

Epoxy Resin Composites with Surface-Modified Silicon Dioxide Nanoparticles: A Review

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ABSTRACT: Surface-modified silica nanoparticles, 20 nm in size and with a very narrow particle size distribution, have been available as concentrates in epoxy resins in industrial quantities for the last 10 years. They can be used in epoxy resin formulations to improve many different properties, including the strength, modulus, toughness, and fatigue performance. In this review, I examine the literature published in the last decade, compare the results with a focus on the mechanical properties, and discuss the mechanisms responsible for property improvements. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1421–1428, 2013

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INTRODUCTION

Epoxy resins are very versatile raw materials for industrial products, from windmill blades to highly sophisticated aerospace parts such as wings or fuselage to coatings and adhesives for construction. They are used in large volumes in generator encapsulations and in microelectronics and UV-cured electronic adhesives. Structural adhesives for automotive or aerospace applications, shipbuilding, or windmill blade construction are mainly based on epoxy resins. Therefore, quite a range of different epoxy resins is available: from low-viscous, short-chain aliphatics such as the diglycidyl ether of hexanediol to high-performance, multifunctional aromatic resins such as triglycidyl ether of aminophenole or tetraglycidyl ether of methyl dianiline (TGMDA). Of course, diglycidyl ether of bisphenol F (DGEBF) and its higher molecular weight variations, epoxidized novolac resins, are of great importance. However, by far, the biggest volume of epoxy resins is produced as diglycidyl ether of bisphenol A (DGEBA), the workhorse of the epoxy industry.

With regard to the many different applications and their substantially different property profiles for the materials used, a big variety of hardeners is used in industrial applications as well. An excellent and very comprehensive overview of the different hardeners used in the industry, their chemical natures, and their network formation was published by Hare^{1,2} some years ago.

Sterically hindered aromatic amines are especially suitable for densely crosslinked, high-glass-transition-temperature (T_g) aerospace formulations; they are typically used in combination with trifunctional or tetrafunctional epoxy resins.

In construction applications, low-viscosity, fast-curing amines are preferred. When they are slowed down to a certain extent, they are the hardener of choice for room-temperature (RT) curing adhesives. Nonstoichiometric hardeners such as dicyandiamide are used in large quantities by the industry for one-part heat-curing structural adhesives.

Hardeners appropriate for composites manufactured by injection methods are mainly amine-based as well, most commonly on isophorone diamine or a combination with short-chain aliphatic poly(ether amines), which tend to have lower crosslink densities but somewhat tougher networks.

Acid anhydrides, being part of the formulation in almost equal amounts to epoxy resins and exhibiting a very low viscosity, are very useful in highly filled encapsulation systems and composites made by filament winding as they lower the viscosities significantly. On curing, they form medium crosslinked resin systems.

In quite a few epoxy resin formulations, fillers are necessary. Fillers improve mechanical properties such as strength, stiffness, and modulus. However, they have a negative impact on the viscosity of the resin, which forbids their use in some applications. Furthermore, they are filtered out by the fabric when the resin formulation containing the filler is subjected to injection manufacturing methods for fiber-reinforced composites. Thus, many applications whose performance could be improved by the use of a filler do not permit the use of classical micrometer-sized fillers, and of course, fillers cannot be used in transparent applications.

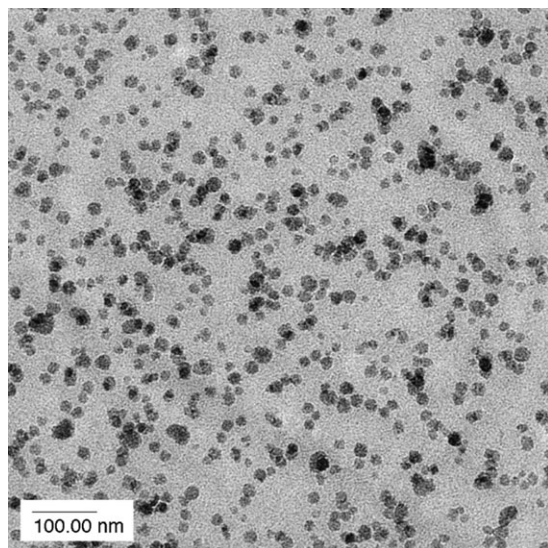


Figure 1. Transmission electron microscopy picture of cured epoxy resin with 5 wt % nanosilica.

In the years 2002 and 2003, the first commercial-grade surface-modified silica nanoparticles were introduced into the market. They were manufactured *in situ* directly in the epoxy resin by a modified sol-gel process and had an average particle size of 20 nm and a very narrow particle size distribution. Odegard et al.³ showed in their article molecular models of such particles and the huge amount of hydroxyl groups on the particle surface. The industrially manufactured particles were surface coated. The hydroxyl groups were reacted with silanes to prevent agglomeration and to compatibilize the particles with the resin. Nevertheless, there were still some remaining free hydroxyl groups, and thus, the particles were slightly acidic. One needs to keep this in mind when looking at the different additives for epoxy resins. The industrial material is very close to the model: isolated spherical particles as concentrates in epoxy resins with an average size of approximately 20 nm. Figure 1 shows a cured epoxy resin with such silica nanoparticles (5 wt %).

They offer several advantages: being 20-nm small and completely monodisperse, they do increase the resin viscosity only slightly at higher concentrations. In contrast to fumed silica, they exhibit no thixotropic properties but behave like a Newtonian liquid. Because of their size, they are transparent and can easily penetrate even close-meshed fabrics in composite manufacturing when they are injected.

Consequently, they are a very attractive raw material for epoxy resin formulators. Today, 10 years later, they are used in many industrial formulations, including encapsulating resins, adhesives, and composites such as automotive parts and machine parts. They improve various properties, including strength, modulus, stiffness, toughness, and scratch resistance. Significant improvements in the fatigue performance were reported when the epoxy resin was modified with nanosilica.

Nevertheless, it difficult to determine the optimum addition level on the function of a resin and hardener system of choice. Different and sometimes even contradicting results have been

published. The aim of this review is to give a comprehensive overview of the actual state of research with a focus on mechanical properties and to provide formulating guidelines.

DISCUSSION

Unless mentioned otherwise, researchers cited used commercial 40 wt % concentrated masterbatches of surface-modified nanosilica in DGEBA with an average particle size of 20 nm and a very narrow particle size distribution. These were then diluted down with commercial epoxy resins to vary the nanosilica concentrations.

The dispersion of the nanosilica was investigated by all researchers and was always found to be homogeneous. Agglomerates or areas with different silica nanoparticle concentrations were not observed.

This behavior was mainly due to the surface coating of the particles as uncoated particles tend to agglomerate. In some rare cases, when nanosilica-containing epoxy resins were cured with amine-functional reactive liquid rubbers, some agglomeration was found. Such exceptions are described in another article currently under preparation.

T_g was not influenced in most cases and sometimes decreased by 1–2°C at very high addition levels of nanosilica. Sanctuary et al.⁴ investigated the complex specific heat capacity and reported that a blend of DGEBA and surface-modified nanosilica behaved in a neutral manner with regard to the glass-transition dynamics of the resin matrix, just like a mixture.

Amine-Cured Epoxy Resins

Aliphatic and Cycloaliphatic Amines as Hardeners. Rosso et al.⁵ investigated the property improvements of piperidine-cured DGEBA by modification with 5 wt % nanosilica. Although the tensile strength remained unchanged, the tensile modulus was increased by more than 20%. The fracture toughness (K_{Ic}) was improved by 70%, and G_{Ic} was improved by more than 140%.

In a continuation of this work, Wetzel et al.⁶ explored the fracture and toughening mechanisms using Al_2O_3 and TiO_2 nanoparticles of similar sizes (ca. 20 nm) in 4,4'-methylene bis(2-methylcyclohexyl-amine) cured DGEBA. They identified crack-deflection processes, crack pinning, and energy dissipation rather than debonding at the particle-resin interface as reasons for the toughness improvements. A very detailed description is given in Wetzel's Ph.D. thesis.⁷

The fracture behavior of piperidine-cured DGEBA with various nanosilica concentrations at high and low temperatures was reported by Deng et al.⁸ They found that the toughness increased significantly at RT and 50°C with a maximum at approximately 5 wt % nanosilica. At 70°C, they found no increase in the modulus or toughness. At 0 and –50°C, the improvements were much smaller; this indicated different mechanisms at different temperatures.

The curing kinetics of a modified DGEBA cured with piperidine were studied by Rosso and Ye.⁹ The addition of 1–5 vol % nanosilica led to a higher reactivity in curing and an alteration

in crosslinking. They suggested the formation of an amino-rich interphase region around the silica nanoparticles, which could have been responsible for the property improvements.

Haupt et al.¹⁰ looked into the tribological properties of DGEBA cured with an aliphatic amine. They found improvements at nanosilica addition levels above 2 vol % and a maximum at 5.5 vol %. The wear resistance was improved by 30%.

DGEBA and DGEBF cured with an accelerated aminoethyl piperazine were the subject of studies by Dittanet.¹¹ She reported an increase in the modulus of 108% for DGEBA and 90% for DGEBF at a 30 wt % addition level of nanosilica. A significant reduction in coefficient of thermal expansion (CTE) was reported as well.

The cyclic fatigue properties of a piperidine-cured DGEBA was studied by Mai et al.¹² They found a fatigue life improvement of 145% with 2 wt % nanosilica, an even slightly higher improvement at 6 wt % nanosilica, but only a 56% improvement at 10 wt % nanosilica. Apparently, there is no linear relationship between the silica content and increased fatigue performance, but a maximum seems to exist at a certain addition level.

Liang and Pearson¹³ investigated the toughening mechanisms of piperidine-cured DGEBA. In addition to 20-nm silica nanoparticles, they used 80-nm particles from a small-scale manufacturer, which might have had a different surface modification. Neither particle sizes influenced T_g (≤ 24.6 wt % of silica). The modulus increased by approximately 20% for both particle sizes. The compressive property and toughness increases were nearly identical as well. The authors concluded that the influence of particle size was negligible in the range of 20–80 nm.

The interactions between silica nanoparticles and diethylene triamine cured DGEBA before and during network formation was the subject of research by Baller et al.¹⁴ In the first stage of isothermal curing, there was no difference between epoxy resins with different nanosilica contents, whereas later in curing, the reaction rate was reduced, probably due to the reduced mobility of the matrix with increased nanoparticle content.

This study was continued by Philipp et al.,¹⁵ and the generalized Cauchy relation was investigated. It seems that the cured epoxy resins with different amounts of nanosilica incorporated behaved similarly to porous silica glasses, and this indicated a perfect distribution of monodisperse silica nanoparticles.

Tsai et al.¹⁶ investigated nanosilica-containing DGEBA cured with a modified isophorone diamine. The modulus was increased up to 19% and K_{1c} was increased by 81% with 40 wt % nanosilica. Again, the improvements increased with increasing nanoparticle addition.

Furthermore, Tsai and Chang¹⁷ explored the damping properties of isophorone-diamine cured DGEBA and reported slightly improved damping properties (+3,24%) at 10 wt % nanosilica addition.

Ye et al.¹⁸ reported increases in the modulus from 2.9 to 3.3 GPa (with 10 wt % nanosilica) and 3.6 GPa (with 20 wt % nanosilica) for a DGEBA resin cured with piperidine.¹⁸ G_{1c} was increased from 238 to 458 and 666 J/m² (improvements of 92 and 180%, respectively).

Liu et al.¹⁹ looked further into K_{1c} of piperidine-cured DGEBA. They found an increase in the modulus and K_{1c} with increasing loading level: 22% increase in the modulus and 304% increase in G_{1c} at 20 wt % nanosilica.

In another study, Liu et al.²⁰ examined cyclic fatigue crack propagation and reported significant improvements in the fatigue lifetimes for 6 and 12 wt % nanosilica. They discussed extensively the contribution of the different toughening mechanisms identified at high and low loading levels.

In continuation of earlier work, Dittanet and Pearson²¹ tried to identify the influence of the nanoparticle size on the toughening of a piperidine-cured DGEBA epoxy resin. They used particles with average sizes of 23, 74, and 170 nm from a small-scale manufacturer and reported improved properties with increasing addition levels of nanosilica. The modulus was increased by approximately 60% at 30 vol % nanosilica addition regardless of the particle size. G_{1c} was improved by 221% for the 23-nm particles, 239% by the 170-nm particles, and 317% by the 74-nm particles. Interesting was the reduction of the CTE size dependence as well; the 23-nm particles performed best.

Mechanisms for the toughening effect of nanosilica were discussed as well, and the model from Kinloch et al.²² was confirmed; see the next two sections in this article. Matrix shear banding was the dominant mechanism, matrix void growth was secondary, and the debonding of silica nanoparticles had only a minor effect.

Table I gives an overview of the increases in the modulus and K_{1c} (at RT) versus addition levels of nanosilica. The same particles were used together with piperidine as a hardener, and identical curing conditions were used.

As a short summary, I concluded that the tensile strength remains more or less unchanged by the addition of silica nanoparticles. At very high addition levels, there may be a slight increase.¹⁹ The modulus increases with increasing concentrations of silica nanoparticles. However, toughness and fatigue improvements have been either reported to increase steadily or have a maximum at 5–6% loading levels.

Poly(ether amine)s as Hardeners. Ma et al.²³ reported for DGEBA cured with a difunctional short-chain poly(ether amine) an increase in the modulus by 32% at a 10 wt % addition level of nanosilica. At a 20 wt % addition level, the modulus increased by 40%. G_{1c} increased by 110 and 274%, respectively. By extensive microscopic work, the initiation and development of a thin dilatation zone and nanovoid formation were identified as the dominant toughening mechanisms.

Kinloch et al.²² investigated DGEBA and a DGEBA/DGEBF blend cured with a difunctional short-chain poly(ether amine). They reported only very small increases in the modulus (17 and 10%, respectively) with 20 wt % nanosilica. Toughness by means of G_{1c} was improved in both cases by approximately 280%. A linear increase with increasing addition level was found. The toughening mechanisms were investigated and compared with theoretical predictions. Localized plastic shear bands initiated by the stress concentrations around the periphery of

Table I. Properties of Piperidine-Cured Epoxy Resins with Various Nanosilica Contents

| SiO ₂ content (wt %) | Modulus (GPa) | | | K _{1c} (MPa m ^{1/2}) | | |
|---------------------------------|---------------|-------------|-------------|---|------|-------------|
| 0 | 2.80 ± 0.03 | 2.86 ± 0.11 | 2.86 ± 0.08 | 0.967 ± 0.07 | 0.89 | 0.95 ± 0.03 |
| 2 | 2.89 ± 0.07 | 2.90 ± 0.06 | 2.88 ± 0.03 | | | 1.01 ± 0.04 |
| 4 | 2.98 ± 0.15 | | 2.93 ± 0.03 | | | 1.14 ± 0.06 |
| 5 | | | | 1.66 ± 0.11 | | |
| 6 | 2.94 ± 0.07 | 2.98 ± 0.08 | 2.98 ± 0.10 | | | 1.26 ± 0.04 |
| 8 | 3.18 ± 0.12 | | 3.10 ± 0.15 | | 1.43 | 1.39 ± 0.07 |
| 10 | | 3.14 ± 0.14 | 3.14 ± 0.14 | | | 1.57 ± 0.02 |
| 12 | | | 3.20 ± 0.05 | | | 1.70 ± 0.05 |
| 20 | | | 3.48 ± 0.14 | | | 2.11 ± 0.01 |
| Reference | 8 | 12 | 19 | 5 | 8 | 19 |

the silica nanoparticles were the main contributor to the increase in toughness. The debonding of the nanoparticles seemed to be less important, as only approximately 15% of the nanoparticles were found to debond. However, the plastic void growth following the debonding contributed to the toughness increase.

DGEBA modified with various amounts of nanosilica and cured with a difunctional short-chain poly(ether amine) was by Tsai et al. as well.¹⁶ They found exactly the same 17% improvement in the modulus at 20 wt % nanosilica like Kinloch et al.²² and a 40% improvement at a 40 wt % loading level. The strength was slightly improved at the 40 wt % level. Three-point bending tests showed an improvement in the flexural strength with increasing addition of silica nanoparticles up to 16%. The toughness increase was found to be very small because of the fact that K_{1c} of the unmodified resin was quite high. The improvements reached a plateau at approximately 10 wt % nanosilica. One has to take into account the fact that the curing conditions were different.

The work of Jajam and Tippur²⁴ focused on a DGEBA blended with 15% *n*-butyl glycidyl ether cured with a commercial hardener formulation consisting of poly(ether amine), trimethyl hexane diamine, benzene-1,3-dimethane amine, nonyl phenol, and substituted phenol. In addition to nanosilica, they tested micrometer-sized spherical glass particles with a mean diameter of 35 μm. They found a linear increase of K_{1c} with increasing addition level for both particles. At 10 vol %, the nanosilica provided a 78% enhancement relative to the 35-μm glass particles. In dynamic fracture tests, both materials showed improved dynamic K_{1c} values with increasing loading levels. However, the nanosilica showed only a minor improvement of 34% at a 10 vol % addition level. In another study,²⁵ it was confirmed that the addition of nanosilica did not necessarily improve the toughness when a fast impact occurred. Nevertheless, it was shown that quite significant improvements could be achieved when commercial resin systems were used, with the hardeners typically being complex amine blends. The effects found for nanosilica modification of epoxy resins have not been limited to model systems.

Aromatic Amines as Hardeners. Kinloch et al.²² also investigated a high-performance, high-*T_g* epoxy resin system similar to the industrial benchmark RTM6.²² Nanosilica-filled TGMMA was cured with a blend of 4,4'-methylenebis(2,6-diethylaniline) and 4,4'-methylenebis(2,6-diisopropylaniline). At a 10 wt % nanosilica loading level, the modulus was increased by 26%, and G_{1c} was increased by 146%, although it was still at a very low level of 172 J/m².

DGEBA cured with 3,3'-diaminodiphenyl sulfone (3,3'-DDS), tested by Rhoney et al.,²⁶ showed a reduction in gel time with increasing silica levels without much change in the cure profile. The *T_g*, determined by thermomechanical analysis, was lowered from 163 to 146°C at approximately 33 wt % nanosilica. The CTEs at 80° (below *T_g*) and 200°C (above *T_g*) were measured, and a reduction of approximately 20% was found for approximately 33 wt % nanosilica.

Ma et al.²³ studied DGEBA cured with 4,4'-DDS. The modulus was increased by 18% at a 10 wt % addition level of nanosilica. Doubling the addition level to 20% increased the modulus by 40% compared to the neat epoxy resin. G_{1c} was improved by 49 and 81%, respectively. Transmission electron microscopy showed some dilatation in the propagated crack-tip area and some nanovoid formation.

The research of Gurung²⁷ was based on a DGEBA cured with 4,4'-DDS as well. An industrially available nanosilica epoxy masterbatch was compared of silica nanopowder modified with aminopropyl triethoxysilane. Gurung reported an acceleration of curing at the beginning of curing caused by the industrial nanosilica as well. A significant drop in *T_g* from 173 to 130°C at approximately 33 wt % nanosilica was found by both thermomechanical analysis and differential scanning calorimetry studies. The modulus was improved by 59%, but the stress at break was reduced by 12%. The industrial material performed better than the "homemade" nanosilica, and this was attributed to a better particle dispersion.

It is interesting to see the effects of the different network densities derived from the two different DDS molecules when they

were modified with the same nanoparticles with regard to the reduction of T_g .

Anhydride-Cured Epoxy Resins

By far, most researchers have worked with anhydride curing agents for various reasons, including their low viscosity and easily controlled curing cycle. The side reactions can also be controlled and can be suppressed with a well-defined curing schedule. Thus, a tremendous amount of test results is available in this field and are described hereafter. All of the anhydride curing agents described were accelerated with very small amounts (e.g., 1%) of ternary amines.

Methylhexahydrophthalic Acid Anhydride as a Hardener

DGEBA epoxy resin. Eger and Schultz²⁸ reported a significant reduction in the viscosity when nanosilica was used in combination with a DGEBA epoxy resin in place of fumed silica. An amount of 25 wt % increased the modulus by 37% and K_{1c} by 72%. A slight increase in the tensile strength was reported as well.

The toughening mechanisms involved were investigated thoroughly by Taylor et al.²⁹ The T_g , determined by differential scanning calorimetry and DMTA, was not affected by the addition of silica nanoparticles. The modulus was increased by 30% at a 20.2 wt % loading level. K_{1c} was improved by 141%. Crack pinning and crack deflection, found often as toughening mechanisms when larger particles are used to toughen epoxy resins, were ruled out. Localized shear banding might have delivered a minor contribution, but debonding of the nanoparticles and subsequent plastic void growth were mainly responsible for the increase in toughness.

Kinloch et al.³⁰ looked into the fatigue performance of such systems. The modulus was increased by 30% and K_{1c} was increased by 73% at 20.2 wt % nanosilica. Cyclic fatigue testing was applied to the compact tension test specimen, and it was found that the addition of nanosilica clearly and significantly improved the fatigue performance: the more, the better.

Zhang et al.³¹ reported an almost linear increase in the modulus with increasing silica nanoparticle content, from 2.75 to 3.95 GPa at a 14 vol % loading level (an improvement of 44%). K_{1c} was improved by more than 50%. The tensile strength was improved only slightly. They reported an observation of a polymer shell around the inorganic particle, as suggested by Wetzel et al.⁶ for other nanoparticles and Zhang et al.³² for SiO₂ nanoparticles.

In another article, Zhang et al.³³ compared industrial silica nanoparticles manufactured by the sol-gel process to fumed nanosilica. The fumed nanosilica increased the viscosity; the maximum loading was 6 vol %. At this concentration, the modulus was increased by 17%, and K_{1c} was increased by 49%. Microscopy revealed particle clusters of 100–200 nm in size. A similar loading level of monodisperse nanosilica yielded the same improvement for the modulus but only a 29% increase in K_{1c} . A further increase in the nanosilica concentration increased the modulus and K_{1c} further.

Kinloch and coworkers^{22,34} observed for a 20 wt % silica nanoparticle modification an increase in the modulus of 30% and an increase in K_{1c} of 73%. A slight decrease in T_g was noted. The observed toughening mechanisms were a debonding of the epoxy

polymer from the silica nanoparticles followed by plastic void growth of the epoxy. Localized plastic shear banding was observed as well. They proposed a model to predict the toughening by nanosilica that correlated well with the experimental data.

In another investigation, Taylor et al.³⁵ looked into the combination of nanosilica and carbon nanotubes (MWCNTs). An addition of 6 wt % nanosilica increased the modulus by 4% and K_{1c} by 9%. Additionally, a concentration of 0.18 wt % multiwalled carbon nanotubes increased the modulus by another 1% and K_{1c} by another 40%. Several different toughening mechanisms were identified.

Zhang et al.³⁶ found the modulus to increase by 31% at a nanosilica addition level of 12 vol %. The strength was increased considerably, by 45%. K_{1c} was improved by 93%, and T_g was only slightly reduced.

Table II gives an overview of the modulus and K_{1c} (at RT) values versus the addition level of nanosilica. The same particles were used in DGEBA as in epoxy resin and were cured with methyl hexahydrophthalic acid anhydride. The curing conditions varied slightly.

In short, I concluded that the tensile strength was slightly improved by the addition of silica nanoparticles at high loading levels. The modulus and toughness increased with increasing concentrations of silica nanoparticles. There seemed to be no maximum addition level.

DGEBF epoxy resin. The effects of the modification of DGEBF with nanosilica were investigated by Zhang et al.³⁷ With increasing nanoparticle content, property improvements were found. At 15 vol %, the modulus was increased by 48%, the strength was increased by 8%, the impact energy was increased by 30%, and K_{1c} was increased by 77%. When testing was done at 80°C instead of RT, the improvements in the strength and modulus were in the same range; the K_{1c} , however, was increased by 125%. Zhang et al. reported different fracture behaviors for the different temperatures. At RT, many dimples were found, whereas at 80°C, a larger smooth zone on the fracture surface was observed. As the dominant toughening mechanism, an enhanced local deformability around the crack tip induced by the silica nanoparticles was identified.

Gu et al.³⁸ examined the mechanical and tribological aspects of modified DGEBF.³⁸ The hardness and modulus increased nearly linearly with increasing nanosilica content. When 15 vol % nanoparticles were used, the modulus was improved by 40%, and the hardness was improved by 33%. The plasticity index decreased first, showed a minimum at 8 vol % nanosilica, and then increased. The friction coefficient showed similar behavior.

Cycloaliphatic epoxy resin. Eger and Schultz²⁸ studied the properties of 3,4-epoxy cyclohexylmethyl-3,4-epoxycyclohexane carboxylate (EEC) modified with silica nanoparticles and fumed silica. At a 40 wt % loading level, the viscosity increased from 0.23 to 2.1 Pa s for the silica nanoparticles and to 43 Pa s for the fumed silica. At 22 wt %, the strength remained unchanged, and the modulus was increased by approximately 40% for both modifications. Fumed silica increased K_{1c} by 45%; silica nanoparticles increase it by 53%. A reduced water absorption was reported.

Table II. Properties of Anhydride-Cured Epoxy Resins with Various Contents of Nanosilica

| SiO ₂ Content (wt %) | Modulus (GPa) | | | | K _{1c} (MPa m ^{1/2}) | | | |
|---------------------------------|---------------|-----------------|------|-----------------|---|-----------------|------|-----------------|
| 0 | 2.96 | 2.75 ± 0.05 | 2.96 | 3.01 ± 0.05 | 0.59 | 0.55 ± 0.12 | 0.51 | 0.46 ± 0.04 |
| 2 | | 2.79 ± 0.09 | | | | 0.57 ± 0.11 | | |
| 4 | 3.20 | | 3.20 | | 1.03 | | 0.64 | |
| 5 | | 3.00 ± 0.07 | | 3.39 ± 0.19 | | 0.68 ± 0.05 | | 0.68 ± 0.02 |
| 8 | 3.42 | | 3.42 | | 1.17 | | 0.79 | |
| 10 | | 3.24 ± 0.04 | | 3.42 ± 0.34 | | 0.71 ± 0.05 | | 0.74 ± 0.04 |
| 14.5 | | 3.56 ± 0.05 | | 3.63 ± 0.11 | | 0.75 ± 0.05 | | 0.80 ± 0.03 |
| 15 | 3.60 | | 3.60 | | 1.29 | | 0.83 | |
| 20 | 3.85 | | 3.85 | 3.95 ± 0.20 | 1.42 | | 0.88 | 0.89 ± 0.05 |
| 22.8 | | 3.95 ± 0.12 | | | | 0.83 ± 0.05 | | |
| Reference | 29, 30 | 33 ^a | 34 | 36 ^a | 29, 30 | 33 ^a | 34 | 36 ^a |

^aRecalculated from the volume percentage.

Zhang et al.³² investigated EEC as well. With a 22.7 wt % silica content, the modulus was found to increase from 3.05 to 4.18 GPa or by 37%. K_{1c} was improved by 76%. Interestingly, the impact strength (by Charpy impact testing) went from 25.6 to 31.4 kJ/m² at a 5.3 wt % nanosilica content to 23.7 J/m² at 22.7 wt % loading. Apparently, a maximum existed. The strength was not affected by the modifications. As a main toughening mechanism, the energy dissipation caused by nanoparticle-induced dimples was claimed.

Bai et al.³⁹ applied dynamic nanoindentation to investigate the triboelastic properties of modified EEC. The storage modulus increased with increasing nanosilica content. The increase was not linear, with a rapid increase first and then a moderate increase at higher loading levels. The absolute values were higher than those found when DMTA or three-point bending tests were used.

Methyltetrahydrophthalic Acid Anhydride as a Hardener. The industrial curing agent used contained a certain amount of tetrahydrophthalic acid anhydride and was accelerated with 1-methyl imidazole. Mahrholz et al.⁴⁰ explored achievable property improvements by nanosilica modification regarding the use of modified resins for injection techniques where low viscosities are indispensable.⁴⁰

They found a slight increase in tensile strength and an increase in the modulus with increasing nanosilica content. At a 25 wt % loading level, an improvement of 36% was found. The impact strength, determined by a Charpy test, showed a maximum improvement at a content of 15 wt % nanoparticles and decreased upon further addition of nanosilica. Shrinkage was reduced by 19%, and the thermal conductivity increased with increasing nanosilica content.

Duwe et al.⁴¹ described a strong increase in the modulus of approximately 50% at 25 wt % nanosilica at RT and at 50°C. Further, they reported an increase in the thermal conductivity. In comparison to SiO₂, they investigated AlN and boehmite modifications as well.

Methylnadic Acid Anhydride as a Hardener. Hodzic et al.⁴² used benzyltrimethylamine as an accelerator for an anhydride

curing agent in their study of static uniaxial compression. In contrast to that of classic micrometer-sized fillers, the addition of nanoparticles enhanced the compressive stress-strain behavior of the cured epoxy resin. A concentration of 13.6 wt % nanosilica increased the compressive modulus by 19%, the compressive strength by 33%, and the strain at break by 76%. Further increases in the nanoparticle concentration caused further property improvements.

In another study, Hodzic et al.⁴³ employed both cylindrical and prismatic test specimens. In both cases, the test specimen with the highest addition level of nanosilica showed the best performance. Enhanced shear deformation of the matrix and the formation of shear bands that influenced the crack propagation were identified as mechanisms of action of the nanoparticles.

Comparison of Different Types of Hardeners

Flemming et al.⁴⁴ summarized the common understanding that a higher crosslink density leads to a higher T_g and typically a higher modulus as well as a reduced elongation at break and an increased brittleness.

The T_g 's reported for the DGEBA/isophorone diamine system were around 80°C. Cured DGEBA/piperidine systems exhibited T_g 's between 80 and 100°C. Short-chain aliphatic poly(ether amine)s as curing agents achieved T_g 's around 80°C as well. For DGEBA cross-linked with methylhexahydrophthalic acid anhydride, the T_g 's were found to range between 150 and 164°C. A 4,4'-DDS hardener yielded in combination with DGEBA T_g 's between 163 and 173°C. DDS or other aromatic amines used in combination with tetrafunctional epoxy resin (TGMDA) achieved T_g 's of up to 260°C.

In Figure 2, the modulus data from Tables I and II and from some literature are given, and a linear interpolation is applied.^{16,22,23} The epoxy resin used for all of the systems was DGEBA. The increase in modulus with increasing nanosilica content was larger for hardeners that form a close meshed network. Piperidine led to polymers with the lowest network density. This was followed by the difunctional poly(ether amine) (here called D 230), methylhexahydrophthalic acid anhydride (MHHPA), and finally 4,4'-DDS.

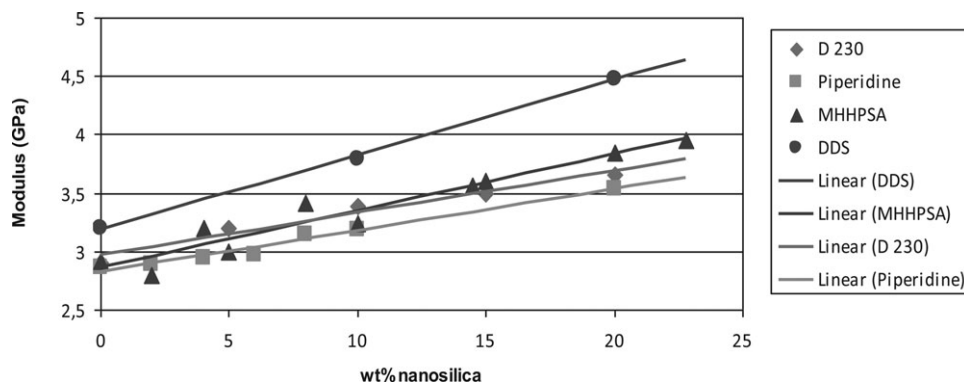


Figure 2. Moduli of epoxy resins with various contents of nanosilica cured with different hardeners. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3 shows K_{Ic} as function of the nanosilica content for these different hardeners. It is evident that hardeners forming a closer meshed network and therefore yielding cured resins with a higher modulus tend to be more brittle and thus have a lower toughness. Again, the toughness increases more or less linearly with increased addition level of silica nanoparticles. The improvements at the same loading level are bigger for systems that already exhibit a higher toughness. This is consistent with the fact that toughening mechanisms are more efficient for polymer matrices with a higher ductility.

As shown in Figure 3, the linear approach did not work for the rather flexible, short-chain poly(ether amine) (D 230) as a curing agent. Here, there seemed to be a maximum; this means that an optimal addition level of nanosilica existed, apparently at lower addition levels. This was consistent with other studies where such a curing agent was used in combination with flexible amine-functional reactive liquid rubbers.⁴⁵

CONCLUSIONS

Taking into account data gathered and published over the last 10 years, I drew the following conclusions:

1. Nanosilica particles are monodisperse, and even at very high concentrations, no agglomerates are found. The rheological properties of the resins are not affected.

2. The particles behave like a filler and do not significantly change the curing characteristics of epoxy resin/hardener blends. Toward the end of the curing cycle, curing is slowed down to a certain extent.
3. Although the topology of the three-dimensional network formed by the crosslinking reaction between an epoxy resin and a hardener is different in the close vicinity of the silica nanoparticles, the general network structure does not seem to change significantly. This could be deduced from the fact that T_g remains the same as for the systems without nanosilica for most curing agents. Furthermore, in most cases, the tensile strength of the cured epoxy resin (determined by lap shear testing) does not change.
4. The modulus increases with increasing addition level of silica nanoparticles in a nearly linear function. At 10 wt % nanosilica, an increase in the modulus of 30–50% can be expected.
5. The compressive strength and the compressive modulus increase as well. Improvements of 10–30% can be expected at a 10 wt % addition level of silica nanoparticles.
6. K_{Ic} increases with increasing level of silica nanoparticles but not always in a linear function. At 10 wt % nanosilica, an increase of approximately 50% can be expected.
7. The toughening mechanisms are the debonding of the epoxy polymer from the silica nanoparticles followed by plastic void growth. Localized plastic shear banding

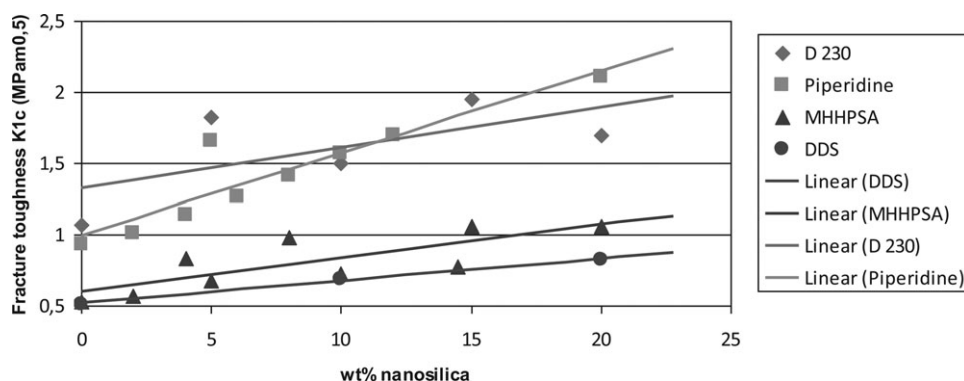


Figure 3. K_{Ic} of epoxy resins with various contents of nanosilica cured with different hardeners. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

contributes as well. Crack deflection does not seem to play a significant role.

- Fatigue performance is improved as well, but there seems to be no linear relationship between the nanosilica content and the level of improvement. Very probably, a maximum exists. At a 10 wt % addition level, an improvement in the fatigue performance of 50–60% can be expected.

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