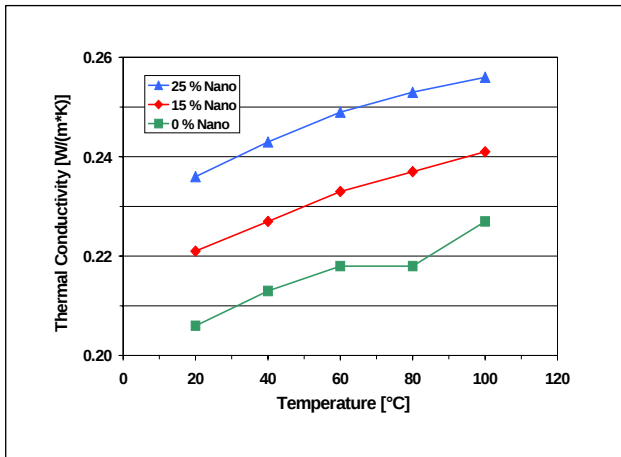


Fig. 8: Thermal conductivity of SiO₂/epoxy resin nanocomposites as a function of temperature.

Interestingly, the thermal conductivity of the nanocomposites was increased by approx. 15 % as compared to the reference (*Fig. 8*). Any improvement of the thermal conductivity leads to a more homogeneous transport of heat into the composite and thus prevents 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 *Fig. 9*. 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 % (G_{12} 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

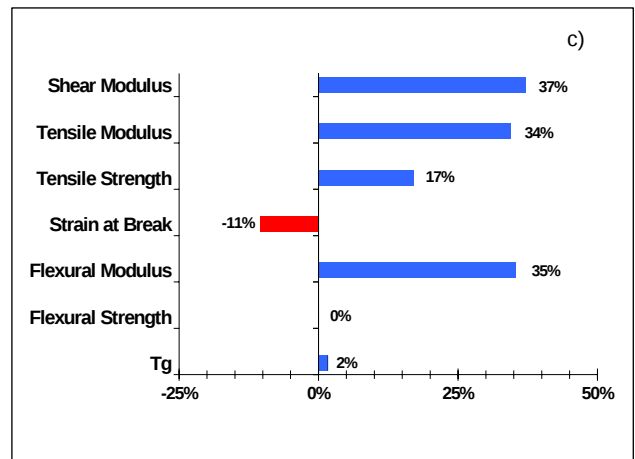
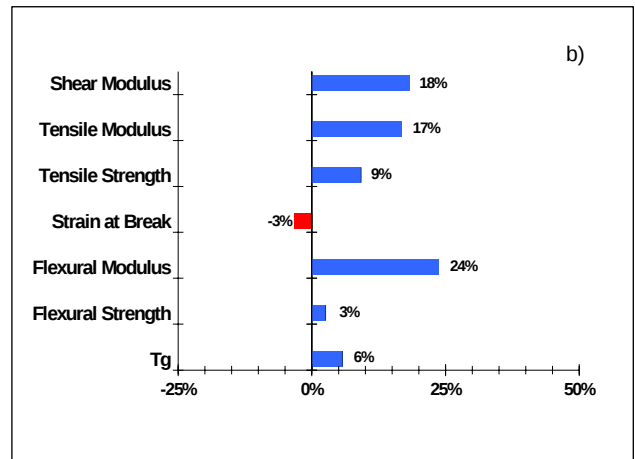
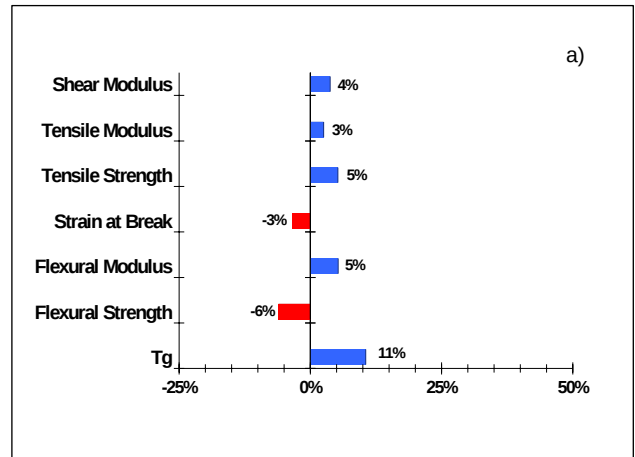


Fig. 9: Mechanical and thermal values of SiO₂/epoxy resin nanocomposites in comparison to the unfilled reference resin on a relative scale (zero corresponds to the reference). SiO₂ content: a) 5 wt.%; b) 15 wt.%; c) 25 wt.%. Reference values absolute: shear modulus: 1202 MPa, tensile modulus: 3345 MPa, tensile strength (ultimate): 76 MPa, strain at break: 2.7 %, flexural modulus: 3576 MPa, flexural strength: 164 MPa, T_g (DSC): 123 °C.

only at nanoparticle contents in excess of 20 wt.% (Fig. 10b). 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 (Fig. 9). 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 (Fig. 10a). 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.% SiO_2 (Fig. 10b). 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.% SiO_2 . This optimum needs to be confirmed in further experiments.

In summary, the structural-mechanical and thermo-physical 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.% SiO_2 . 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 4.2.

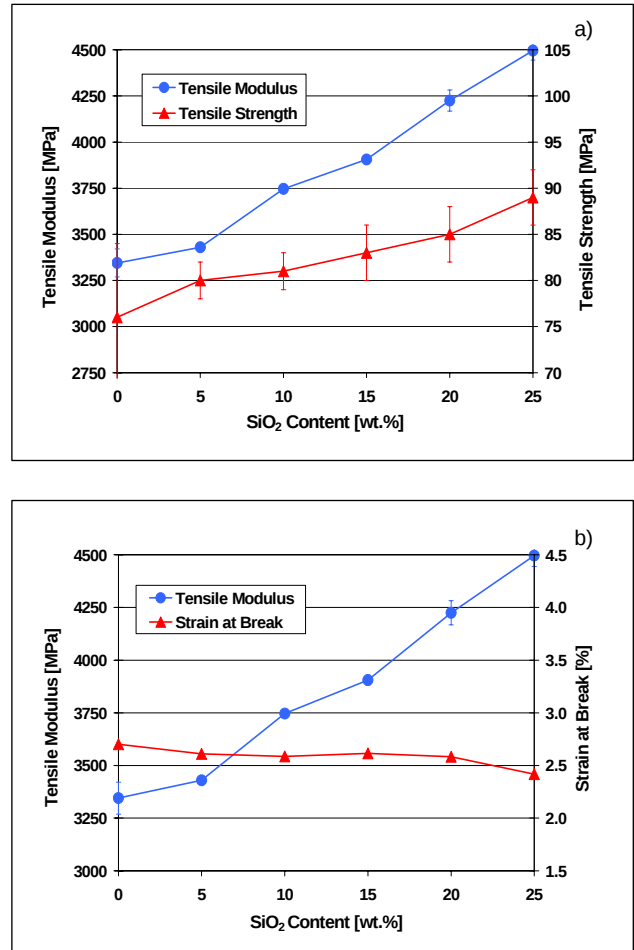


Fig. 10: Tensile characteristics vs. SiO_2 content of SiO_2 /epoxy resin nanocomposites.

4.2 GFR Nanocomposite Results

Subsequently the SiO_2 nanocomposites were used as a new matrix system for GFRP composites. On the basis of the preliminary results obtained with the SiO_2 -modified nanocomposites (see Chapter 4.1), 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 Fig. 11 and 12.

¹ Matrix density measurements: EP reference: 1.21 g/cm³; EP nanocomposite (25 wt.% SiO_2): 1.34 g/cm³.

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 SiO_2 nanoparticle-filled GFRP plates as compared to the unfilled reference is evident (see Table 1 and Figure 11ab). 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 SiO_2 content (Fig. 11b 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 (Fig. 11ab).

The small difference in density between the unfilled GFRP reference ($\rho = 2.05 \text{ g/cm}^3$) and the GFRP composite with 25 wt.% SiO_2 ($\rho = 2.10 \text{ g/cm}^3$) is consistent with lightweight design. However, a further increase of the SiO_2 fraction may be reason for concern due to the aspects of process technique and a detrimental effect on the structure as mentioned in Chapter 4.1. For this reason, the optimum of the material so far is being limited to a nanofiller content of up to 25 wt.% SiO_2 (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.% SiO_2 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

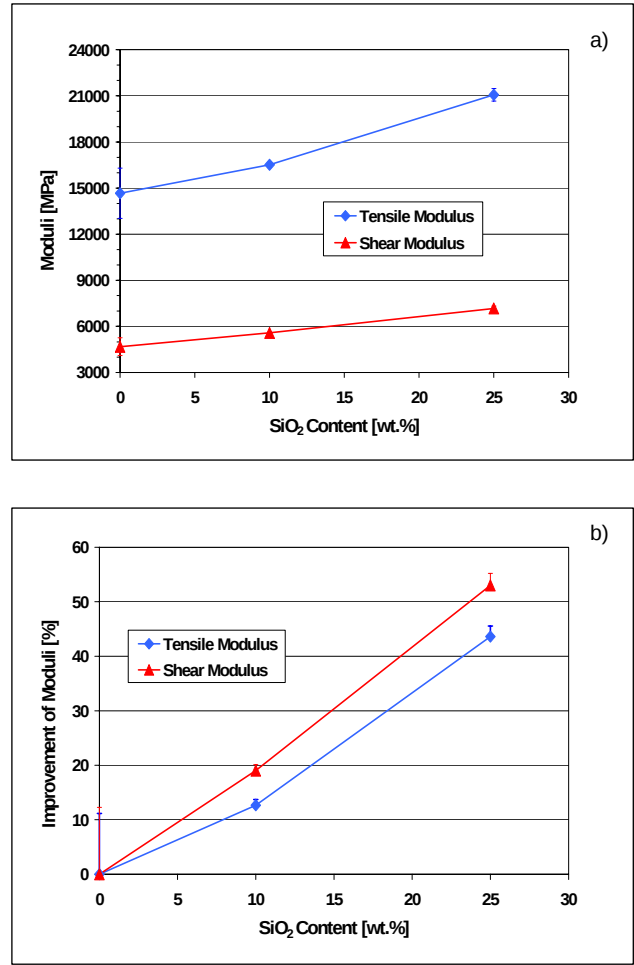


Fig. 11: Stiffness of GFRP composites with varying nanoparticle content absolute (a) and relative (b). Nanoparticle content: 0–25 wt.% SiO_2 relative to epoxy resin. GF content: 60 vol.% fabric ($\pm 45^\circ$); matrix: epoxy resin.

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.% SiO_2 (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 (Fig. 12). Whereas the reference material shows a broad transition from the damage-free (linear-elastic) to the damaged area, the nanofilled 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 $\varepsilon > \text{approx. } 0.4 \%$, whereas this is observed with the nanomaterial only from $\varepsilon > \text{approx. } 0.6 \%$. 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).

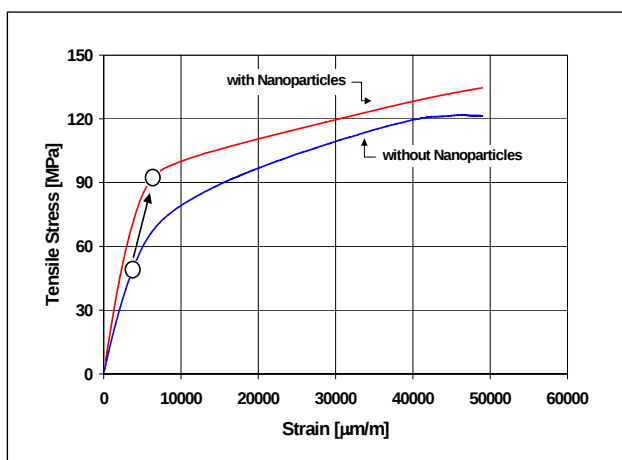


Fig. 12: Stress-strain diagram from tensile tests of filled and unfilled GFRP composites. Nanoparticle content: 25 wt.% SiO₂ relative to epoxy resin. GF content: 60 vol.% fabric ($\pm 45^\circ$); matrix: epoxy resin.

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.

5 Summary

Future fibre composite materials for use in aerospace applications 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 SiO₂ nanocomposite shows that it is possible to directly improve the performance parameters of the polymer matrix (improvement of the mechanical and thermo-physical 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/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 composites. The greater damage tolerance – measured under static conditions – should also lead to an improved composite behaviour under dynamically changing 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 (e.g. by using the LRI technique) make this new class of materials particularly interesting for use in many aerospace applications.

6 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 materials of aerospace structures, 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.

Actually spherical and layered silicates, POSS (Polyhedral Oligomeric Silsesquioxanes) and carbon nanotubes (CNT) are currently undergoing intensive research as interesting nanoparticle classes for space structures [7]. 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)

7 References

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