COMPRESSIVE STRENGTH: THE KEY TO FUTURE CFRP PRODUCTION

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OVERVIEW

Besides the prepreg technology as manufacturing technology for carbon fibre reinforced composites (CFRP), the wish for cost-efficient production and reduced process times has led to the well established injection technologies, e.g. liquid resin infusion technology (LRI). material performance of component parts, The manufactured by using LRI does not completely reach the one, which can be attained in prepreg technique. The compression properties have to be named as one of the main decreased material parameters compared to prepregs. To compensate these deficits an innovative solution was invented at the DLR. Institute of Composite Structures and Adaptive Systems. By using LRI and nanoparticles filled epoxy matrix, an enormous improvement of the composite quality can be achieved. Surface modified boehmite nanoparticles and SiO₂ nanoparticles reduce the epoxy resin shrinkage and enhance its strength and stiffness considerably. Thus, the residual stress is reduced and the mechanical properties are improved. Due to that new matrix quality, the CFRP compression properties are significantly enhanced without adverse impact on other material characteristics. CFRP with boehmite filled matrices demonstrate even disproportionate increases of compression properties compared to the resin enhancements. It is assumed, that the surface functionalisation of the boehmite particles leads to a stronger fibre-matrix adhesion and therefore to a reduction of the inter-fibre fractures and exponantiate all resin improvements. The improved material properties of the fibre reinforced nanocomposites as well as the costefficient manufacture generates a new class of materials particularly interesting for use in many aerospace applications.

1. INTRODUCTION

For use in aerospace applications, CFRP must have a very high degree of capability, reliability and safety and must be cost-efficient. To achieve these goals it is essential to figure out an optimized combination of fibre composite material and its manufacturing process. At present the prepreg technique is the most common manufacturing technology for high-performance composites in aerospace. However, in spite of the good composite quality, the extreme production costs are a grave disadvantage. Injection techniques have proven to be good alternatives over the past few years [1-3]. Compared to the prepreg technique, the crucial factors of the injection method are the lower manufacturing costs as the result of using cost-efficient resins and semi-finished fibre products. Though, the property level of composites manufactured with the injection method is still not completely comparable with the one of the prepreg

composites. Present results carry the assumption, that the deficit in compression strength and transverse tensile strength is based on lower stiffness and higher volume shrinkage of the polymer systems which leads to residual stress in the laminate. In order to prevent these lower material properties, the DLR Institute of Composite Structures and Adaptive Systems has figured out an innovative way. The goal is to eliminate the disadvantages of the injection technique during the manufacture of highperformance fibre composites and simultaneously improve the composite material qualities. By adding nanoparticles (1-100nm) to the resin as filler for high-performance matrices, remarkable improvements in the mechanical and thermo-physical properties of the polymer are obtained. These nanocomposites offer increased strength, stiffness, reduced matrix shrinkage and lower thermal expansion of the polymer matrix. The dimension of matrix improvement due to nanoparticles is decisively affected by the degree of dispersion. Therefore an optimized dispersion technology for different nanoparticles, depending on their character, size, aspect ratio and surface modification was developed and is still in process. If an efficient dispersion is achieved, the polymer matrices will effectively be reinforced, leading to higher performances in the composite. For the manufacturing process of CFRP with nanoparticle reinforced matrices the Single-Line-Injection technique (SLI) that was developed and patented at the institute [3] is used. This paper gives a status report of the workings so far and first eminent results in this new research field.

2. MATERIALS AND METHODS

Two various nanoparticles are investigated for materials reinforcement in that study. A system based on silicon dioxide (SiO₂), a commercially available nanoparticleformulation (master batch), and boehmite epoxy nanoparticles, available as powder are characterised. The SiO₂ particles were manufactured by means of a sol-gel technique and grew directly in the polymer matrix [4]. Their size can be adjusted through quenching processes (d=8-50nm). An established and aviation-approved anhydridecuring epoxy resin was used as the polymer matrix and cured in a standard cycle. The surface modified (aminosulfonic acid) boehmite particle clusters (d=40µm), consisting of 14nm size primary particles, had to be dispersed at the institute. The same neat epoxy resin was used as dispersion medium (matrix) and than cured in same cycle.

In order to receive optimised parameter separation in CFRP, different unidirectional CF fabrics with various geometrical imperfections and sizings but comparable material properties were investigated. The SLI procedure was chosen to fabricate the laminates. The curing cycle was identical to the one, used for the pure resin. Both nanoparticle filled matrix systems were used to investigate

material properties of nanocomposites compared to neat resin, as well as for the comparison of nanoparticle reinforced CFRP and neat resin injected carbon fabric.

3. PREPARATION AND CHARACTERIZATION

3.1. Nanocomposites

For the boehmite nanocomposites, a certain dispersion technology had to be gualified. By using a combination of dissolver and bead mill, high shear forces are provided to desagglomerate the boehmite clusters. In order to obtain a detailed view on the particle size distribution of the dispersion, the boehmite/epoxy mixture was injected into a rotating disc centrifuge, which measures via light absorption the particle sizes [5]. Thus, the adequate milling time for the system could be determined. A high loaded master batch was manufactured. The boehmite/epoxy dispersion was than mixed with a certain part of neat resin in order to produce various nanoparticle concentrations. Subsequently the dispersions were directly introduced into the resin-curing agent system and cured in casting moulds. Supplemental to the dispersion characterisation by disc centrifuge, the cured samples were observed by scanning electron microscopy (SEM) to obtain a further view on the particle size distribution and the type and shape of the nanoparticles The nanoparticle reinforced samples and neat epoxy resin samples as references were than characterised in terms of their thermo-physical and mechanical properties. Tensile, impact and fracture toughness tests in accordance with the German industry standard DIN were performed in order to determine essential parameters of the materials In addition, the viscosities, resin shrinkage and glass transition temperatures (DSC) were determined. Thus, we managed to receive the influence of the concentration of nanoscaled boehmite on the range of properties of the reaction resin.

The particle size distribution of the SiO_2 /epoxy formulation was controlled by photon cross correlation spectroscopy (PCCS) [6, 7]. Afterwards, portions of the preconditioned master batch of silicon dioxide (40wt. %) were mixed with a certain part of neat resin and introduced directly into the resin-curing agent system in order to also produce various nanoparticle concentrations. Subsequently, the resin formulations were cured in casting moulds. The matrix systems were characterised accordingly to the methods used for the boehmite nanocomposites.

3.2. Carbon-Fibre-Reinforced Nanocomposites

Selected nanocomposite formulations were then used as novel matrix systems for CFRP composite materials. The composites were manufactured according to single line injection technique (SLI). Unidirectional CF fabrics were selected as the reinforcement material. The fibre volume fraction of the CFRP was comparable with negligible variations from 59 to 61vol. % in all cases. The novel fibrereinforced nanocomposites were subjected to extensive mechanical testing. As described in precedent chapters, the deficits compared to laminates consisting of prepregs are mainly present in compression properties. Thus, Celanese tests were performed to detect at high sensitivity the influence of the nanoparticles on the properties of the composites. For quantification of the improvement of the properties, conventional CFRP composites, without filler, were manufactured from each fabric to serve as reference materials.

4. RESULTS AND DISCUSSION

4.1. Nanocomposites

4.1.1. Dispersion - Particle Size Distribution

The predispersed nanoparticulate SiO_2 formulation was mixed into the epoxy resin by using a magnetic stirrer. 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. 1).



FIG 1. Particle Size Distribution and integral particle size distribution of SiO2 particles by PCCS

SEM 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 Fig. 2).



FIG 2. SEM image of a SiO₂-epoxy nanocomposite (25wt. %)

For the surface modified boehmite nanoparticles a new dispersion technology was invented, introducing high shear forces into the formulation in order to separate the functionalised primary particles. Therefore boehmite powder was added to neat epoxy resin and stirred in dissolver. Afterwards the mixture was dispersed in bead mill to achieve a homogeneous, nanoscaled suspension.

By using a rotating disc centrifuge the changing particle size distribution of the mixture during the dispersion process can be measured. As can be seen in Figure 3, after 90 minutes milling time the particles cannot further be separated, they reagglomerate. That can be explained by the proceeding decompose of the particle agglomerates to smaller particles. At certain particle sizes, the attracting energies exceed the repulsive energies [8]. Hence, 90 minutes milling time is chosen to disperse the boehmite particles.



FIG 3. Particle size distribution of boehmite particles by disc centrifuge after different hours milling time



FIG 4. SEM image of a boehmite-epoxy nanocomposite (15wt. %)

After curing, the distribution is verified by SEM observation (Fig. 4), as it has been accomplished to the SiO_2 formulation. That demonstrates 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 thermo-physical and mechanical analysis.

4.1.2. Thermal Properties

Isothermal viscosimetry was used to investigate the injectability of the nanocomposites. The increase of the filler content up to 25wt. % SiO₂ and 15wt. % boehmite at a typical injection temperature of 80 °C, leads to a reduction in pot life (Fig. 5). However, the reduction in pot life as well as the small increase in initial viscosity are negligible and are no problem for production purposes

(Fig. 5; Limiting viscosity number line at 500mPas; applies to SLI technique). With regard to a normal injection time of maximum 30 minutes, there are no remarkable differences. This shows that the injectability is retained in the modified resins.



FIG 5. Isothermal viscosity-time curves of SiO₂/epoxy resin with varying filler contents at 80°C and a shear rate of 4/s

The glass transition temperature (Tg) was determined by DSC. Interestingly, the Tg can be increased with SiO_2 nanoparticles, but decreases again with increasing filler content though none of the values was lower than the reference resin value of 123 °C. The Tg of boehmite nanocomposites increases also with low filler content, but drops below the Tg of the neat resin (Fig. 6). Some studies [9] indicate to that phenomenon a weaker filler-matrix adhesion. Possible other reason can be found in rising humidity in the composite with higher particle content. Currently, that effect is not clear and further studies are needed.



FIG 6. Differences in glass transition temperature with various filler contents of boehmite and SiO₂

Measurements of the density showed chemical resin shrinkage to be reduced by approx. 50% at a nanoparticle content of only 25wt. % (Fig. 7). Concerning the non-linear thermal expansion of the nanoparticle reinforced resins, it can be assumed that the thermal shrinkage, in addition to the chemical shrinkage, can be reduced disproportionate. Nanocomposites also present earlier starting cross linking which leads to a more gentle curing process. The enormous reduced resin shrinkage and the gentle curing process causes the reduced internal mechanical stress (shrinkage stress) in the composite, which improves the applicability of the material (higher tolerance to damage).



FIG 7. Normalized volume shrinkage of SiO₂ nanocomposites with different particle contents at RT

4.1.3. Mechanical Performances

The results of the mechanical tests versus pure resin are shown in Fig. 8. The increase in stiffness and strength of the SiO₂ nanocomposites with increasing silicon dioxide content is clearly evident. The filler content of up to 25wt. % SiO₂ investigated in this study improved the tensile modulus by up to 34% and the tensile strength (ultimate) up to 17%. The stiffness of nanocomposites containing boemite particles is increased by 24% while the tensile strength gained 12%. The fracture toughness, only investigated with SiO₂ nanocomposites, rises with rising filler content over 70% enhancement. Concerning the strain at break, all samples containing SiO₂ reached higher the boehmite nanocomposites. values unlike to Consequently for SiO₂ nanocomposites, improved stiffness and strength can be implemented without any loss (compared to neat resin) of essential material properties. Both the strength and the stiffness values show a continuous linear increase over the range of filler contents investigated (Fig. 8). 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 20wt. % SiO₂ and 10wt. % boehmite (Fig. 8). However, this negative effect is more than compensated by the significant increase in the stiffness and strength of the polymer matrix in such a matter that the current maximum for the material was limited to a filler content of up to 25wt. % for SiO2 and 15wt. % for the boemite particles. If this maximum presents also the optimum, that needs to be confirmed in further experiments.



SiO₂ /Boehmite Content

FIG 8. Normalized values of nanocomposites based on neat epoxy data

In summary, the structural-mechanical and thermophysical properties of a high performance epoxy resin were improved significantly with the use of different reasonably-priced nanoparticle systems. The limit of optimal usage range of the EP resin tested in the present study is at a nanofiller content of 25wt. % SiO₂ and 15wt. % of boehmite. A further increase of the filler fraction is expected to cause problems related to process technique (dispersability and reduced pot life) and to induce effects that are detrimental to the structure of the material (increasing brittleness of the matrix). The slight increase in the density of the matrix can be disregarded in this context and does neither contradict the aspect of lightweight design nor the overall consideration of the CFRP composite in Chapter 4.2.

4.2. Carbon-Fibre-Reinforced Nanocomposites

Subsequently the SiO₂ and boehmite nanocomposites were used as new matrix systems for CFRP composites. On the basis of the preliminary results obtained with the SiO₂-modified and boemite-filled nanocomposites (see Chapter 4.1), the nanoparticle content was selected to 25wt. % (relative to the EP resin) of silicon dioxide and 15wt. % of boemite. The CFRP laminates were manufactured using resource-efficient resin injection technique (SLI). The fibre volume fraction was measured by incineration of small samples of each laminate. All laminates exhibit fibre volume fraction between 59vol. % and 61vol. %, which represents the aeronautic standard. Samples of each laminate were tested in Celanese-compression tests. The structural-mechanical results obtained with the CFRP laminates are shown in Fig. 9.



FIG 9. Normalized values of CFRP nanocomposites based on CFRP with neat epoxy

Compression tests indicate multiaxial stress to the laminate. The microstructure shows failure based on strength and rigidity. Hence, the stiffness and strength of the matrix and the fibre matrix adhesion is of great interest. These material properties are considerable enhanced by nanoparticles. Therefore the compression tests are well suited for nanoparticle reinforced fabrics and supplemental to that, the compression properties are one of the most decreased materials properties in CFRP manufactured by injection technology.

The significant increase in the strength with SiO_2 and boehmite matrices (SiO_2 : + 33%; boehmite: + 31%) and strain at break (SiO_2 : + 31%; boehmite: + 22%) of the SiO_2 nanoparticle-filled CFRP laminates as compared to

the unfilled reference is evident (Fig. 9). In general there is an increase of the strength and strain at break values of every laminate containing nanoparticles. Enhancements of all properties present the woven fabrics with SiO₂ and boehmite fillers. In all cases, the increasing strength and strain at break can be ascribed to higher stiffness and reduced resin shrinkage of the nanoparticle reinforced matrix, which leads to reduced residual stress. These matrices can carry higher shear loads to the fibres and prevent micro-buckling by bearing the fibres up to higher loads. That mechanism is demonstrated by the woven fabrics, while interfering crimps rest between the plies of the unwoven fabrics. Both, the SiO2 and boehmite filled matrices increase the stiffness of the woven fabrics. The absolute values of all CFRP are presented in Table 1. Concerning the woven fabrics, the enhancements relating to the values of the nanocomposites do not confirm. The increase of the compression properties of the CFRP filled with 15wt. % boehmite is compared to 25wt. % SiO₂ filler content in relation to their pure resin properties clearly disproportionately high. The aminosulfonic acid as surface modification of the boehmite nanoparticles is assumed to cause that enormous enhancement of properties. That acid seems to have a positive influence on the fibre matrix adhesion and accordingly reduces inter-fibre fractures and delaminations. The general performance of the both, the SiO₂ and the boehmite composites 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). The expansion of the damage-free range, measured under static conditions, can be expected also to improve the properties of the composite vibration stability. These considerations as well as the influence of different surface acids need to be confirmed in further studies.

Para meter	Ref. Fabri c 1	Fabri c 1 SiO2	Ref. Fabri c 2	Fabri c 2 SiO2	Ref. Woven Fabric	Woven Fabric, SiO2	Woven Fabric, Boeh mite	
Youngs Modulus [GPa]	124	121	111	108	115	119	126	
Compression Strength [MPa]	987	1144	777	876	855	1137	1123	
Strain at Break [%]	0,82	1,00	0,73	0,85	0,77	1,01	0,94	

TAB 1. Compression Parameter, 25wt. %SiO2 and 15wt. % boehmite, different fabrics

The results of the nanoparticle reinforced CFRP are very good reproducible. The variances are at the same level as the ones of the pure CFRP. That indicates high dispersion quality and therefore a very homogeneous particle distribution within the composite. Fig. 10 presents the matrix of a SiO₂ reinforced fibre composite. As a result, local inhomogeneities due to filtering effects can be excluded. This demonstrates that we successfully achieved the targeted manufacture of fibre-rein-forced nanocomposites by means of an injection technique.



FIG 10. SEM image of the matrix of CFRP with SiO₂reinforced epoxy resin (25wt. %)

Figure 11 presents fibres and matrix of different CFRP compression test samples, both outside the fracture zones. On the left side there can clearly be seen inter - fibre fractures, while the right matrix is still in good order. The left picture represents a CFRP without nanoparticles, while the fibres on the picture on the right side are surrounded by nanoparticle reinforced CFRP. The stronger adhesion is obvious.



FIG 11. SEM-image of debonding (woven UD fabric without nanoparticle filled matrix) (left) and strong fibre matrix adhesion (woven UD fabric with nanoparticle filled matrix) (right)

5. SUMMARY

Future fibre composite materials for use in aero-space 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 help to meet these central requirements. The examples of a SiO_2 and boehmite nanocomposites show that is possible to directly improve the performance parameters of the polymer matrix (improvement of the mechanical and thermo-physical parameters, reduction of resin shrinkage). The

nanoparticle reinforced resin 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 particularly be disproportionately transferred to fibre composite structures that were made with the SLI technique. Depending on the fabric, enhancements of compression strength and strain at break about 30% were realized. The stiffer nanoparticle filled matrices with reduced resin shrinkage prevent microbuckling and delaminations at early stage. Thus, the residual stress is reduced and the mechanical properties are improved. The significant increase of all parameters with the boehmite filled matrix is assumed to a perfect suitable surface modification of the nanoparticles. That aminosulfonic acid leads to a stronger fibre-matrix adhesion and therefore to a reduction of the inter-fibre fractures and improvement of the over-all material performance in comparison to unfilled fibre composites. The greater damage tolerance, measured under static conditions, should also lead to improved composite vibration stability. The increased 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 costefficient 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 as well as the optimization of the nanocomposites. Particularly the transferability of each of the new resin characteristics, concerning especially the surface modification influence, to high performance composites (CFRP) needs to be researched.

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