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Improving mechanical properties of fiber-reinforced composites based on epoxy resins containing industrial surface-modified silica nanoparticles: review and outlook

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Abstract

Surface-modified silica nanoparticles, 20 nm in diameter and with a very narrow particle size distribution, are available as concentrates in epoxy resins in industrial quantities since 10 years. They improve many different properties like strength, modulus, toughness and fatigue performance. Some of these improvements can be found for fiber-reinforced composites as well. In this review, the research results obtained with commercial silica nanoparticles published in the last decade are studied, results are compared with a focus on mechanical properties and the mechanisms responsible for the property improvements are discussed. Silica nanoparticles present only in the interface between fibers and resin matrix might be a very promising approach for future cost-sensitive applications.

Keywords

Epoxy, silica nanoparticles, toughening, fiber-reinforced composites

Introduction

The use of fiber-reinforced composites is the key to lightweight construction, which is indispensable for modern life. Aerospace, automotive, shipbuilding or railway, rotor blades for wind energy generators or sports equipments – the applications for fiber-reinforced composites are manifold. Glass or carbon fibers, woven, unidirectional or multiaxial, are the most common reinforcements. Thermoplastic or thermosetting materials are used as matrices.

In many high-performance applications epoxy resins are used as matrix materials. All known manufacturing technologies for fiber-reinforced composites are used in the industry in combination with epoxy resins. Ski poles are made by using filament winding of carbon fibers in combination with anhydride cured epoxy resins. Machine parts are manufactured by using amine cured glass fiber prepregs. Profiles are produced by pultrusion using liquid resin systems. Aerospace parts are made by using carbon fiber prepregs based on tetrafunctional epoxy resins cured with aromatic amines in an autoclave. The most popular manufacturing technologies are injection technologies like resin transfer moulding (RTM), single-line injection (SLI), vacuum-assisted resin transfer moulding (VARTM) etc. due to the relatively short manufacturing cycles. Rotor blades for wind energy generators are manufactured mainly by using vacuum-assisted infusion techniques. However, the viscosities of the resin systems used for injection technologies need to be low.

In engineering composite parts, e.g. a crank shaft for a sports car, the reinforcing fiber or fabric are non-woven and their orientation towards the force along the part are of utmost importance. However, the choice of resin and hardener is important as well – to match performance as well as production cycle needs. Of course any improvement of the resin performance is welcome to help to improve the performance of the composite parts.

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Mineral fillers like calcium carbonate or quartz powder can improve mechanical properties of epoxy resins like strength, stiffness and modulus. However, they do increase the viscosity of the resin significantly. Due to their size, typically microns, they cannot be used in injection manufacturing methods because they are filtered out by the fabric upon injection. In prepreg manufacturing they tend to sediment in the process. Thus in most composites applications no mineral fillers are used.

In the years 2002/2003, the first commercial grades of surface-modified silica nanoparticles were introduced into the market. They are manufactured in situ directly in the epoxy resin by a modified sol–gel process. The spherical particles have an average diameter size of 20 nm and a very narrow particle size distribution.[1] Figure 1 shows the particle size distribution determined by small angel neutron scattering (SANS).

In a recent, extensive review, the property improvements of epoxy resins modified with silica nanoparticles have been investigated.[2] Incorporated into cured bulk epoxy resins, regardless of the hardener choice, they do improve several properties like strength and modulus (as expected for mineral particles). Furthermore, they improve toughness which is less obvious, but a known effect when using glass microspheres in epoxy formulations. Cyclic fatigue performance can be improved significantly, by several hundred percent.

Used in resin systems for composite applications, they offer several advantages: being 20 nm small and completely monodisperse, they do increase the resin viscosity only slightly at higher addition levels. In contrast to fumed silica they do not exhibit thixotropic properties but behave like a Newtonian liquid. Due to their size they can easily penetrate even close-meshed fabrics in composites manufacturing when being injected. Figures 2 and 3 show TEM pictures of glass fiber reinforced composites (GFRC) made by using an epoxy resin containing silica nanoparticles.[3] The laminates have been made by using VARTM. The uniform dispersion of the particles is evident and the difference in size between fiber and particle is obvious – thus it is self-explaining why there is no gradient in nanosilica distribution even after quite a distance from the point of resin injection.

Further, the silica nanoparticles can be used in prepreg manufacturing as they do not sediment – in contrast to larger particles. Being completely transparent, they can even be used in composite parts where the surface appearance matters, e.g. in sports car parts like roofs or car body side panels as well as interior surfaces or in sporting equipment like golf clubs, helmets or ski poles.

As silica nanoparticles are a very attractive raw material for epoxy resin formulators, they are used today, 10 years later, in many industrial composites applications. They improve various properties like tensile strength, tensile modulus, flexural stiffness, toughness and scratch resistance.

Very important for many applications is the significant improvement of fatigue performance that the nanosilica modification of the epoxy resin provides to the fiber-reinforced composite part. Thus many

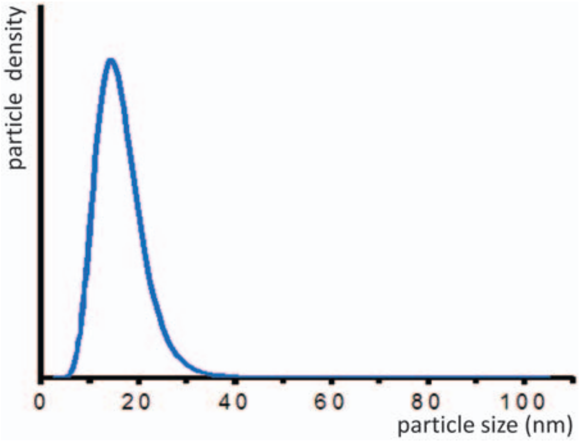

Figure 1. Particle size distribution of silica nanoparticles determined by SANS.

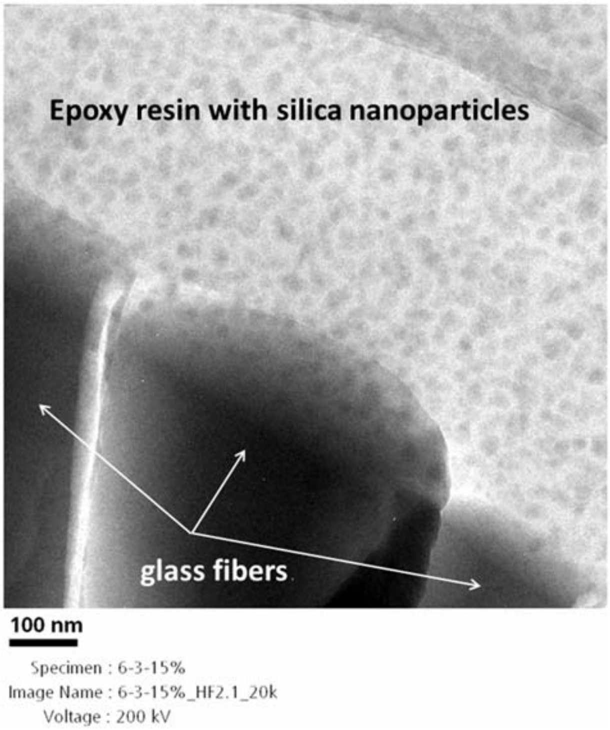

Figure 2. TEM picture of GFRC with 15 wt% silica nanoparticles.

fiber-reinforced composites in automotive, machine building or recreational equipment do contain silica nanoparticles. Aerospace applications will follow soon.

Nevertheless, it is a difficult task to determine the optimum addition level in function of resin and hardener used. Very often the improvements found for a modified bulk resin[2] are not translated into the fiber-reinforced composite made from this resin.

Mechanical properties of fiber-reinforced materials like tensile strength and tensile modulus or compressive strength and compressive modulus are considered to be fiber-dominated. Other properties like fracture toughness (K_{Ic}) and fracture energy (G_{Ic}) are considered to be matrix-dominated, as the crack is inserted into the test specimen in between the layers of fibers. Compressive properties (before and after impact) are influenced by both fiber and matrix.

The fiber or fabric or textile used as reinforcement is therefore a further variable which needs to be taken into consideration. Of course many research results have never been published but converted into industrial formulations.

The aim of this review is to give a comprehensive overview regarding the actual state of research, to understand the mechanisms of property improvements of bulk resins as well as laminates and to provide formulating guidelines. First results for laminates with nanosilica at the fiber/matrix interface are presented.

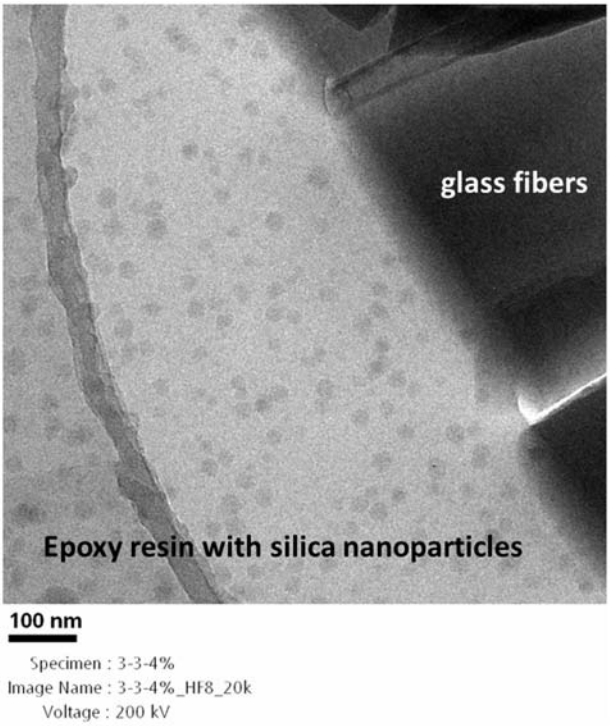

Figure 3. TEM picture of GFRC with 4 wt% silica nanoparticles.

Discussion

If not mentioned otherwise, the researchers cited used commercial 40% (by weight) concentrated masterbatches of surface-modified nanosilica in diglycidyl ether of bisphenol A (DGEBA) with an average diameter of 20 nm and a very narrow particle size distribution. These were then diluted using commercial epoxy resins to vary the nanosilica concentrations.

All investigations revealed a very good dispersion of the nanosilica particles; typically determined by transmission electron microscopy (TEM).

Glass fiber-reinforced epoxy resin composites

Amine-cured epoxy resin systems. Tsai et al.[4,5] prepared laminates by impregnating one layer of unidirectional (UD) glass fiber (E-glass) and subsequent addition of further layers until 12 layers have been impregnated. Cure was performed in a press under vacuum. The DGEBA epoxy resin was cured with an industrial isophoronediamine. They reported an increase in fracture energy (G_{Ic}) of the bulk resin by 47% at a loading level of 10 wt% nanosilica and by 84% at 20 wt% nanosilica. G_{Ic} of the laminate was increased from 0.83 kJ/m^2 to 0.90 kJ/m^2 at 10 wt% silica nanoparticles in the resin, which equals an improvement of only 8%. At 20 wt% an increase in G_{Ic} of 15% was reported.

In continuation of this work they investigated in-plane shear strength and off-axis compressive strength.[6] DGEBA and a short-chain polyether diamine as curing agent were blended to prepare thin laminates (1.45 mm, 5 layers of UD, 10° off axis). Again hand lay-up and cure under pressure and vacuum were used. The in-plane shear strength was increased from 23.7 MPa to 27.5 MPa at 5 wt% silica nanoparticles to 30.1 MPa at 10 wt% and 29.6 MPa at 20 wt% loading level. This equals improvements of 16%, 27% and 25%, respectively.

To test the off-axis compressive strength thick laminates (6.15 mm, 22 layers of UD, 0°, 5°, 10°, 15° and 90° off axis) were prepared. The unmodified control was compared to a system with 20% of silica nanoparticles. The improvements were different for the different fiber orientations: +7% at 0°, +17% at 5°, +6% at 10°, +6% at 15° and +2% at 90°. For 0° the failure mechanism was dominated by fiber splitting. At 90° the out-of-plane shear failure mechanism was observed. For 5°, 10° and 15° the main failure mode was microbuckling where improvements can be expected to be found as the silica nanoparticles do increase the modulus of the epoxy resin matrix.

Tate et al.[7] used a commercial epoxy resin system, aliphatic amine cured, which they modified with silica nanoparticles. They used a −45°/90°/+45° bidiagonal stitched bonded fabric (E-Glass) and VARTM to prepare the laminates (5.95 mm, 8 layers of fabric). Tensile strength was improved from 92.1 MPa to 122.4 MPa at 6 wt% silica nanoparticles, which equals an improvement of 33%. At 7 wt% 109.5 MPa and at 8 wt% 101.4 MPa could be achieved. A similar behaviour was found for the modulus which increased from 10.3 GPa to 13.2 GPa at 6 wt% nanosilica, again an improvement of 29%; 7 wt% and 8 wt% achieved only 12.8 GPa and 11.7 GPa, respectively; which might indicate the existence of a plateau in performance. Or, there might be further improvements found at 10 wt% or 15 wt% addition levels – which have not been investigated.

The interlaminar shear strength (ILSS: ASTM D 2344) showed the same tendency: it went up from 24.5 MPa to 31.0 MPa (+27%) with 6 wt% silica nanoparticle modification. With 7 wt% and 8 wt% 30.1 MPa and 29.8 MPa were obtained. A slightly different picture was found for flexural strength and flexural modulus. Strength increased from 146 MPa to 177 MPa to 181 MPa and 180 MPa. Modulus was improved from 25.0 GPa to 29.5 GPa to 30.5 GPa to 30.7 GPa for 6 wt%, 7 wt% and 8 wt% nanosilica.

In a different investigation we found in three-point-bending tests with laminates made by an anhydride cured system a plateau in performance improvements as well, at about 8 wt% of silica nanoparticles.

Anhydride-cured epoxy resin systems. If not mentioned otherwise, the systems investigated are all based on DGEBA, cured with methyl hexahydrophthalic acid anhydride; accelerated with a very small amount of a ternary amine.

Mahrholz et al.[8,9] published very early promising results. They made laminates with a bidirectional glass fiber at +45°/−45° orientation using the SLI technique. At a 20 wt% addition level of silica nanoparticles, the tensile strength was improved by 25%, tensile modulus was increased by 64% and the shear modulus was increased by 75%.

Kinloch et al.[10] prepared 7-mm laminates consisting of 16 plies of unidirectional glass fibres at 0°. Resin infusion under flexible tooling (RIFT) was used to manufacture the laminates, with an infusion temperature of 50°C. At 10 wt% silica nanoparticles in the matrix glass transition temperature (T_g) was lowered by 2°C, flexural modulus was slightly lowered from 39.7 GPa to 38.5 GPa (equals −3%). The interlaminar fracture energy G_{Ic} was increased from 330 J/m^2 to 1015 J/m^2, which equals an improvement of 207%. G_{IIc} was improved slightly from 1300 J/m^2 to 1380 J/m^2; which is equal to +6%.

In continuation of this work, they manufactured quasi-isotropic plates, 4-mm thick with 8 plies of glass fibers with a 0°/0° interface and performed ballistic impact testing.[11] The delaminated area of the nanosilica-containing laminates was always larger than for the unmodified control - for all impact energies tested. It seemed like the presence of nanosilica did not improve laminate properties regarding fast impact.

Sprenger et al.[12] tested similar laminates with a falling dart impact test (30 J) and could not detect any improvements. The delaminated area had exactly the same size with or without silica nanoparticles present in the resin - see Figure 4. Unfortunately, the compression after impact (CAI) test results have not been released for publication.

Kuehn et al.[13] found slightly improved CAI properties for laminates with nanosilica as will be shown in the chapter carbon fiber-reinforced composites.

The question which mechanisms of toughness improvements by silica nanoparticles apply to fiber-reinforced composites and whether they work at high speed impact will be discussed later.

Manjunatha et al.[14] investigated the tensile fatigue behaviour. They used a fabric with a +45°/−45° pattern, laid up 16 ply in a quasi isotropic sequence (+45°/−45° alternating with 90°/0°). Infusion temperature was 50°C. The tensile strength was increased from 365 MPa to 381 MPa (+4%); modulus was increased from 17.5 GPa to 18.8 GPa (+7%). The 10 wt% silica nanoparticles improved significantly the fatigue performance of the laminate. At a very high stress (225 MPa), the number of cycles until failure was more than doubled.

Further investigations compared the improvements in strength and modulus to the changes of the bulk resin system.[15] Bulk strength increased by 19%, laminate strength by 4%. Bulk modulus was increased by 17%; laminate modulus by 7%. The fatigue life of the

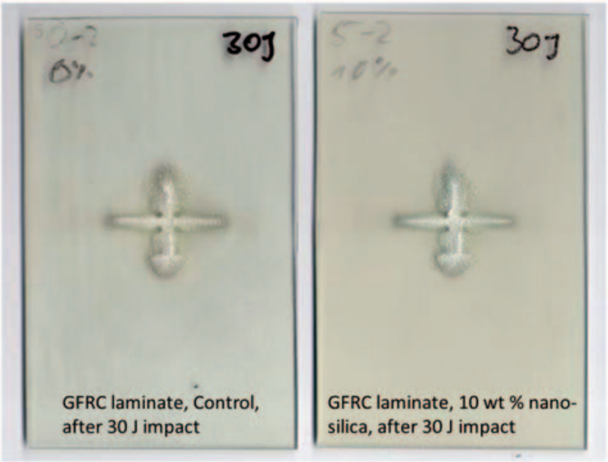

Figure 4. Photograph of GFRC after impact testing without and with nanosilica.[12]

bulk epoxy is three to four times higher for the resin with 10 wt% silica nanoparticles than for the unmodified control, as can be seen in Figure 5. The same improvement was found for the laminate. From investigations using transmission optical microscopy, it was found that the crack density after a given number of cyclic loadings was much lower. The nanosilica apparently suppresses the matrix cracking and reduces the crack growth rate which results in an enhanced fatigue life.

Kinloch, Taylor and their team prepared UD GFRCs, 12 ply, 6-mm thick and investigated the toughness[16]; 10 wt% silica nanoparticles increased the G_{Ic} from 330 J/m^2 to 1015 J/m^2, this equals an improvement of more than 200%. The bulk resin G_{Ic} was improved by 130% at 11 wt% nanosilica. They reported small agglomerates of silica nanoparticles for the bulk resin, which seemed to have no negative influence on performance. Quasi-isotropic laminates, 8 ply, 4-mm thick by using a biaxial stitched fabric laid up to give a 0°/0° interface across the fracture plane were prepared. Interestingly the G_{Ic} was lowered by the nanosilica modification from 718 J/m^2 to 626 J/m^2 (−13%). This is very probably due to the different fibre architecture. Figure 6 compares the fracture surfaces of laminates without and with silica nanoparticles. Crack propagation was in the direction of the fibers; from left to right. Disregarding the different magnifications, there seems to be no big difference for the fracture surface; both exhibit brittle failure with little plastic failure.

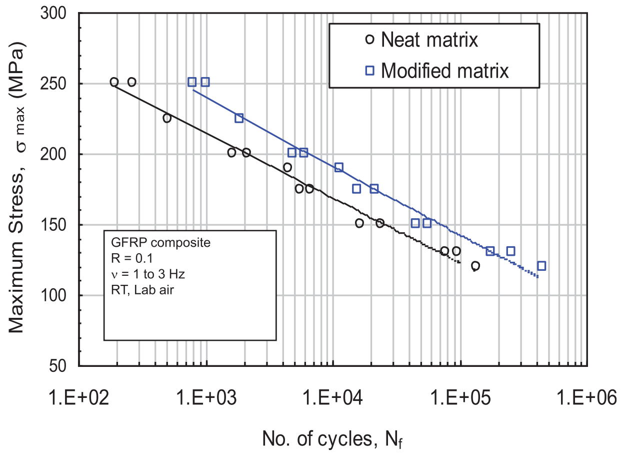

Figure 5. Stress versus lifetime for a GFRC with epoxy resin matrix; unmodified and with 10 wt% nanosilica.[15]

Carbon fiber-reinforced epoxy resin composites

Amine cured epoxy resin systems. Caccavale et al.[17] made laminates by using VARTM to infiltrate 18 layers of T300 carbon fiber in a 90°/0° lay-up. As curing agent a commercial polyamine hardener was used. The dispersion of the nanosilica in the epoxy resin was found to be very well. Fracture toughness (K_{Ic}) for the bulk resin was increased by 11% at an addition level of 3.7 wt% silica nanoparticles to 1.01 MPam$^{1/2}$. No improvement was found in the laminate, however. The initiation value of G_{Ic} was decreased by 9%; the propagation value increased by 4%, which is within the standard deviation. Impact testing showed a slight decrease of energy absorption. ILSS was increased slightly. The tests were performed for wet conditions as well, but the changes by the nanosilica addition were similar.

In the thesis more details were given.[18] Cyclic fatigue performance was not improved either by the silica nanoparticles addition. Improvements of the matrix properties could not be transformed into improvements of the laminate.

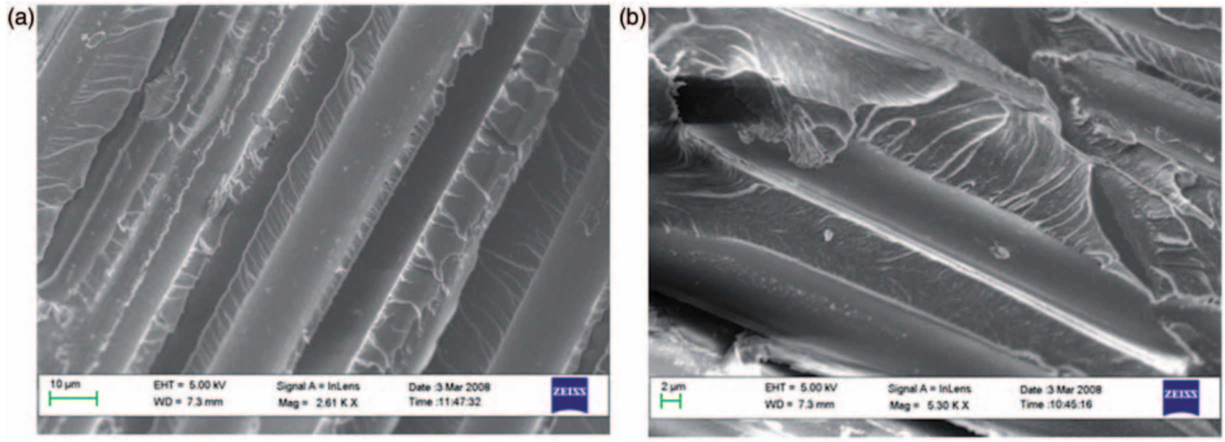

Figure 6. Scanning electron micrographs of fracture surfaces of quasi-isotropic GFRC with epoxy resin matrix: (a) unmodified and (b) with 10 wt% nanosilica.[16]

The conclusion drawn was that these properties are fiber-dominated and not improved by the nanosilica addition. However, it should rather be said that the nanosilica had no influence on toughness and fatigue performance in this case. Or, eventually higher loading levels of nanosilica are necessary to see an effect.

Tang et al.[19] used piperidine as curing agent and vacuum-assisted resin infusion (VARIM) to prepare laminates. The unidirectional carbon fiber fabric used was UT70-20 (24 layers for ILSS testing and 20 layers for mode I and mode II testing) and the resulting fiber volume fraction was 65%. The tensile strength of the bulk epoxy was increased from 64.8 MPa to 69.4 MPa at 10 wt% nanosilica and to 72.4 MPa at 20 wt% loading. Tensile modulus increased from 2.9 GPa to 3.3 GPa to 3.6 GPa. G_{Ic} increased from 237.9 J/m^2 to 457.9 J/m^2 at 10 wt% nanosilica to 666.4 J/m^2 at 20 wt% nanosilica. These are improvements of 93% and 180%, respectively.

The laminates with the modified resins were tested extensively. The G_{Ic} of the laminate (at crack propagation) was improved from 995 J/m^2 to 1007 J/m^2 at 10 wt% nanosilica and to 1203 J/m^2 at 20 wt%; an improvement of 1% and 21% only. The ILSS was lowered by the nanosilica addition by 3% and 12%. G_{IIc} was lowered as well – from 969 J/m^2 to 929 J/m^2 and to 750 J/m^2 (−23%). The conclusion drawn was that especially for the high concentration of 20 wt% of silica nanoparticles the shear strength of the matrix was reduced.

Liu et al.[20] investigated laminates made from plain woven carbon fibers, 18 ply, with a fiber volume fraction of 60%. Piperidine was used as curing agent, VARIM as manufacturing method. G_{Ic} of the laminate was improved by approx. 24% for 4 wt%, 6 wt%, 8 wt% and 12 wt% silica nanoparticles, whereas the G_{Ic} for the bulk resin is increased linearly with increasing nanosilica level for more than 100%. This could indicate a plateau in performance improvements already at 4 wt% nanosilica. Of course it has to be taken into account that woven fabrics have a big influence on G_{Ic}, which might ''hide'' some effects of the silica nanoparticles.

A completely different test specimen and totally different properties were studied by Zhang and his team.[21] They prepared short carbon fiber-reinforced epoxy resins; cured with a cycloaliphatic amine. Tenax A-385 short carbon fibers with an average diameter of 7 μm and a length of 40−70 μm were added at 10 vol% as well as 8 vol% graphite flakes. Silica nanoparticles were introduced in addition levels of 1–5 vol%. The distribution of the nanosilica was uniform; strength and modulus were increased. However, the main topic of the investigation was related to the wear properties on both rough and mirror-polished surfaces. The coefficient of friction was lowered significantly by the spherical nanosilica particles. The wear rate was improved by approximately 50%. A maximum in performance improvements was found for 3 vol% silica nanoparticles which equals approx. 5 wt%.

Sprenger et al.[22] used tetraglycidyl ether of methylene dianiline epoxy resin (TGMDA), cured with sterically hindered aromatic amines and 8 plies of 439 T fabric to prepare laminates by RTM. Fibre content was 60%. The bulk resin fracture energy was increased from 180 J/m^2 to 320 J/m^2 at 10 wt% nanosilica and lowered again to 160 J/m^2 at 19.5 wt%. The fracture energies of the laminates however were reduced significantly by more than 60% for 5 wt% and 10 wt% of silica nanoparticle addition; the laminate with 19.5 wt% was only slightly inferior to the control.

Falling dart test with 30 J impact showed no significant differences in delaminated areas for the laminates with different concentrations of nanosilica and without nanosilica. This confirms other findings for fast impact testing of GFRCs. Apparently the mechanisms of toughening found for cured epoxy resins modified with nanosilica in bulk does not apply for fiber-reinforced composites made from nanosilica containing epoxy resins; at least not for fast impact.[2] This will be discussed later.

Hackett et al.[23] studied spherical functionalized silica nanoparticles from a different source with a particle size of 84 nm. They were manufactured as well by a sol−gel method and dispersed in an epoxydized phenol novolac resin. They prepared prepregs using dicyandiamide as curing agent together with a urea accelerator and TR50S carbon fiber; 12 plies with a 0° orientation were used to prepare the laminate for compression testing; 24 plies for the flexural test specimens.

The modulus of the bulk resin was increased with increasing nanosilica addition level by more than 100% at 45 wt% nanosilica. G_{Ic} was increased by approx. 50%. Bulk strength remained unchanged up to 35 wt% and then increased slightly. The compressive strength of the laminate was increased from 1.8 GPa to 2.0 GPa at 45 wt% nanosilica which equals an improvement of 11%. At 15 wt% 1.8 GPa or an improvement of 3% were found. Flexural modulus was found unchanged even at very high addition levels of silica nanoparticles and is apparently fiber-dominated. The flexural strength was increased from 1.5 GPa to 1.9 GPa at 45 wt% (an improvement of 26%). At 15 wt% the improvement found was approximately 10%.

In continuation of this work they investigated TGMDA cured with 4,4′-diaminodi-phenylsulfone (DDS) and modified with 45 wt% of silica nanoparticles from a different source with an average particle size of 154 nm.[24] The bulk resin modulus was increased from 3.8 GPa to 7.8 GPa at 45 wt% nanosilica; fracture toughness from 0.57 MPam$^{1/2}$ to 0.76 MPam$^{1/2}$.

The coefficient of thermal expansion was reduced from 40 to 25 µm/m/°C due to the fact that 45% of organic resin and hardener had been replaced by inorganic filler. Prepregs and then laminates were made with 38 wt% silica nanoparticles, but no reference data without silica were provided. The laminate was reported to have a high strength, high compressive strength and a high modulus.

Furthermore, a DGEBA-based system was evaluated. At 43 wt% of nanosilica the tensile modulus was doubled from 3.1 GPa to 6.3 GPa, the strength was increased moderately from 56.8 MPa to 67.2 MPa and the fracture toughness was increased from 0.51 MPam$^{1/2}$ to 0.72 MPam$^{1/2}$; an improvement of 41%. Prepregs and laminates were made and tested: at 43 wt% silica nanoparticles the shear modulus was increased from 3.7 GPa to 5.1 GPa. Shear strength was improved from 53.7 MPa to 61.6 MPa and the compressive strength from 0.7 GPa to 1.0 GPa.

In recent papers they revealed more details: imidazole was used as hardener.[25,26] The prepregs were prepared using T300-3 k and T700-12 k 2 × 2 twill carbon fabrics. Four types of laminates were made, three with T300: 8 ply 0° for compression tests, 14 ply 0° for flexural testing, 36 ply +−45° for in-plane shear. The fourth was made from 1 layer T300 followed by 6 and 8 layers of T700 and finally a last layer of T300. Nanoindentation tests showed an increased strength and hardness. Vickers hardness tests revealed similar improvements.

Chiu et al.[27] investigated the property improvements of CFRC by polyacrylonitrile (PAN) nanofibers. As second control they used a system containing 5 wt% of the commercially available nanosilica. The modification with the PAN-nanomats did not really show any improvements, whereas the addition of silica nanoparticles did improve the G_{Ic} by 25–41% (depending on the fiber reinforcement and the resin/hardener system).

Anhydride cured epoxy resin systems. Soutis at al.[28] worked with DGEBA cured with 1-methyl-5-norbornene-2, 3-dicarboxylic acid anhydride (NMA) accelerated with a small amount of ternary amine. Eight layers of HTS40 12 K carbon fibres were wound dry on a frame, impregnated and cured using vacuum bag technology. The compressive properties for different addition levels of silica nanoparticles were investigated. The compressive modulus increased with increasing nanosilica content from 85.7 GPa to 132.4 GPa at 11.7 vol% nanosilica; which equals an improvement of 54%. The compressive strength increased quickly from 825.9 MPa to 1150.6 MPa at 2.1 vol%, then to 1268 MPa at 5.5 vol% (54% improvement) and finally dropped to 1172 MPa at 11.7 vol% silica nanoparticles. Strain at break did not change significantly. It is clear that the presence of nanosilica in the resin improves the compressive properties of a laminate significantly. This finding is used in quite a few industrial applications, like composite leaf springs.

Thunhorst et al.[29] used methyltetrahydrophthalic acid anhydride (MTHPA) and DGEBA to formulate a resin/hardener blend designed for pultrusion. It contained 32.6 wt% of nanosilica from a different manufacturer with a particle size of probably 86 nm.[23] Standard 12 K tows were used to prepare pultruded rods with an average fiber volume of approx. 64% and an average diameter of 1.27 cm. They reported significant processing improvements through reductions in pull force, enabling slight increases in fiber volume and line speed increase. Improvements of up to 10% were found for modulus and flexural failure stress, however this could be the result of higher fiber volumes rather than the nanosilica addition.

Sprenger et al.[30] had chosen accelerated methylhexahydrophthalic acid anhydride to cure DGEBA. The G_{Ic} of the bulk resin was increased from 100 J/m^2 to 205 J/m^2 at 4 wt% nanosilica to a plateau around 400 J/m^2 for 7.5 wt% and 11.2 wt% – an improvement of 300%. Six plies of carbon-fiber fabric were used to prepare 3-mm laminates with a 60% fiber content using VARTM technology. The flexural modulus of the laminate was improved by 2.5% from 24.5 GPa to 25.1 GPa at 12 wt% nanosilica. G_{Ic} was increased from 430 J/m^2 to 550 J/m^2, which equals an improvement of 28%.

Hsieh et al.[16] investigated the same system. The G_{Ic} of the bulk resin was increased from 77 J/m^2 with increasing silica addition level to 212 J/m^2 at 20 wt% nanosilica, which represents an improvement of 175%. Modulus was improved from 2.96 GPa to 3.85 GPa at 20 wt% nanosilica. Laminates were prepared by stacking a linen woven carbon fiber fabric (0°/90° weave) and using VARTM. The modified system contained 12 wt% silica nanoparticles. G_{Ic} was increased from 439 J/m^2 to 489 J/m^2, a minor improvement of only 11%. Figure 7 shows the fracture surfaces of the laminates with the unmodified and modified epoxy resin matrix. Apparently, the presence of silica nanoparticles has no significant influence on the fracture behaviour in this fiber-reinforced system.

The research of Liu and his team[31] was based on DGEBA as well and used a blend of methylhexahydrophthalic acid anhydride and sebacic anhydride as hardeners. The tensile strength of the bulk resin was increased from 74.0 MPa to 79.7 MPa at 2 vol% nanosilica and to 86.7 MPa at 14 vol% nanosilica. The elastic modulus was increased from 2.6 GPa to 2.8 GPA (at 2 vol% SiO_2) respectively 3.8 GPa at 14 vol% SiO_2. Single T-300 carbon fibers were embedded into the center of the test specimen mold. Single-fiber fragmentation tests were performed.

The critical break density (number of breaks / mm at failure) of the fiber was improved by 19% at 2 vol%

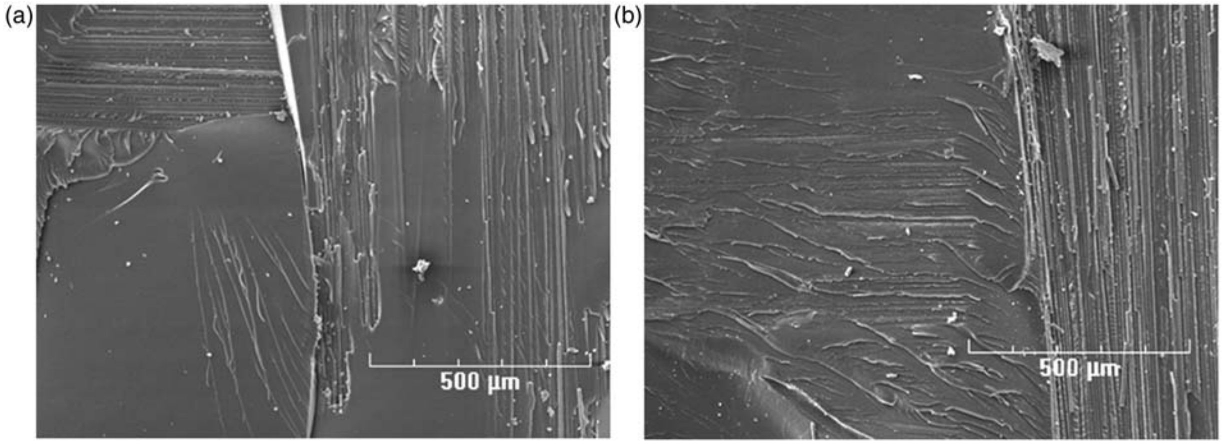

Figure 7. Scanning electron micrographs of fracture surfaces of CFRC with an epoxy matrix: (a) unmodified and (b) with 12 wt% nanosilica.[16]

and by 27% at 14 vol% nanosilica. The interfacial shear strength was calculated and showed improvements of 21% and 30%, respectively. Taking into account the results of micro-Raman spectroscopy and SEM microscopy, they concluded, two effects to be responsible: the stress transfer from matrix to fiber is made more efficient by the nanosilica particles and the nanoparticles increase the interfacial frictional stress between fiber and matrix.

Kuehn et al.[13] prepared quasi-isotropic test specimen with 4 mm thickness using 16 ply of carbon fiber fabric AUW 797-1. DGEBA containing 25 wt% silica nanoparticles was cured with MTHPA. They reported identical delamination areas for both control and modified epoxy resin at different impact energies of 20 J, 30 J and 40 J. However, the compressive strength was approx. 7% higher for the nanosilica-containing laminate after 20 J impact and approx. 5% higher after 40 J impact.

Comparison between bulk and laminate property improvements

By the addition of silica nanoparticles strength and modulus of cured bulk epoxy resins were increased, of course, depending on the epoxy resin/hardener combination, by different magnitudes.

Summing up the many details provided in the paragraphs before, it can be concluded that regardless of the fiber or fabric or nonwoven used as reinforcement and their orientations in the laminate the composite modulus is not or only slightly improved by the presence of silica nanoparticles in the epoxy resin. A similar trend was observed for the tensile strength of laminates made from woven textiles or UD laminates tested in fiber direction. These properties are fiber-dominant. Tensile tests with UD laminates in other directions than the fiber direction could reveal an effect of the nanosilica added.

Unfortunately, very often either bulk or laminate properties were studied by the researchers, but not both. Few report G_{IIc} data. Thus, Table 1 gives an overview of the G_{Ic} data provided by the researchers who investigated both bulk and laminate properties. It becomes evident that the significant improvements found for the modified bulk resins are not reflected in the fiber-reinforced laminates.

This raises question regarding the toughening mechanisms which apply for the fiber-reinforced materials and how they differ from the toughening mechanisms of cured bulk resins.

Mechanisms of toughening

The mechanisms for the property improvements of bulk epoxy resins have been well investigated and are fully understood.[2] Two main toughening mechanisms have been identified for silica nanoparticles: localised shear-bands initiated by the stress concentrations around the periphery of the nanoparticles and the debonding of the silica nanoparticles followed by subsequent plastic void growth.

In a fiber-reinforced system, additionally mechanisms like fiber bridging and fiber debonding may play a certain role; fiber pullout probably a minor one.

Mircroscopical studies of fracture surfaces revealed some differences between the laminates with nanosilica and without nanosilica at typical addition levels around 10 wt%. The fracture failure mode changes from interface failure between glass or carbon fiber and epoxy matrix to a combination of interface failure and matrix failure for the laminates with nanosilica.[4,6,16,19]

This might explain why the improvements in toughness found are relatively small compared to bulk resins,

Table 1. G_{Ic} of various bulk resins and laminates.

Reference	4, 5	4, 5	19	19	30	16	16	16
Resin/ hardener	DGEBA/ IPD	DGEBA/ IPD	DGEBA/ Piperidine	DGEBA/ Piperidine	DGEBA/ Anhydride	DGEBA/ Anhydride	DGEBA/ Anhydride	DGEBA/ Anhydride
Nanosilica (wt%)	10	20	10	20	11	11	12	20
Bulk G_{Ic} (J/m^2)	280	350	458	666	400	183	–	212
Improvement (%)	+47	+84	+92	+180	+300	+138	–	+175
Fiber reinforcement	Glass	Glass	Carbon	Carbon	Carbon	–	Carbon	–
Composite G_{Ic} (J/m^2)	900	950	1007	1203	550	–	489	–
Improvement (%)	+8	+15	+1	+21	+28	–	+11	–

DGEBA: diglycidyl ether of bisphenol A.

as the major failure "source" is still the failure at the interface between fiber and resin matrix.

Another issue to take into account is the effect of strain rate – G_{Ic} testing versus falling dart test. There is abundant literature available and discussing it would go beyond the scope of this paper. Jacob et al.[32] published a comprehensive overview for various fiber-reinforced composites.

As the modification of the matrix resin apparently has a rather small effect on fiber matrix adhesion, this could explain why we found no difference in delaminated area between control and modified system for the falling dart tests.

How much silica nanoparticles do you really need – and where?

A very interesting and promising aspect was researched by Gao et al.[33] They investigated changes in laminate properties when the silica nanoparticles are only present in the interphase between fiber and resin. Fiber sizings containing 1% of 22 nm silica nanoparticles without surface modification from a different source were prepared and applied to the unsized glass fibers. An increase in fiber surface roughness was observed. They reported superior interphase performance compared to the unsized control: strength, debonding and total energy absorption were improved. Failure modes were studied by SEM and it was found that the crack was deflected which apparently increased energy consumption.

Similar to Gao et al., Yang et al.[34] investigated changes in laminate properties with silica nanoparticles only present in the interphase between fiber and resin. They made composites based on tetrafunctional epoxy resin (TGMDA) cured with DDS. Unsized carbon fibers were prepared and treated with a sizing agent based on an epoxy resin that contained 3 wt% silica nanoparticles with an average diameter of 20 nm and a surface treatment with a silane coupling agent. Then the fibers were impregnated, prepregs made and cured in a mould.

An increase in ILSS was reported: +14% compared to unsized fibers and +5% compared to a sizing without nanosilica. They concluded that the interfacial adhesion between the fiber and the matrix is increased. The crack propagation path in the sizing layer was found to be changed by the presence of the nanosilica.

We started research activities in this area as well: composites plates of unidirectional ([0/0]) and quasiisotropic ($[+45/-45/0/90/-45/+45/90/0]_5$) layups were manufactured by resin infusion using flexible tooling method. Stitched +45/−45 and unidirectional glass fiber fabrics were supplied by Saertex. A two-part epoxy resin system (Epikote MGS RIMR 135 +Epikure MGS RIMH 137 from Momentive) was used as matrix material. Before infusion the glass fibers were dipped in an aqueous emulsion of a silica nanoparticle containing epoxy resin and dried subsequently to obtain a defined amount of epoxy resin on the fabric.

The first tests performed were fracture toughness tests. Figure 8 shows the improvements in G_{Ic} of the laminates made from pretreated UD. An additional level of 1.5 wt% aqueous emulsion equals 0.36 wt% silica nanoparticles on fiber weight; 4 wt% equal 1.12 wt% silica nanoparticles on fiber weight.

Additionally, an increase in the adhesion between fibers and matrix was indicated by the presence of a significant amount of resin bonded on the fibers when the fracture surfaces of the modified samples were observed, a feature that was not observed in the case of control fracture surfaces.

Next property to be investigated will be the fatigue performance. And the question, if some or most of the SiO_2 nanoparticles are washed off the fabric and dispersed into the matrix during the resin infusion process or if the stay at the interface fiber-matrix needs to be addressed.

If more data will confirm that for substantial improvements of the laminates it will be sufficient to apply thin layers on the fabric, this will be of huge commercial interest. Calculated on total it would

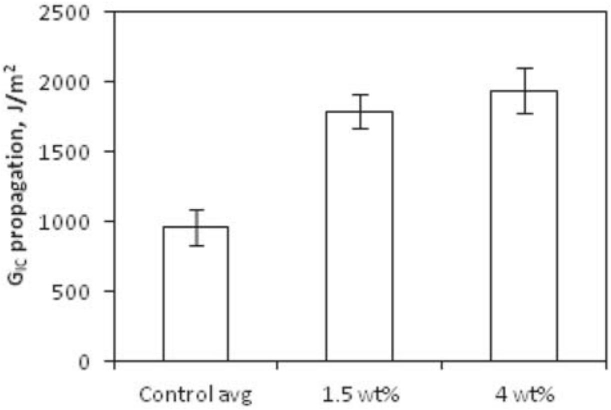

Figure 8. G_{Ic} of pretreated glass fiber reinforced composites made from commercial unmodified epoxy resin.

mean that far less than 1 wt% silica nanoparticles would be enough, which is negligible from a cost aspect – compared to modify the whole resin matrix.

Of course this field needs further future research to fully understand such systems.

Conclusions

1. Significant improvements in strength, modulus and toughness were found for bulk epoxy resins modified with silica nanoparticles. When these resins are used as matrix for fiber reinforced composites much smaller improvements were found.
2. Not taking into account the reinforcing fibers, their volume fraction and orientation respectively the layup used and disregarding the hardeners used a general outline can be given: typical improvements found for fiber-reinforced composites with an epoxy resin matrix modified with 10 wt% – 20 wt% of silica nanoparticles are increases of 5–25% in fracture toughness.
3. Most significant improvements are found for the compressive properties and for the fatigue performance.
4. Consequently many industrial composite parts today are based on epoxy resins modified with silica nanoparticles – glass fiber-reinforced as well as carbon fiber-reinforced.
5. Improving laminate properties by using silica nanoparticles in the sizing seems to be a very cost-efficient route, which needs further evaluation.
6. To push the performance levels of fiber-reinforced systems further, especially regarding toughness and fast impact, the combination of classical toughening methods with the silica nanoparticle modification is the next logical step in technology development.[35] This will be the subject of future investigation.

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Conflict of Interest

None declared.

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