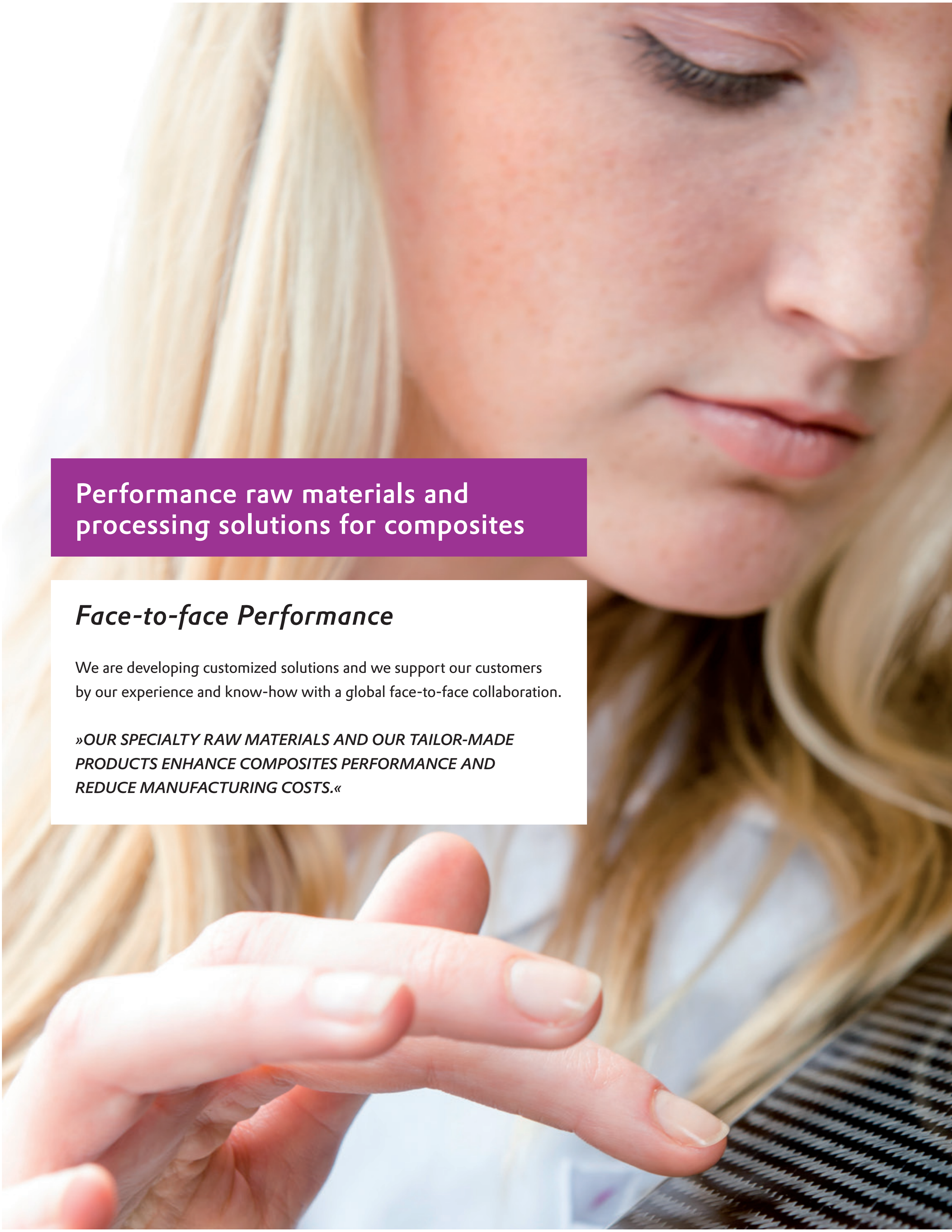
Fiber-reinforced composites

Products for efficiency and performance of thermosetting matrices

Leading Beyond Chemistry



Performance raw materials and processing solutions for composites

Face-to-face Performance

We are developing customized solutions and we support our customers by our experience and know-how with a global face-to-face collaboration.

»OUR SPECIALTY RAW MATERIALS AND OUR TAILOR-MADE PRODUCTS ENHANCE COMPOSITES PERFORMANCE AND REDUCE MANUFACTURING COSTS.«

DEPENDING ON THE APPLICATION AND DESIRED MODIFICATION, DIFFERENT PRODUCTS CAN BE USED FOR IMPROVING THE PERFORMANCE OF THERMOSETTING RESINS AND COMPOSITES MADE THEREOF OR IMPROVING THE PROCESSABILITY OF THERMOSETS AND TEXTILES:

4 Toughening epoxy resins with copolymers

7 Toughening epoxy resins with core shell elastomers

9 Modifying epoxy resins with nanoparticles

12 Improving performance with hybrid epoxy resins

14 Process additives for epoxy resins, vinyl ester resins and unsaturated polyester resins

TOUGHENING EPOXY RESINS WITH COPOLYMERS

ALBIPOX®

- Improved impact resistance over a wide temperature range (easier finishing)
- Damage-tolerant systems; improved fatigue performance
- Improved interlaminar shear strength, better fiber adhesion
- Higher pressure resistance (e.g. in pipes)
- Excellent tackifiers for prepregs and dry textiles

Exclusively tailored, customer-specific products are also available for special applications on request.

To modify an existing system, part of the epoxy resin is replaced by ALBIPOX® 1000 or ALBIPOX® 2000 (see also application remarks below). If blending is not possible, the ready-to-use ALBIPOX® 3001 can be employed. ALBIPOX® 8001 is added in small amounts (typically 3 – 10 wt%) to increase the tack of prepregs or textiles to the desired level.

PROPERTY IMPROVEMENTS

Epoxy resins have a substantial disadvantage: their brittleness. This disadvantage can be more than compensated by an elastomer modification (so-called "toughening" or impact resistance modification). In contrast to an elastification, the elongation at break of the cured modified resin does not increase.

The toughening of epoxy resins proves to be difficult, however. The use of flexible hardeners or the addition of non-reactive flexibilizers significantly impairs a number of important properties such as tensile strength and modulus, thermal and chemical resistance as well as thermo-dimensional stability.

These negative effects can be avoided by toughening with copolymers based on reactive elastomers. However, the pure liquid elastomers are only slightly miscible with epoxy resins, if at all. The different ALBIPOX® grades are reaction products between epoxy resins and an elastomeric copolymer. Hereby, an epoxy resin is reacted with a high amount of the reactive liquid elastomer. After the reaction, the elastomer molecules are epoxy functional and will be chemically bonded to the resin matrix during curing.

ALBIPOX® products are miscible with all epoxy resins in any ratio.

ALBIPOX® products can be used by epoxy resin formulators like a modular system. There are no limitations in hardeners used.

As the glass transition temperature of the liquid rubber used ranges at -40 °C to -50 °C, the significantly improved properties are also found at these low temperatures. An additional advantage is the improved processability of the modified laminates, thereby avoiding splintering on mechanical finishing. The shrinkage is also reduced, as the rubber domains can absorb the internal stresses arising during curing.

►►►

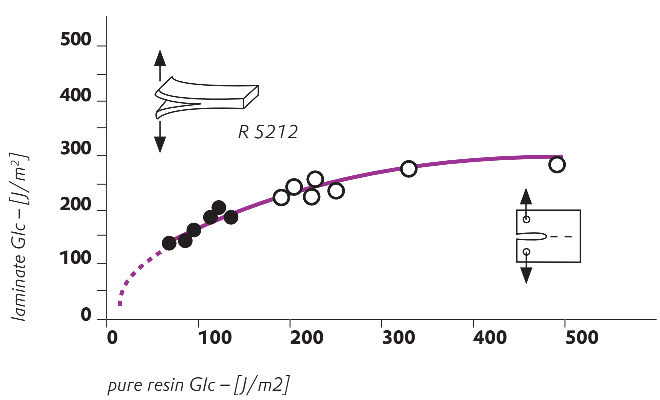
Product overview

Technical data [1]

PRODUCT NAME	NBR* [wt %]	BASE RESIN	EEW [g/equiv.]	DYN. VISCOSITY, 25 °C [mPa·s]	CHARACTERIZATION
ALBIPOX® 1000	40	DGEBA	330	200,000	standard type
ALBIPOX® 2000	40	DGEBA	330	400,000	standard type
ALBIPOX® 3001	15	DGEBA/ DGEBF	215	22,000	application-ready resin
ALBIPOX® 8001	10	DGEBA	210	400,000 4,000 (at 80°C)	very efficient tackifier

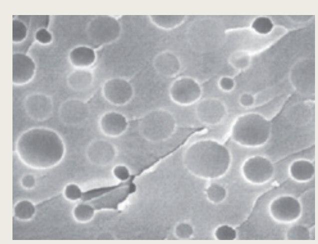
* NBR = nitrile butadiene rubber
[1] no specification

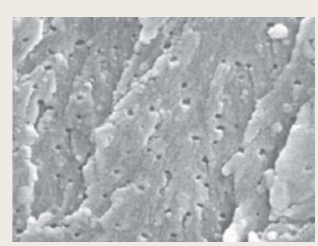
Figure 1
shows the effect of such a resin modification on the laminate



● standard epoxy resins
○ new epoxy resins with improved toughness. C-fibre: T300

Figure 2
microscopical images of rubber domains in toughened epoxy resin





HOW IT WORKS During curing, a phase separation of the elastomeric parts occurs regardless the chemical nature of the hardener and the curing temperatures. This results in finely dispersed rubber domains which are homogenously distributed across the resin. As can be seen in Figure 2, the domain size typically is in the range between 0.2 – 4 µm.

►►► For the most part, the rubber domains consist of the relatively long molecules of the elastomer used, and are chemically bonded to the matrix via their epoxy groups at the phase boundary. If a force is now applied to the cured resin system, it can be dissipated uniformly in all directions when encountering a rubber domain.

If a crack has already occurred, it is prevented from further growing: the elastomer particles stretch perpendicular to the direction of tear and are not torn out, as they are bonded chemically to the matrix. Figure 2 shows the uniformly distributed rubber particles in the epoxy matrix (mechanism see also Fig. 3).

APPLICATION REMARKS

Part of the epoxy resin in a given formulation is replaced by the ALBIPOX® grade selected. The correct ratio of rubber to epoxy is crucial for successfully improving an epoxy resin formulation. Normally, optimum results are obtained with 10 – 15 phr rubber (i.e. 10 – 15 parts rubber on 100 parts resin).

The amount of hardener is adjusted to the altered epoxy equivalent weight of the new resin mixture. An adjustment is not required for non-stochiometric hardeners such as dicyandiamide. Fillers and other recipe components are used as before.

If the viscosity of the ALBIPOX® grade selected is too high for handling in production, we recommend to preheat to 70 – 80 °C.

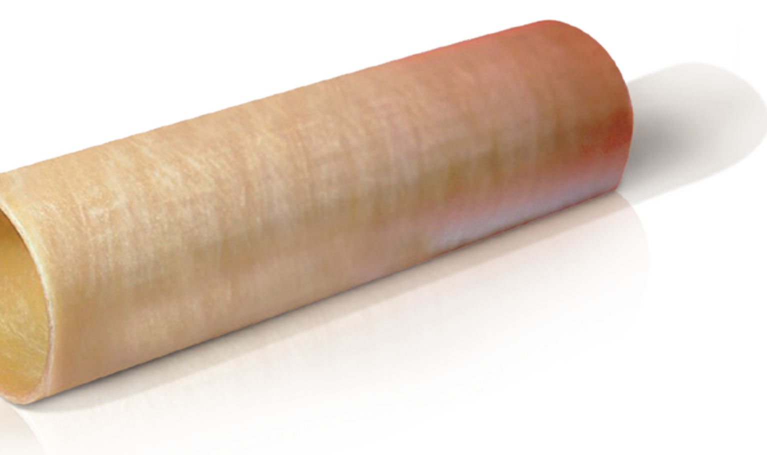
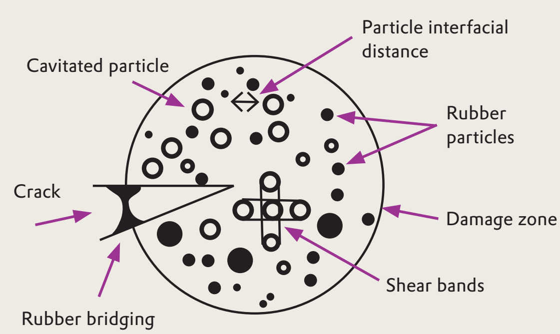


Figure 3
mechanisms of rubber toughening according to Kinloch et al., J. Mat. Sci 27, 2763-2769 (1992)



Sample calculation for the epoxy equivalent when using ALBIPOX® 1000:

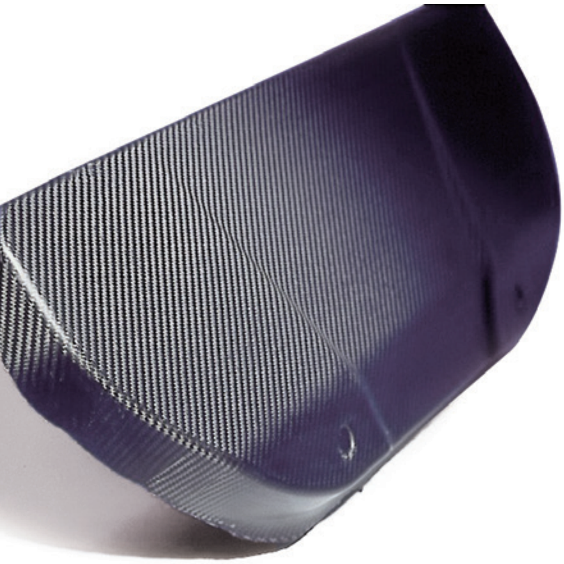
	Original formulation	10 phr NBR*	12 phr NBR*	15 phr NBR*
Standard DGEBA (EEW 185)	100	85	82	77.5
ALBIPOX® 1000 (EEW 330)	–	25	30	37.5
Total parts by weight	100	110	112	115
EEW	185	206	210	216

* NBR = nitrile butadiene rubber

TOUGHENING EPOXY RESINS WITH CORE-SHELL ELASTOMERS

ALBIDUR®

- Improved impact resistance over a wide temperature range down to -100 °C
- Negative coefficient of thermal expansion, significantly reduced shrinkage
- Moderate viscosity increase on addition, no loss in modulus or Tg
- Damage-tolerant systems, improved fatigue performance



PROPERTY IMPROVEMENTS
Besides the low viscosity of ALBIDUR®, further advantages are the high thermal stability (up to 200 °C) and the excellent low temperature toughening (below - 100 °C). Electrical properties, UV and ozone stabilities are improved significantly as well.

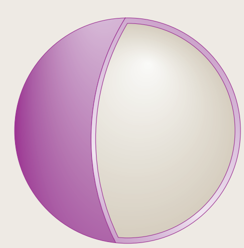
In contrast to the ALBIPOX® products, unsaturated polyester resins (UP) and vinyl ester resins (VE) containing silicone core-shell particles are available as well within the ALBIDUR® product range.

ALBIDUR® products are miscible with all epoxy resins in any ratio.

ALBIDUR® products can be used by epoxy resin formulators like a modular system. There are no limitations in hardeners used.

HOW IT WORKS ALBIDUR® products consist of a reactive resin in which fully-cured silicone elastomer particles of a defined size (0.1 - 1 µm) are finely dispersed. The silicone elastomer particles have an organic shell comprising reactive groups, here epoxy groups (Fig. 4). The toughening mechanisms are the same as in Chapter 1, however the silicone rubber particles are already present and do not form upon cure. Thus glass transition temperature (Tg) and modulus are less affected by the toughening.

Figure 4
schematic representation of a core-shell particle
core: silicone rubber
shell: compatible surface with epoxy groups



Product overview

Technical data [1]

	SILICONE RUBBER [wt %]	BASE RESIN	EEW [g/equiv.]	DYN. VISCOSITY, 25 °C [mPa·s]
ALBIDUR® EP 2240 A	40	DGEBA	300	35,000

[1] no specification

MODIFYING EPOXY RESINS WITH NANOPARTICLES

NANOPOX® HP

- Significantly improved fatigue performance
- Improved modulus and flexural strength, increase in toughness
- Significantly improved compressive strength
- Lower CTE, reduced shrinkage
- Very low viscosity, thus suitable for injection processes
- Improved surface quality, no fiber-printthrough (Class A)

Product overview

Technical data [1]

PRODUCT NAME	BASE RESIN	EEW [g/equiv.]	DYN. VISCOSITY, 25 °C [mPa·s]	CHARACTERIZATION
NANOPOX® HP 100	DGEBA	295	60,000	standard type
NANOPOX® HP 120	DGEBA/F	290	45,000	crystallization-free
NANOPOX® HP 110	DGEBF	275	20,000	standard type
NANOPOX® HP 131	EEC	220	5,500	for cycloaliphatic epoxy formulations, UV-curable
NANOPOX® HP 140	epoxidized Novoloac	310	20,000 (at 50 °C)	high performance novolac, high Tg and modulus

Special tailor-made grades are available on request.
[1] no specification

HOW IT WORKS NANOPOX® F products are epoxy resins containing amorphous silica nanoparticles with a spherical shape. Supplied as concentrates, they can be used like standard epoxy resins and be blended with all standard epoxy resins. No special dispersing or mixing equipment is necessary. These particles have diameters around 20 nm and a very narrow particle size distribution (Fig. 6). They are uniformly and agglomerate-free dispersed in the resin, as can be seen in Figure 7. The result are resins with a comparable low viscosity, although they contain 40 wt% silica nanoparticles.

Figure 6
particle size distribution determined by SANS

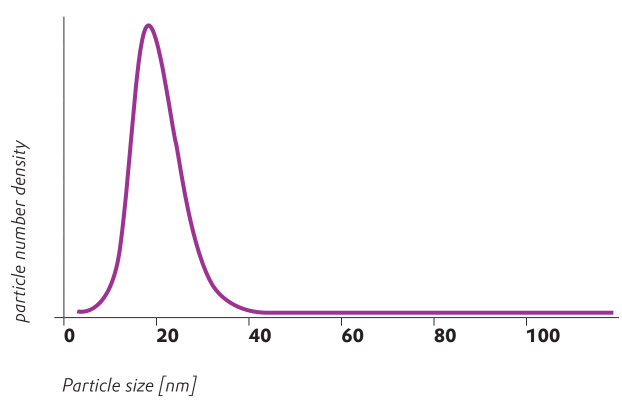


Figure 7
TEM images of cured NANOPOX® samples showing the excellent dispersion of SiO_2 nanoparticles

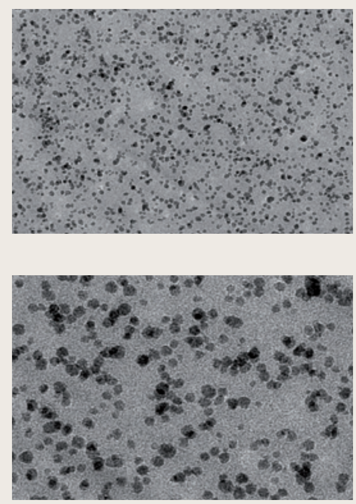
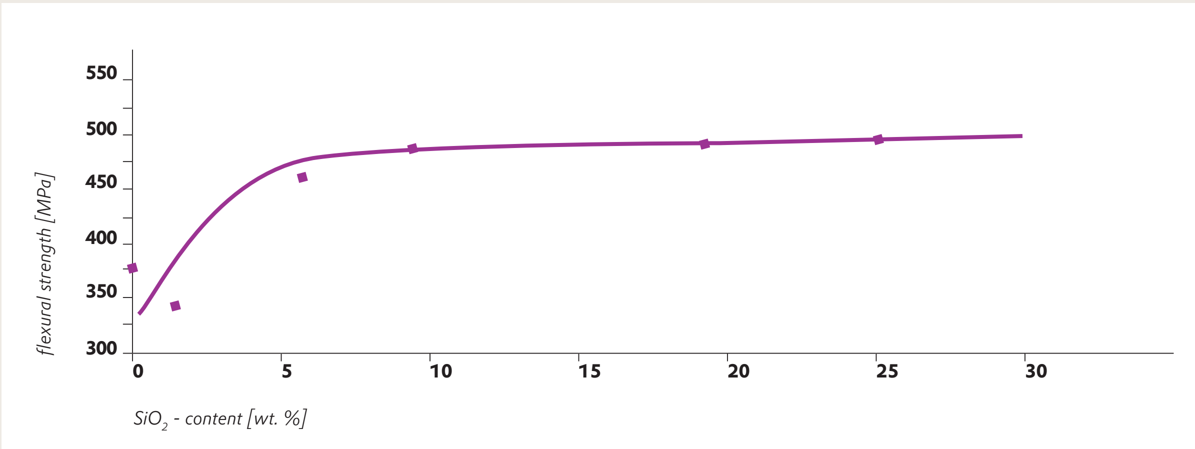
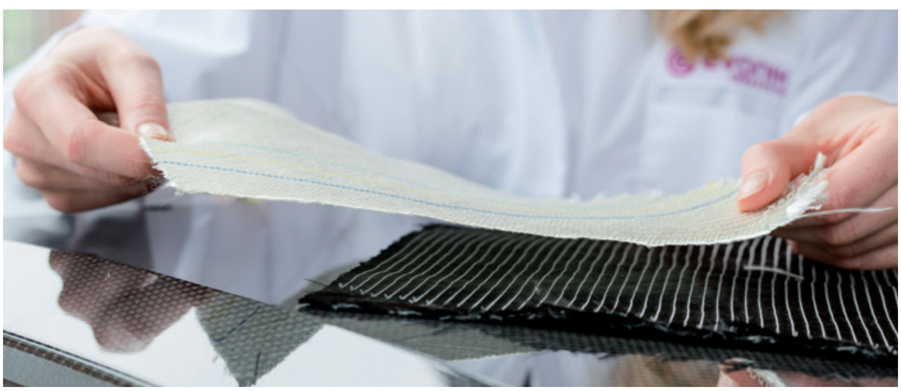


Figure 5
flexural strength of a GFRC improved by nanosilica addition





PROPERTY IMPROVEMENTS

Modifying epoxy resins used to manufacture fiber-reinforced composites with about 10 wt% silica nanoparticles significantly enhance their properties. Compressive strength and bending strength are improved. Fatigue performance is improved by magnitudes, thus providing much longer service lifes for composites parts. With increasing nanoparticle content the shrinkage (or CTE) is considerably reduced which enables a Class A surface to be attained. Silica nanoparticles do increase toughness as well, not to the extent to a rubber-toughening, but by 30 – 40 %. The complex mechanisms are well understood by now.

Figure 5 shows the flexural strength of a glass fiber-reinforced laminate manufactured using VARTM (DGEBA, anhydride cured, 60 % GF). Due to their small size and the absence of any larger aggregates, the nanoparticles can easily penetrate all fiber structures, even close-meshed fabrics without compromising the impregnation by excessive viscosity. Therefore all state-of-the-art manufacturing processes like resin infusion (RI respectively VARI), RTM or VARTM, filament winding or pultrusion can be used. Furthermore the silica nanoparticles do not sediment, thus they are very favourable for the use in prepreg manufacturing.

Mechanical treatment of cured epoxy resins containing silica nanoparticles, e.g. the sawing of laminates or the polishing of fiber-reinforced composites does not release isolated nanoparticles. They remain embedded in much larger polymer fragments; thus standard dust protective gear is sufficient.

IMPROVING PERFORMANCE WITH HYBRID EPOXY RESINS

ALBIPOX® F

- Outstanding fatigue performance
- Extremely tough and stiff resin systems
- Excellent fiber-wetting

PROPERTY IMPROVEMENTS

By combining both rubber-toughening and the modification with silica nano-particles, tough and stiff fiber-reinforced composites with outstanding fatigue performance can be manufactured. The drawbacks of rubber-toughening like lower modulus are overcompensated by the nanosilica. Fracture toughness is increased further, as there exists a synergy between both modifications. The ALBIPOX® F products are especially suitable for heavy-duty applications or ballistic applications (Fig. 8).

Product overview

Technical data [1]

PRODUCT NAME	Base resin	EEW [g/equiv.]	Dyn. viscosity, 25 °C [mPa·s]	CHARACTERIZATION
ALBIPOX® F 080	DGEBA/F	330	70,000	standard type for anhydride cure; can be diluted down

Special tailor-made grades are available on request.
[1] no specification

HOW IT WORKS ALBIPOX® F products are epoxy resins containing amorphous silica nanoparticles and CTBN adducts. The mechanisms of rubber-toughening apply, as well as the mechanisms of toughening with silica nanoparticles. Between both mechanisms a synergy exists, which results in materials with no microcrack formation and an outstanding fatigue performance.

PROCESS ADDITIVES FOR EPOXY RESINS, VINYL ESTER RESINS AND UNSATURATED POLYESTER RESINS

TEGOPREN®, TEGOMER®, TEGO® Antifoam

- Improved wetting of glass fibers
- Improved filler and flame retardant dispersion, reduced sedimentation
- Defoamers, prevention of air bubble formation
- Improved scratch resistance of surfaces
- Internal release agents

PROPERTY AND PROCESSING IMPROVEMENTS

By using small amounts of these additives in thermosetting resin formulations (typically 0.1 – 0.8 %) the manufacturing process of fiber-reinforced composites can be made easier. If such an additive is used as internal release agent, demolding even without using an external mold release agent is no problem anymore. Surface properties like scratch resistance can be increased significantly. The use of defoamers reduces the amount of bubbles or pores in a fiber-reinforced composite, which consequently exhibits better mechanical performance.

INTERNAL RELEASE AGENT

Especially in fast manufacturing processes like VARTM efficient demoulding is necessary. Time and cost-intensive external mold release agents cannot be used. Therefore internal release agents are part of the epoxy resin formulation. They offer several advantages:

- fast demoulding of the composite part
- superior surface appearance of the composite part
- no negative effects on paintability of the composite part
- no negative effects on processability of the epoxy resin

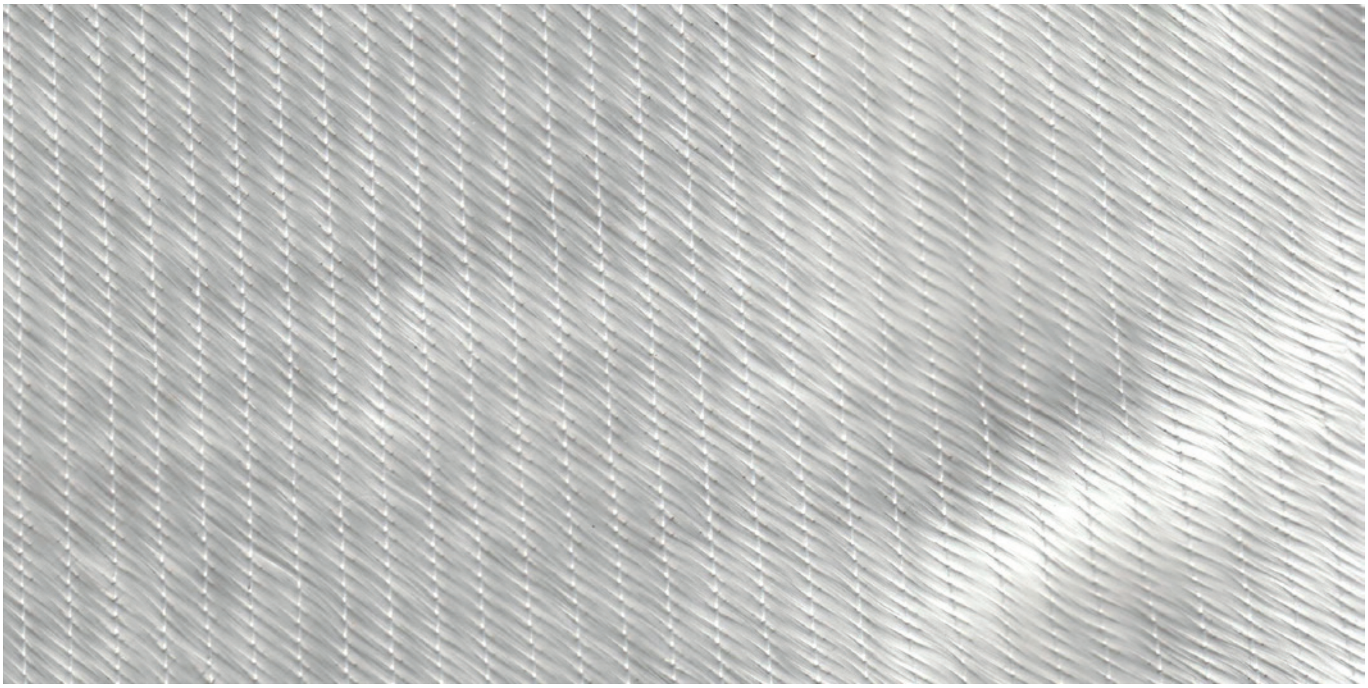


Figure 9
cured epoxy resin without additive and with 0.3 % TEGOMER® DA 626

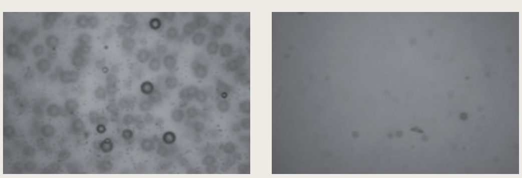


Figure 10
cured UPES resin without additive and with 0.2 % TEGOMER® D 2345

Product overview

Technical data[1]

PRODUCT NAME	CHEMICAL COMPOSITION	CHARACTERIZATION
TEGOMER® DA 626	Polymeric structure	dispersing agent, defoamer
TEGOPREN® 6875	Alkyl-modified siloxane	dispersing agent, improved scratch resistance
TEGOMER® M-SI 2650	Organo-modified siloxane containing non-reactive aromatic groups	internal release agent, dispersing agent

[1] no specification

Internal release agent

RESIN	FIRST RECOMMENDATION	SECOND RECOMMENDATION
Standard epoxy resins	0.1 – 0.2 % TEGOMER® M-Si 2650	
Standard UP resins	0.1 – 0.2 % TEGOMER® M-Si 2650	0.1 – 0.2 % TEGOPREN® 6875

SCRATCH RESISTANCE

Just think about public transportation – and the scratch resistance of panels made from SMC becomes an imminent issue. Figure 11 shows the possible improvements. Low addition levels of 0.3 – 0.6 % can already yield significant improvements.

For the modification of unsaturated polyester resins based on orthophthalic acid we recommend these products:

Scratch resistance

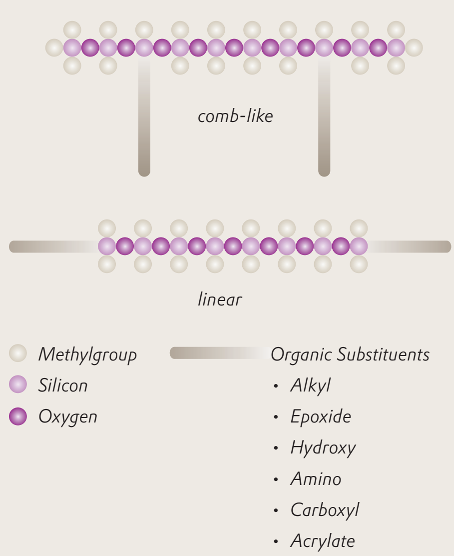
CURING AGENT	RECOMMENDATION
Methylethylketone peroxide (MEKP)	TEGOMER® M-Si 2650 TEGOPREN 6875
Dibenzoyl peroxide (BPO)	TEGOPREN 6875

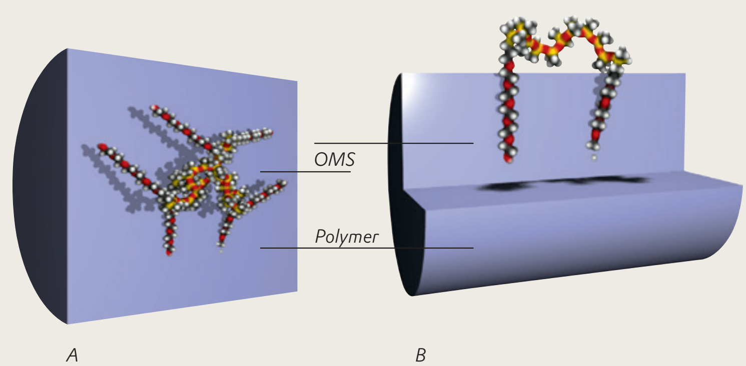
[1] no specification

HOW IT WORKS Organo-modified siloxanes (OMS) consist of a siloxane backbone with attached organic groups. The organic groups ensure a permanent functionalization of the polymer without bleeding of the OMS. Different molecular architectures of OMS derivatives are available. Figure 12 shows the comb-like as well as the linear structure of the OMS together with the possible functional groups. By varying the density and nature of the attached organic groups the OMS called TEGOMER® or TEGOPREN® are tailor made products to the final application. Figure 12 shows the functionalization of a polymer matrix with OMS. These derivatives can either work for bulk modification (case A) or for surface modification (case B).

Figure 11
scratch resistance of cured unsaturated polyester with 0.4 % TEGOMER® M-Si 2650 / without additive

Figure 12
schematic illustration of the structure of an OMS and its interaction with a polymer





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