



## Feature article

## Epoxy resins modified with elastomers and surface-modified silica nanoparticles



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## ABSTRACT

Epoxy resins are inherently brittle. Thus they are toughened with reactive liquid rubbers or core–shell elastomers. 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. Some of the drawbacks of toughening, like lower modulus or a loss in strength can be overcompensated when using nanosilica together with these tougheners. Apparently there exists a synergy as toughness and fatigue performance are increased significantly. In this article the literature published in the last decade is studied with a focus on mechanical properties. Results are compared and the mechanisms responsible for the property improvements are discussed.

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## 1. Introduction

Epoxy resins are used for many years in a multitude of industrial products, like structural automotive adhesives, high performance fibre reinforced composites, electrical and electronic applications, heavy duty protective coatings and many more. However, they are very brittle and therefore in most commercial formulations tougheners are used.

Since the seventies and eighties of last century the use of reactive liquid rubbers as tougheners for epoxy resins became industrial standard. Carboxy terminated butadiene acrylonitrile copolymers (CTBNs) are reacted with an excess of epoxy resin to form a so-called adduct, an epoxy-rubber–epoxy terpolymer. These are soluble in epoxy resins, whereas the pure rubber is not. Upon cure and subsequent formation of the three-dimensional network, the rubber molecules become insoluble again, phase separate and form small rubber domains or particles within the cured polymer matrix. These rubber particles are chemically linked to the polymer. Since the very early work of Kinloch and his team the mechanisms of rubber toughening have been the subject of intensive research and are well understood [1,2].

An excellent review was published recently [3].

However, the phase separation and domain formation depend on the cure speed, cure temperature and the curing agent itself. The acrylonitrile content of the copolymer has an influence on the particle size as well. Furthermore not all long-chain rubber molecules participate in the phase separation, some of them are crosslinked randomly into the epoxy polymer matrix. Consequently the network density is lowered, which results in a lower strength and a lower modulus, and, of course, in a lower glass transition temperature ( $T_g$ ). Another issue is the relatively high viscosity of epoxy resins containing reactive liquid rubbers which prohibit some applications where low viscosities are required.

To overcome these disadvantages core–shell elastomers (CSRs) have been developed in the 1980s–1990s. Instead of forming a second phase upon cure the rubber particles were added from the beginning. They consist of an elastomeric, rubber-like core of approx. 90 nm; typically a butadiene homopolymer or a butadiene–styrene copolymer with a random copolymer shell of 10–20 nm which is compatible with the epoxy resin [4,5]. They will be referred to as CSR Type I. Others are based on polyacrylate cores and have a diameter in the range of 300–400 nm [6]. They will be referred to as CSR Type II. If these core–shell particles are dispersed in epoxy resins, the viscosities of modified resins are much lower compared to epoxy resins modified with reactive liquid rubbers. The toughening effects are independent from the curing agent and the cure schedule. Sometimes strength and modulus are lowered,

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but not to the same extent as with reactive liquid rubbers. The use in high temperature applications however is limited, as the shell tends to soften at higher temperatures followed by a drastic loss in strength and modulus of the cured polymer.

Another CSR development in the mid-1980s created a material which can be used at elevated temperatures as well [7,8]. This was achieved by reducing the thickness of the shell to a molecular monolayer – the result is rather a core–skin than a core–shell material. These epoxy-functional CSR with a polysiloxane core and an average diameter around 500–700 nm are very efficient tougheners over a very broad range of temperatures [9]. They will be referred to as CSR Type III. Fig. 1 shows the unstained SEM picture of the fracture surface of an anhydride cured epoxy resin containing 5.5 wt% of CSR Type III. The morphology looks very similar to the pictures taken from polymers toughened with reactive liquid rubbers (CTBNs). The rubber domains are very uniform.

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 and have an average diameter of 20 nm as well as a very narrow particle diameter distribution.

These particles are completely monodisperse and 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. Due to their size they are transparent and can easily penetrate even close meshed fabrics in composite manufacturing when being injected. The property improvements which can be achieved by modifying epoxy resins with these silica nanoparticles, like modulus, toughness and fatigue performance, have been the subject of intensive research in the last decade [10]. The mechanisms how nanoscaled spherical fillers can improve epoxy polymer properties have been identified; however the contribution of each one might be of a different proportion depending on the hardeners used to form the three-dimensional network upon cure. Fig. 2 shows the excellent dispersion and the very narrow particle diameter distribution of the spherical nanosilica.

The combination of reactive liquid rubbers or core–shell elastomers and silica nanoparticles as an additional modifier in epoxy resin systems yields additive and sometimes synergistic property improvements. It becomes possible to formulate tough and stiff materials. Therefore such hybrid systems are used in many industrial epoxy formulations today. The aim of this article is to give a

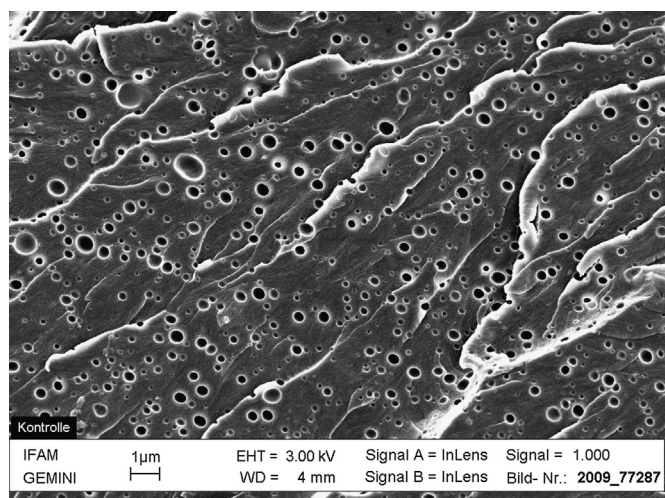


Fig. 1. SEM image of an epoxy polymer with 5.5 wt% CSR Type III.

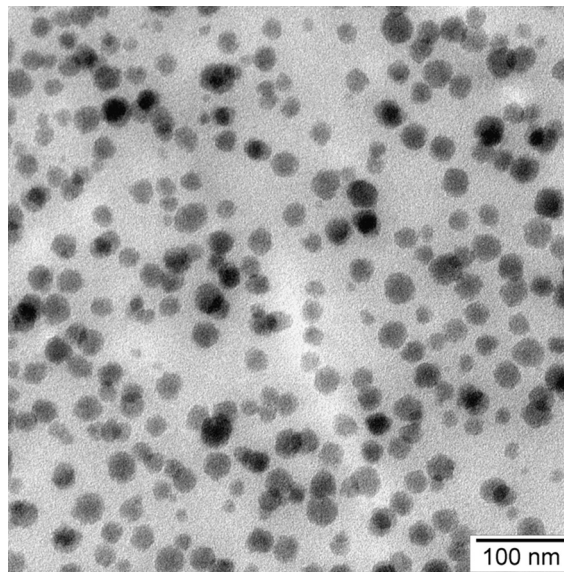


Fig. 2. TEM image of an epoxy polymer with approx. 20 wt% silica nanoparticles [11].

comprehensive overview of the actual state of research regarding the various different aspects and to provide formulation guidelines.

## 2. Discussion

If not mentioned otherwise, the researchers cited used commercial 40% (by weight) concentrated masterbatches of surface-modified nanosilica in DGEBA from one supplier. These particles have an average diameter of 20 nm and a very narrow particle diameter distribution. They were then diluted down using commercial epoxy resins to vary the nanosilica concentrations.

### 2.1. Epoxy resins modified with reactive liquid rubbers (CTBNs) and silica nanoparticles, amine cured

The diglycidyl ether of bisphenole A (DGEBA) is the most commonly industrially used epoxy resin. Thus most of the research work was performed using DGEBA.

At first the silica nanoparticles, after being commercially available, had been added to epoxy formulations containing CTBNs to reduce the loss in strength and modulus caused by the rubber modification without increasing the viscosity. Very soon in some applications a synergy between elastomeric tougheners and silica nanoparticles was discovered and patented consequently [12].

However, as will be shown in this article, the synergy is not necessarily related to morphology and sometimes only found for one polymer property or not at all.

One of the first industrial applications where nanosilica was used together with reactive liquid rubbers were structural epoxy adhesives. We found an increase in adhesive lap shear strength at low addition levels of nanosilica (<2 wt%) of a one-component, heat-curing adhesive [13]. The toughness seemed not to be increased further compared to the formulation without nanosilica. This might be due to the fact that the curing agent of this adhesive, dicyandiamide, forms very close-meshed molecular networks. The CTBN rubber in the formulation had 26% acrylonitrile in the copolymer.

In another study we used a rubber with 18% of acrylonitrile and a commercial amine curing agent based on 2,2'-dimethyl-4,4'-methylene-bis(cyclohexyldiamine) and isophorone-diamine. We found that the loss in modulus caused by the rubber modification

could be compensated by the addition of nanosilica for rubber concentrations up to approx. 7 wt% [14]. The  $G_{IC}$  of the unmodified polymer was increased from 609 J/m [2] to 1223 J/m [2] by the addition of 4.6 wt% CTBN and increased further to 2059 J/m [2] for a system containing 4.1 wt% CTBN and 2 wt% of nanosilica. This indicates the existence of an optimum nanoparticle content which might be different for each different polymer system defined by resin and hardener.

Caccavale studied epoxy resin systems modified with the same rubber and cured with another commercial polyamine hardener [15]. The loss in modulus due to a 7.3 wt% rubber modification was only partially compensated by the addition of 3.7 wt% nanosilica and still approx. 6% lower than the control.  $T_g$  was lowered significantly by 19 °C.  $K_{IC}$  of the hybrid however was increased by 136% (dry conditions) respectively 154% (wet conditions). Microscopical investigations revealed a good dispersion of both silica nanoparticles and rubber domains formed upon cure. Moisture absorption of the hybrid system was higher than for the unmodified epoxy and this could be assigned to the CTBN modification.

Tsai et al. based their research upon the same rubber with 18% acrylonitrile in the copolymer and isophorone diamine as a hardener [16]. They reported a fair dispersion of both rubber domains formed upon cure and silica nanoparticles. The modulus of the unmodified system was lowered by 10 wt% of CTBN from 3.25 GPa to 2.63 GPa compared to the control and brought back to 3.18 GPa by the addition of 10 wt% nanosilica. Similar behaviour was found for the tensile strength – a loss of approx. 20% for the rubber-modified polymer and approx. 3% for the hybrid. Fracture toughness by means of  $G_{IC}$  was increased by 516% to 1170 J/m [2] by the addition of the rubber. The hybrid system achieved only 930 J/m [2]. This indicates a tough and stiff system, but no synergistic effects.

In another study they tested the damping properties at room temperature of these systems [6]. The glass transition temperature ( $T_g$ ) of the rubber is below – 30 °C; the  $T_g$  of the cured epoxy polymer is estimated to be above +100 °C. The loss factors reported were 2.95% for the unmodified system, 3.12% for 10 wt% of rubber, 3.51% for 10 wt% of nanosilica and 3.88% for the hybrid with 10 wt% of both. Modulus was reduced by 17.3% by the CTBN, increased by 8.74% by the nanosilica and only 5.3% lower for the hybrid. As damping properties were best for the hybrid there might be a synergy.

Pearson et al. reviewed the improvements obtained by the addition of spherical glass beads with an average diameter of 2 and 50  $\mu\text{m}$  to rubber toughened epoxies, and compared them to their results with the spherical silica nanoparticles of 20 nm diameter [17]. Additionally they investigated silica nanoparticles of 80 nm in diameter; those were supplied by a different manufacturer. A significant increase in fracture toughness and fracture energy with a maximum at approx. 5 vol% of nanosilica was found. Variations of the rubber content revealed larger improvements at lower rubber levels than for high rubber concentrations. This might eventually be caused by the observed nanosilica agglomeration at very high rubber concentrations.

In the basic study they published further details [18]. The rubber used contained 18% acrylonitrile in the copolymer. Piperidine was the curing agent of choice. Compressive moduli are improved only slightly compared to the unmodified control when nanosilica is added; with the values being lower for the 20 nm particles than for the 80 nm particles. The 80 nm particles seem to have a smaller effect on the toughness; the addition level of the rubber dominates. The 20 nm particles, however, do increase the fracture toughness up to a maximum at approx. 6 vol% nanosilica. Looking at the fracture energy of 3250 J/m<sup>2</sup> for the unmodified system containing approx. 21 vol% of CTBN, the 80 nm particles increase the fracture energy up to 4310 J/m<sup>2</sup> at 1.5 vol% addition level. The 20 nm

particles show with 5720 J/m<sup>2</sup> a maximum at 3.1% addition level. A similar toughness was found with 12 and 17 vol% rubber. Pearson observed agglomerate formation (clustering) of the nanosilica particles at rubber concentrations above 12 vol%.

Robinette and his group used two commercial epoxy resin formulations which contain a CTBN adduct in the resin part [19]. They modified the resin part with nanosilica and adapted the amount of amine-based hardener accordingly. The tougher, low  $T_g$  system called SC-15 showed an increase in modulus from 2.37 GPa to 2.96 GPa at 15 wt% addition level of nanosilica. This equals an improvement of 25%.  $T_g$  seemed to be nearly unaffected.  $G_{IC}$  however, increased from 900 J/m<sup>2</sup> to 1020 J/m<sup>2</sup> at 1 wt% nanosilica.

For higher loading levels the  $G_{IC}$  was more or less at 800 J/m<sup>2</sup>. In contrast, the high  $T_g$  system SC-79 showed no increase in modulus at first, then a somewhat higher modulus at 7.5 and 10 wt% addition level, then a drop in modulus again. The glass transition temperature was lowered with increasing nanosilica concentration from 180 °C to 162 °C at 15 wt% nanoparticles.  $G_{IC}$  was increased from 180 J/m<sup>2</sup> to 380 J/m<sup>2</sup> at 10 wt%, then drops again to 250 J/m<sup>2</sup> at 15 wt%. Apparently both systems have an optimum nanosilica addition level, however at totally different concentrations. Fig. 3 shows the good distribution of the nanosilica and the typical rubber domains formed upon cure. It is interesting to see that no silica nanoparticles are trapped in the rubber domains upon their formation during cure.

Sun et al. worked with the SC-79 epoxy resin system as well [21]. Modulus increased with increasing nanosilica addition level up to approx. +40% for a 15 wt% loading level. Flexural strength and strain at break showed a similar behaviour. Additionally they investigated combinations with other nanoparticles like alumina or carbon nanofibers but could not find further improvements.

Another team investigating the SC-79 two part epoxy system was the group of Renukappa et al. [22]. They focused on tribological and electrical properties and reported a maximum for strength at 10 wt% nanosilica. Wear resistance was increased significantly and showed a maximum at 10 wt% as well. Dielectric strength, arc and track resistance were improved first with increasing the nanosilica content, showed a maximum at 15 wt% and decreased with 20 wt% below the level of the unmodified control.

In continuation of this work Ranganathaiah et al. reported a linear increase in modulus with increasing nanosilica content from 2.97 GPa to 3.55 GPa at 20 wt% [23]. Strength exhibited a maximum at 10% again. They concluded that 10 wt% is the optimum loading

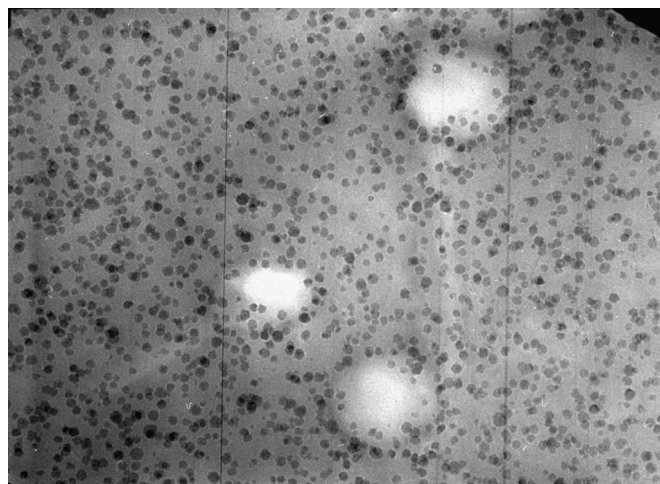


Fig. 3. TEM picture of epoxy polymer modified with reactive liquid rubber (CTBN) and nanosilica [20].

level as for 15 and 20 wt% agglomerates had been observed (by TEM) which could explain the lower performance. Volume resistivity and surface resistivity had been investigated as well.

Tetrafunctional epoxy resins, cured with sterically hindered aromatic amines are used in high performance aerospace applications. We examined such a system and observed a further increase in toughness by the addition of 10 wt% nanosilica to the reactive liquid rubber modified system [24]. The loss in modulus due to the rubber modification was overcompensated by the nanosilica. Thus a tough and stiff resin system could be formulated. Dry  $T_g$  was not affected by the modifications; however the wet  $T_g$  (after two weeks at 70 °C and 100% relative humidity) was the lowest for the hybrid system.

## 2.2. Epoxy resins modified with styrene–butadiene rubber (SBR) and silica nanoparticles, amine cured

Gope et al. studied an epoxy resin cured with triethylenetetramine, which was modified with a styrene–butadiene rubber up to 1.5 wt% and silica nanoparticles at up to 2 wt% [25]. The silica nanoparticles with an average diameter of 130 nm – it is unclear if they were surface modified or not. They reported a very good dispersion of both rubber and nanosilica as well as improved mechanical properties. Wear properties have been improved significantly by the nanosilica addition (up to 4 times lower).

## 2.3. Epoxy resins modified with reactive liquid rubbers (CTBNs) and silica nanoparticles, anhydride cured

In an early investigation we used the reactive liquid rubber with 18% acrylonitrile in the copolymer and methylhexahydrophthalic acid anhydride (MHHPA) accelerated with a small amount of a ternary amine [26]. Modulus was lowered by the rubber modification and increased again by the nanosilica addition to the level of the unmodified system. This system had a fracture energy ( $G_{IC}$ ) of 103 J/m<sup>2</sup>, which was increased to 406 J/m<sup>2</sup> by the addition of 9 wt% CTBN. Adding 4.5 wt% nanosilica pushed the  $G_{IC}$  to 917 J/m<sup>2</sup>; 9 wt% nanosilica to 973 J/m<sup>2</sup>. Compared to the control this is an increase of approx 850%. The glass transition temperature dropped by the rubber modification from 143 °C to 133 °C. The nanosilica addition had no influence on  $T_g$ .

Manjunatha et al., working with the same system, investigated the cyclic fatigue behaviour [27]. Tensile strength and modulus of the polymer were lowered by the rubber addition and increased by the nanosilica addition. The system with 9 wt% CTBN and 10 wt% nanosilica had approx. 10% lower strength and modulus. The cyclic loading tests at different stress levels showed a clear shift towards much more cycles before failure for both the rubber and the nanosilica modified polymer. However, the hybrid performed best and gave a 6–10 times enhancement of fatigue life.

Kinloch, Taylor et al. used the same system and reported significant improvements in toughness [28]. Though the modulus of the hybrid system was slightly lower than for the unmodified system (–4%), the fracture energy  $G_{IC}$  was significantly increased by the addition of 9 wt% CTBN and further increased by the nanosilica addition. A maximum was found at 15 wt% nanosilica: 965 J/m<sup>2</sup> compared to 77 J/m<sup>2</sup> for the control which equals an improvement by 1150%. At 20 wt% nanosilica the toughness shifts to lower values. Interestingly the formation of small silica agglomerates was observed, but did not seem to affect the rubber domain formation nor the performance of the cured resin.

Zhang, Tang et al. used a powdered CTBN rubber for their study, together with accelerated methylhexahydrophthalic acid anhydride [29]. They reported well dispersed rubber particles and well dispersed silica nanoparticles. No agglomerate formation could be

observed. The elastic modulus of all hybrid formulations was lower than for the unmodified system with a modulus of 3.01 GPa; except for the formulation with 7 vol% nanosilica and 2 vol% rubber which achieved a modulus of 3.25 GPa.  $G_{IC}$  of the control was 62 J/m<sup>2</sup> and increased to 186 J/m<sup>2</sup> for 7 vol% nanosilica and 2 vol% rubber. 2 vol% nanosilica and 7 vol% rubber gave a further increase to 371 J/m<sup>2</sup>. However, the best overall performance was shown for the system with 4.5 vol% silica and 4.5 vol% rubber with a  $G_{IC}$  of 306 J/m<sup>2</sup> (equals an improvement of approx. 394%), a slightly lower modulus (–4%) and the highest impact energy of all systems tested. 31.29 kJ/m<sup>2</sup> compared to 16.2 equals an improvement of approx. 93%. The glass transition temperature was reported to be unaffected by the modification which indicates a particulate nature of the rubber similar to core shell materials.

In another study they evaluated a carboxy-terminated polyurethane-co-polyether block copolymer as a toughener together with silica nanoparticles [30]. As curing agent accelerated methylhexahydrophthalic acid anhydride was used. TEM microscopy revealed a good dispersion of both rubber domains formed upon cure as well as for the silica nanoparticles. The tensile strength was slightly lower for the elastomer modified system and increased for the hybrid systems compared to the unmodified control. A reduction in modulus from 3.01 GPa to 2.50 GPa at 9 vol% elastomer was observed. With 9% nanosilica this loss was overcompensated to 3.20 GPa; at 12% nanosilica even to 3.40 GPa.  $K_{IC}$  was more than doubled from 0.46 MPam<sup>1/2</sup> to 1.00 MPam<sup>1/2</sup> by the toughener and further increased with increasing concentration of silica nanoparticles. The hybrid system with both 9 vol% exhibited a  $K_{IC}$  of 1.2 MPam<sup>1/2</sup>, the system with 9 vol% elastomer and 12 vol% nanosilica achieved 1.33 MPam<sup>1/2</sup>. This equals an improvement of 189%.

## 2.4. Epoxy resins modified with silica nano-particles, cured with amines and amino-functional reactive liquid rubbers (ATBNs)

Totally different systems can be achieved when amine functional reactive liquid rubbers are used to modify an epoxy resin. They are used as part of the hardener blend in 2 part epoxy formulations, e.g. structural adhesives. Compared to epoxy resins modified with CTBN adducts a much smaller percentage of the rubber molecules phase separate and form rubber domains. A large proportion is crosslinked randomly into the polymer and lowers the crosslink density significantly – with the known effects of a much lower  $T_g$ , lower modulus, increased elongation at break, increased toughness etc.

Kinloch et al. used a combination of an amine terminated reactive liquid rubber with 17% acrylonitrile in the backbone together with a commercial polyamidoamine as a curing system [31]. The lap shear strength of adhesive joints of untreated aluminium alloy was increased significantly at low nanosilica addition levels of approx. 1 wt%. Roller peel tests showed significant improvements as well with a maximum around 2 wt% nanosilica.  $G_{IC}$  was increased from 1200 J/m<sup>2</sup> for the rubber toughened system to a maximum of 2300 J/m<sup>2</sup> at 4.6 wt% silica nanoparticles.

In continuation of this work we varied the rubber level of the formulations and found similar behaviour: there was always a significant property improvement at low addition levels of nanosilica (1–4 wt%) [32]. The same was found for roller peel tests at different temperatures (substrate chromic acid etched aluminium) as well as for wedge impact test with adhesive joints of degreased steel. Most striking were the results of the adhesive fracture energy test where the  $G_{IC}$  was doubled from 1200 J/m<sup>2</sup> to 2400 J/m<sup>2</sup> by the addition of approx. 1 wt% nanosilica.

Further work with a different hardener composition (amine functional reactive liquid rubber, amine functional polyether, polyamidoamine and isophorone diamine) showed similar results

[33]. The mode I fracture energy was increased from 2256 J/m<sup>2</sup> to a maximum 4550 J/m<sup>2</sup> at 6 wt% nanosilica addition level. Lap shear tests of adhesively bonded glass-fibre reinforced composites gave comparable behaviour.

Atomic Force Microscopy (AFM) investigations revealed a different morphology than for the CTBN modified resins. When an epoxy resin system containing both the CTBN adduct and the nanosilica is cured, the rubber domain formation upon cure seems not to be affected by the presence of the nanosilica. Agglomeration of the nanosilica does either not occur or only small agglomerates are found [21,28], which seems not to affect the performance of such systems. An aspect which will be discussed when looking into the synergy between CTBN and silica nanoparticles.

If an epoxy resin containing nanosilica is cured with an amine blend containing amine functional reactive liquid rubber, the phase separation and rubber domain formation become quite irregular at higher nanosilica concentrations. Furthermore it seems that partial agglomeration of the silica nanoparticles is induced, with large agglomerates formed; nevertheless superior mechanical properties were found [33]. These irregular morphologies need further investigation in the future.

## 2.5. Epoxy resins modified with core–shell elastomers (CSRs) and silica nanoparticles, amine cured

### 2.5.1. CSR Type I

Mai et al. studied the cyclic fatigue behaviour of an epoxy resin system modified with a core–shell elastomer characterized by a particle diameter of approx. 110 nm [34]. Piperidine was used as a curing agent. They reported a reduction in strength by the addition of the core–shell rubber, which was not improved by the addition of the 20 nm silica nanoparticles. The loss in modulus however was compensated; it dropped from 2.86 GPa to 2.25 GPa at 10 wt% elastomer and was brought back to 2.81 GPa with 10 wt% nanosilica. The silica nanoparticles increased the fatigue life whereas the core–shell particles decreased it. Thus the hybrid system did not perform better than the neat polymer. Toughness was increased from 277 J/m<sup>2</sup> to 1250 J/m<sup>2</sup>.

This work was continued by Liu et al. [35]. They looked further into toughness and toughening mechanisms. Core–shell particles and silica nanoparticles were well distributed, as TEM microscopy revealed.  $G_{IC}$  for the unmodified resin was 277 J/m<sup>2</sup>. The elastomer addition increased  $G_{IC}$  with raising addition level. At 10 wt% core–shell the  $G_{IC}$  was 1930 J/m<sup>2</sup>. An increase in toughness with the addition of nanosilica was found as well. At 10 wt% nanosilica  $G_{IC}$  was 690 J/m<sup>2</sup>. The hybrid system with 10 wt% of both modifications had the highest toughness of 2480 J/m<sup>2</sup>. This seems to imply an additive behaviour, no synergistic effects. However a good balance between toughness and modulus could be achieved. As major toughness contributors nano-silica debonding and bridging before pullout and core–shell rubber cavitation and matrix plastic shearing were identified. They claimed that nanosilica and core–shell elastomer act independently during crack growth.

Furthermore they examined cyclic fatigue crack propagation of this hybrid system and observed a synergistic effect on the fatigue crack growth threshold [36]. The unmodified epoxy polymer has a  $\Delta G_{th}$  of 44 J/m<sup>2</sup>; 6 wt% core shell increases it to 47 J/m<sup>2</sup>. The modification with 6 wt% nanosilica results in 65 J/m<sup>2</sup>, whereas the hybrid with 6 wt% of both achieves 102 J/m<sup>2</sup>; an improvement of 132% compared to the control.

### 2.5.2. CSR Type II

Tsai et al. used the larger Type II particles and isophorone diamine as a hardener [16]. TEM microscopy showed a good dispersion of both silica nanoparticles and elastomer particles as

well. The modulus was reduced from 3.25 GPa to 2.73 GPa by the addition of 10 wt% core shell particles and brought back to 2.97 GPa by further addition of 10 wt% silica nanoparticles. The tensile strength was reduced by approx. 27% by the elastomer and this reduction was not changed by the nanosilica addition – though the system modified only with nanosilica exhibited no loss in strength. The fracture toughness of the epoxy resin was determined to be 190 J/m<sup>2</sup>. It was increased by a 10 wt% core–shell modification to 1420 J/m<sup>2</sup>. A modification with 10 wt% of nanosilica achieved 280 J/m<sup>2</sup>. The hybrid system with 10 wt% of both modifications achieved only 1030 J/m<sup>2</sup>. A good balance between toughness and modulus, but no synergistic effects.

In continuation of this work Tsai et al. investigated the damping properties at room temperatures and found a 42% improvement of the loss factor for the hybrid system [6].

### 2.5.3. CSR Type III

Palinsky reported about the modification of a commercial reactive transfer moulding (RTM) resin based on tetraglycidyl ether of methyl dianiline (TGMDA) and cured with sterically hindered aromatic amines [37]. By modifying this resin system with the core–shell elastomer strength and modulus were not affected, however the (dry)  $T_g$  was lowered by 12 °C.  $K_{IC}$  was increased from 0.69 MPam<sup>1/2</sup> to 0.90 MPam<sup>1/2</sup> which equals an improvement in toughness by 30%. Further modification with silica nanoparticles did not affect strength but increased the modulus by 12%.  $K_{IC}$  was not increased further, however the glass transition temperature was lowered by another 16 °C. The addition level of both modifications was not communicated.

In a very detailed study Walter et al. [38] investigated an epoxy resin system cured with a commercial aliphatic amine hardener. They found significant improvements in  $K_{IC}$  by adding 3–8 vol% of core shell elastomer with only small losses in modulus. Nanosilica addition up to 8 vol% increased both modulus and  $K_{IC}$  by 25–50%. The combination of both modifications showed further small increases in  $K_{IC}$ . The morphology of the polymer containing 8 vol% core–shell rubber and 5.5 vol% nanosilica can be seen in Fig. 4, respectively. 3 vol% core–shell rubber and 5.5 vol% nanosilica can be seen in Fig. 5. As the different magnifications show, both nanoparticles and elastomer particles are well dispersed.

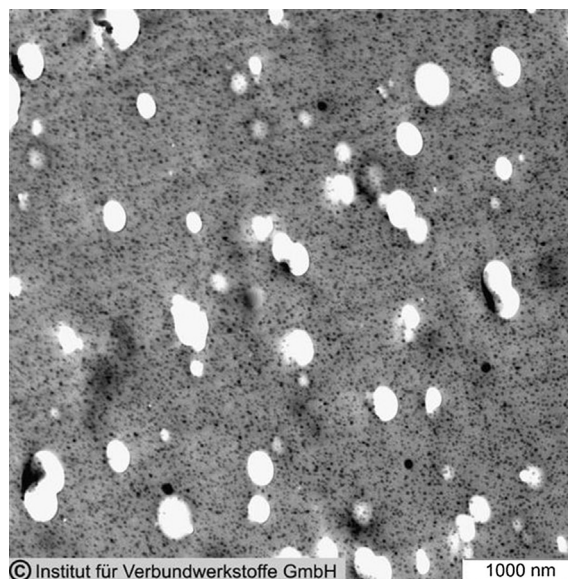
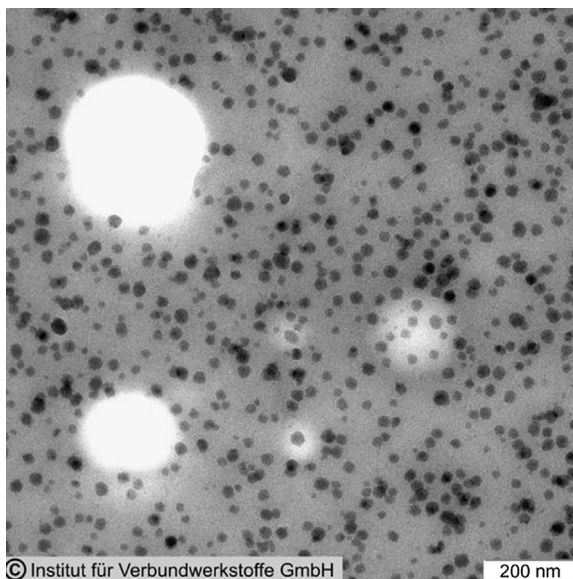


Fig. 4. TEM picture of epoxy polymer modified with 8 vol% Type III core–shell elastomer and 5.5 vol% silica nanoparticles [11].



**Fig. 5.** TEM picture of epoxy polymer modified with 3 vol% Type III core-shell elastomer and 5.5 vol% silica nanoparticles [11].

In continuation of this work Schlarb et al. studied the abrasive properties of the cured epoxy resin systems [39]. The addition of core-shell elastomer increases the abrasion whereas the nanosilica lowers the abrasion up to 30%. The hybrid performed like the unmodified epoxy resin system.

Botsis et al. investigated cycloaliphatic polyamine cured epoxy resin [5]. They observed a good dispersion of both rubber and nanoparticles as well. A small decrease in the coefficient of thermal expansion (CTE) was found for the nanosilica addition; the core-shell particles slightly increased the CTE. The hybrid behaves pretty much like the unmodified resin.

## 2.6. Epoxy resins modified with core-shell elastomers (CSRs) and silica nanoparticles, anhydride cured

### 2.6.1. CSR Type I

Taylor et al. used DGEBA cured with accelerated methylhexahydrophthalic acid anhydride for their studies [40]. The strength was lowered from 83 MPa to 69.5 MPa by the addition of 9 wt% core-shell elastomer. Further modification with 9 wt% silica nanoparticles increased the strength slightly to 73 MPa. The rubber addition reduced the modulus from 2.05 GPa to 1.7 GPa. The addition of nanosilica brought the modulus back to 1.9 GPa. The toughness of the core-shell modified polymer was increased from 1.18 MPam<sup>1/2</sup> to 1.58 MPam<sup>1/2</sup>. This equals an improvement of approx. 34%.

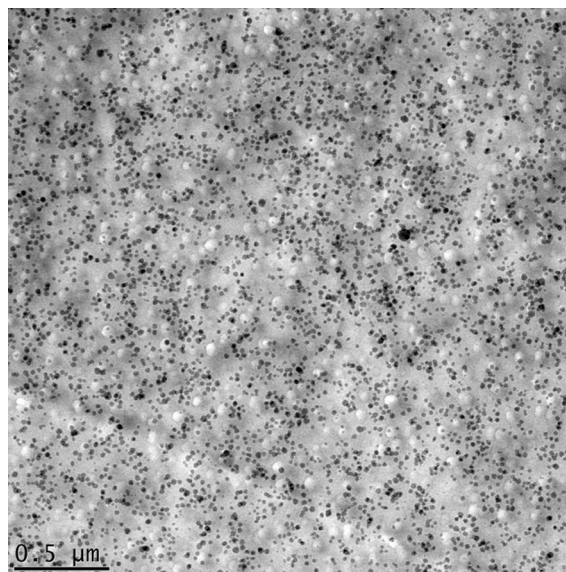
TEM investigations showed again uniform dispersion of both the 20 nm silica nanoparticles and the 110 nm core-shell rubber particles, as can be seen in Figs. 6 and 7 for different magnifications.

### 2.7. Short overview of improvements achieved

Having discussed all research results in detail, Table 1 gives an overview of the results of some selected references; regardless of the resin/hardener combination.

As can be seen, the modulus of the hybrids is a few percent lower than for the unmodified systems; especially for higher rubber or elastomer levels.

Toughness is improved significantly; especially for higher elastomer concentrations very high values can be obtained. Of course



**Fig. 6.** TEM picture of epoxy polymer modified with 9 wt% Type I core-shell rubber and 6 wt% silica nanoparticles.

the absolute value is depending on the resin/hardener combination of the formulation.

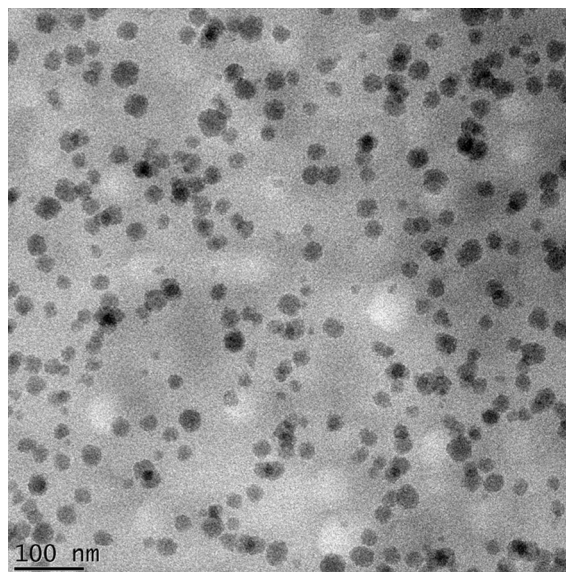
All systems are tough and stiff, which means that the best of both modifications is found in the hybrid systems.

Additionally the fatigue performance of such formulations is outstanding.

### 2.8. Synergy or no synergy?

If Figs. 3–7 are compared, the morphology of the fracture surfaces looks identical, though the elastomer particles have different sizes. However, what looks the same, behaves differently regarding micro-mechanics.

We found in our investigations with the Type III core-shell rubber no synergy between core-shell particles and silica nanoparticles. Toughness increases compared to the control were



**Fig. 7.** TEM picture of epoxy polymer modified with 9 wt% Type I core-shell rubber and 6 wt% silica nanoparticles.

**Table 1**  
Overview of property improvements of epoxy polymers achieved by hybrid modification.

Resin/Hardener	Modifications	Modulus (GPa)	Improvement versus control	$G_{IC}$ (J/m <sup>2</sup> )	Improvement versus control	Ref.
DGEBA MHHPA	4.6 wt% CTBN, <sup>a</sup> 8.5 wt% nanosilica <sup>a</sup>	2.89	−4%	241	+289%	[29]
DGEBA MHHPA	9 wt% CTBN, 9 wt% nanosilica	2.77	−6%	683	+787%	[28]
DGEBA MHHPA	9 wt% CTBN, 15 wt% nanosilica	2.85	−4%	965	+1153%	[28]
DGEBA commercial amine I	Unknown, but low % CTBN, 10 wt% nanosilica	3.25	−21%	380	+111%	[19]
DGEBA commercial amine II	11.3 wt% CTBN, 5.7 wt% nanosilica	2.68	−22%	1843	+203%	[14]
TGMDA aromatic amines	8 wt% CTBN, 10 wt% nanosilica	3.37	+4%	708	+302%	[24]
DGEBA piperidine	10 wt% CSR I, 10 wt% nanosilica	2.78	−3%	2480	+795%	[35]
DGEBA isophorone diamine	10 wt% CSR II, 10 wt% nanosilica	2.97	−9%	1030	+442%	[16]
DGEBA commercial amine	5.1 wt% CSR III, <sup>a</sup> 11 wt% nanosilica <sup>a</sup>	3.50	+9%	1851	+300%	[38]

<sup>a</sup> Recalculated from vol%.

additive. Similar findings have been reported by Liu et al. for Type I core–shell rubbers except for fatigue performance where a synergy seems to exist [35,36]. Tsai et al. could not confirm the existence of a synergy for Type II core shell particles either [16].

Apparently the well known mechanisms of rubber toughening with particulate rubbers and the mechanisms of nanosilica toughening do not significantly interact with each other, though interactions at the tip of a crack forming should be expected.

No agglomeration was reported for all systems containing both core shell rubber particles and silica nanoparticles.

The toughness of a hybrid resin based on core–shell rubbers is the added toughness of the nanosilica modification plus the core–shell elastomer modification; regardless of the rubber particle size or chemistry.

In contrast we always found a synergy in toughening between reactive liquid rubbers and nanosilica. Others, like Zhang confirmed the existence of a synergy. Though the morphology looks the same, here the mechanisms of rubber toughening with reactive liquid rubbers and nanosilica toughening are interacting somehow.

Some researchers noticed the presence of small agglomerates or clusters of nanosilica in their cured resin systems containing reactive liquid rubber [18,21,27,28].

This raises two questions. First, do agglomerates have an influence on the performance of the cured epoxy polymer? Second, do the agglomerates have any influence on the synergy found between CTBN adducts and silica nanoparticles? Could they be the reason?

Pearson investigated two different sizes of nanosilica (20 and 80 nm) in piperidine cured epoxy resin [41]. They reported a negligible effect of the particle size on fracture toughness and compressive properties. Thus it seems to be a fair assumption to consider these small agglomerates or clusters as somewhat larger nanoparticles which do not or nearly not affect the performance of the cured epoxy polymer.

Recently Pearson studied the hybrids based on the two different particle sizes and reactive liquid rubber [18]. He found no considerable effect of particle size on the toughening of the hybrid nor could he confirm a synergy.

A correlation between very high, synergistic values of  $G_{IC}$  and the observation of small nanosilica agglomerations or clusters could not be established.

It is well known that the  $G_{IC}$  of rubber toughened epoxy polymers increases dramatically with a lower crosslink density [42]. This is the reason why many industrial formulations contain the CTBN rubber adduct along with a small amount of a solid DGEBA with a higher molecular weight. The long chain molecules of the solid epoxy resin lower the crosslink density to a certain extent and make the resin matrix more ductile as well as the rubber toughening more efficient.

When silica nanoparticles are added to an epoxy resin modified with CTBN, the proportion of rubber molecules not participating in

the phase separation upon cure increases with increasing addition level of nanosilica [28]. If more long flexible rubber molecules are crosslinked randomly into the polymer matrix, the crosslink density is lowered and the ductility of the matrix is increased – thus making the rubber toughening more efficient. This could be the explanation of the synergistic improvement of  $G_{IC}$  and fatigue performance for hybrid systems based upon the combination CTBNs and nanosilica.

As indication for the lower crosslink density can be seen the development of the glass transition temperature [28]: The addition of nanosilica does not lower the  $T_g$  compared to the unmodified epoxy polymer system. This is different for the CTBN modified system. At a 9 wt% rubber addition level the  $T_g$  is 150 °C. Further addition of silica nanoparticles lowers the  $T_g$  to 145 °C at 10 wt% and to 140 °C at 20 wt%.

Though the difference in  $T_g$  might seem small, this is not unusual as minor changes in crosslink density can have a big impact on toughness. Pearson reported for two rubber toughened epoxies with a small difference in crosslink density and a difference in  $T_g$  of only 5 °C an increase in fracture toughness by factor three [42].

Still there is a need for additional research to explain the synergy, like the nature of interactions at the tip of a forming crack.

### 3. Conclusions

Taking into account all the data accumulated, a couple of conclusions can be drawn:

- The combination of rubber toughening and silica nanoparticles offers the possibility to formulate tough and stiff epoxy resin systems; regardless of the hardener used.
- Losses in modulus due to a modification with reactive liquid rubbers or core–shell rubbers can be compensated to a large extent, sometimes even completely by the addition of nanosilica.
- Losses in strength caused by core–shell elastomer modification cannot always be compensated by the silica nanoparticles.
- Lower glass transition temperatures caused by the toughener are not improved by the nanosilica addition – no increases in  $T_g$  can be achieved.
- Toughness of hybrid systems is always higher as for only rubber-toughened epoxy resin systems.
- Toughness increases of epoxy resins containing reactive liquid rubbers are synergistic. Improvements of 80%–300% can be achieved for amine cured epoxies and of 300%–1200% for anhydride cured epoxies.
- Similar improvements can be achieved for the cyclic fatigue performance.
- Typical addition levels providing best performance, high toughness and stiffness as well as very high fatigue

performance are 5–10 wt% core–shell elastomer or 5–15 wt% reactive liquid rubber combined with 5–10 wt% of silica nanoparticles.

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