Structural Adhesives

Products for efficiency and performance of thermosetting and UV-curing matrices

Leading Beyond Chemistry

Performance raw materials for structural adhesives

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 STRUCTURAL ADHESIVES PERFORMANCE.«

DEPENDING ON THE APPLICATION AND DESIRED MODIFICATION, DIFFERENT PRODUCTS CAN BE USED FOR IMPROVING THE PERFORMANCE OF ADHESIVES BASED ON THERMOSETTING RESINS AND UV-CURABLE RESINS SYSTEMS.

ADHESION – THE MODERN WAY TO CONNECT

In former times welding seams, screws or rivets have been always the first choice for a durable and sufficient connection of different elements. Today the adherence of components plays a major role for more and more applications and industries.

The business line Interface & Performance of Evonik offers a broad range of binders and additives to fulfill the modern needs of adhesion:

Hybrid Adhesives & Sealants Our silane modified polymers are superior binders for your hybrid adhesive to achieve your desired mechanical and environmental profile.

Water based Adhesives Our specialty additives reduce foaming and improve wetting of your dispersion based on, for example acrylic, SBR, PU or PVAc polymers.

Silicone Adhesives & Sealants We supply the raw materials and formulation support for your silicone needs.

Structural Adhesives & Sealants We offer toughening, fatigue improvement, deaeration and dispersing agents for your adhesive and resin systems, be it based on epoxies, acrylics, or PU.

MODIFYING HEAT AND ROOM TEMPERATURE CURING EPOXY ADHESIVES WITH NANOPARTICLES

NANOPOX® A

- Significantly improved fatigue performance
- Increase in toughness, reduced CTE
- Improved modulus, particularly high lap shear and peel strengths

PROPERTY IMPROVEMENTS
The performance of structural adhesives can be significantly improved by modifying them with silica nanoparticles. Typically part of the epoxy resin used in the adhesive formulation to be improved is replaced by NANOPOX®. Simple blending is sufficient, no special dispersing equipment is necessary. In many adhesive formulations addition levels of 5 – 15 wt% NANOPOX® (which equal 2 – 6 wt% nanosilica) are sufficient. Especially the fatigue performance is increased considerably.

Structural epoxy adhesives toughened with reactive liquid rubbers (CTBN-adducts) or core-shell materials can be further improved by the addition of silica nanoparticles. Figure 1 shows the results of the wedge impact test (DIN EN ISO 11343) of a 2 part epoxy adhesive on oil-treated automotive steel as substrate. The impact resistance is increased by an additional 40 – 150 %; lap shear strength and peel strength are improved as well.

Product overview

Technical data[1]

PRODUCT NAME	BASE RESIN	EEW [g/equiv.]	DYN. VISCOSITY, 25 °C [mPa·s]	CHARACTERIZATION
NANOPOX® A 410	DGEBA	295	60,000	standard type
NANOPOX® A 510	DGEBF	275	45,000	standard type
NANOPOX® A 611	EEC	220	4,000	cycloaliphatic epoxy, UV-curable

* (all products contain 40 wt% SiO_2 nanoparticles). Special tailor-made grades are available on request.
[1] no specification

HOW IT WORKS NANOPOX® A 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. 2). They are uniformly and agglomerate-free dispersed in the resin, as can be seen in Figure 3. As a consequence these resins have a comparable low viscosity, although they contain 40 wt% silica nanoparticles

Figure 1
2-part adhesive impact resistance as function of the nanoparticle content

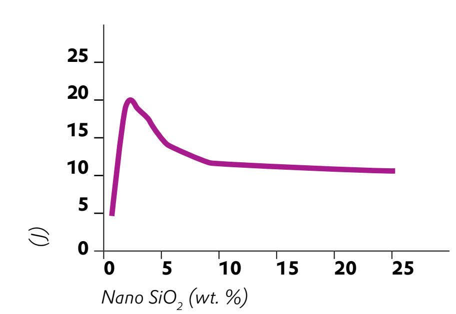


Figure 2
particle size distribution determined by SANS

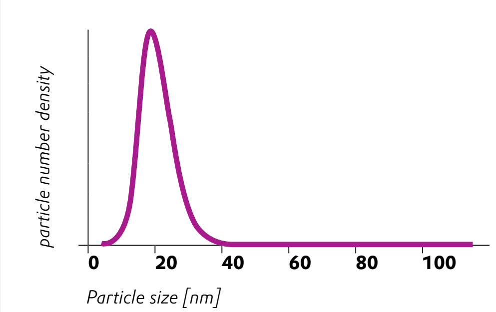
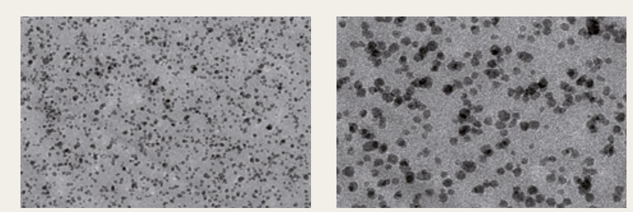


Figure 3
TEM images of cured NANOPOX® samples showing the excellent dispersion of SiO_2 nanoparticles



Acrylic monomers and oligomers modified with silica nanoparticles

MODIFYING UV-CURED OR RADICALLY CURED ADHESIVES WITH NANOPARTICLES

NANOCRYL® A

- Significantly improved tear resistance, fracture toughness and modulus
- Highly filled, transparent adhesives can be formulated
- Significantly improved adhesion to inorganic substrates (e.g. glass)

PROPERTY IMPROVEMENTS
The products are highly transparent and do not show any sedimentation, i.e. the processability remains essentially unchanged compared to the respective base monomer or oligomer. The transparency of a given formulation remains unchanged as well after a modification with NANOCRYL® A. The performance however, is improved significantly: Thermal expansion and internal stress are reduced. Tear resistance, fracture toughness and modulus are increased. Thermal ageing is reduced, heat conductivity is increased, barrier properties against gases, water vapor and solvents are increased.

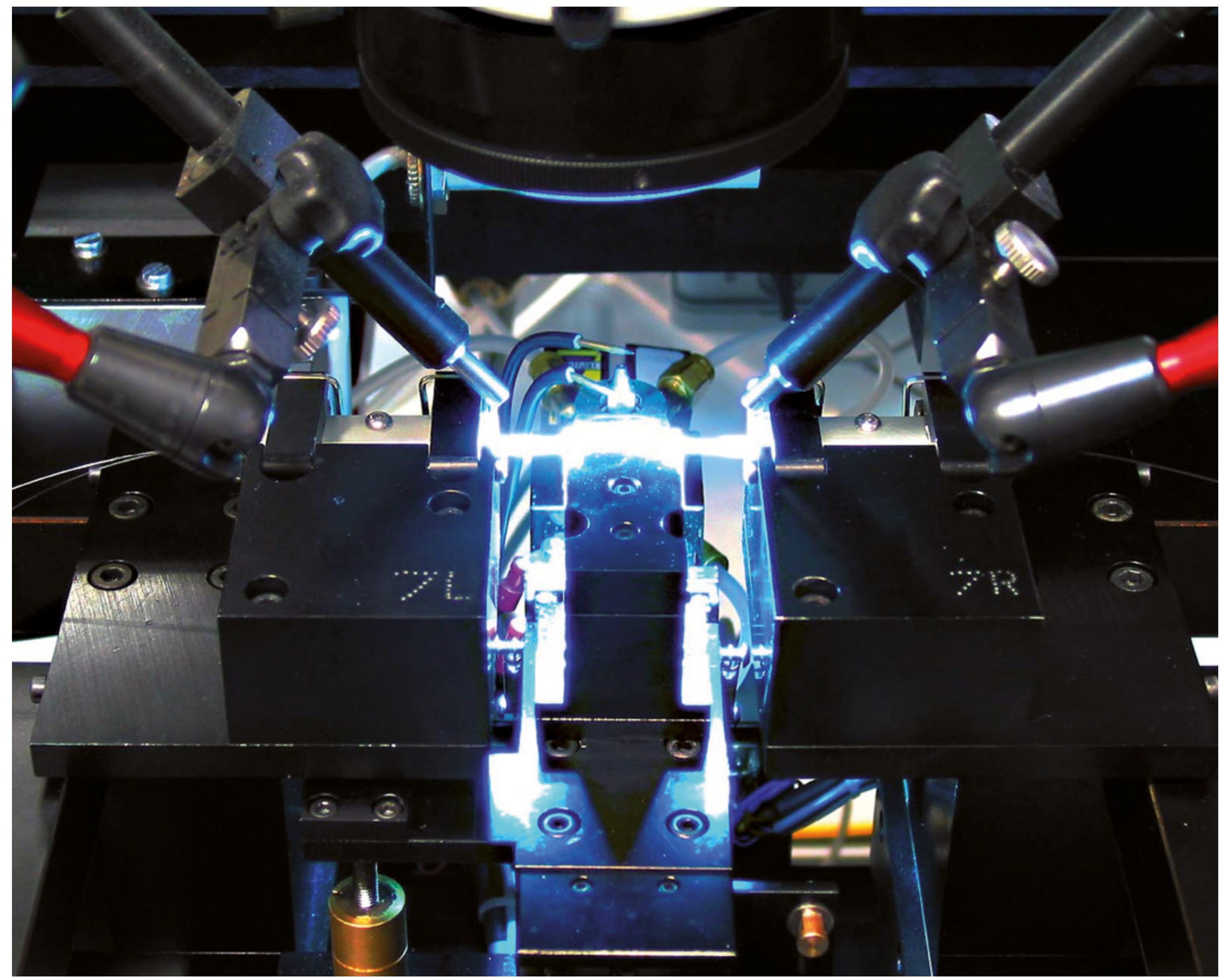
NANOCRYL® A products are compatible with most acrylate monomers and oligomers. Nevertheless compatibility with the individual formulation components should be tested separately prior to the recipe development. They can be used as delivered or as additive. The total silica content required in a formulation depends on the desired property profile. NANOCRYL® A products can be used as well in formulations containing conventional fillers like quartz powder, Al_2O_3 or others. The nanosilica particles will then fill the space between the microparticles. This enables the formulator to increase the total filler content without increasing the viscosity and push modulus, bending strength and other properties further.

Product overview

Technical data [1]

PRODUCT NAME	MONOMER	CHARACTERIZATION	DYN. VISCOSITY, 25 °C [mPa·s]
NANOCRYL® A 210	HDDA	Hexandioldiacrylate	175
NANOCRYL® A 215	TPGDA	Tripropylenglycoldiacrylate	200
NANOCRYL® A 220	TMPTA	Trimethylolpropanetriacrylate	3,300
NANOCRYL® A 223	TMPEOTA	Ethox. Trimethylolpropanetriacrylate	1,000

* (all products contain 50 wt% SiO_2 nanoparticles). Special tailor-made grades are available on request.
[1] no specification



Source: Dr. Hönle AG

MODIFICATION OF REACTIVE RESINS WITH NANOPARTICLES

NANOPOL® A

Product overview

Technical data [1]

PRODUCT NAME	SiO_2 CONTENT [wt%]	SOLVENT	DYN. VISCOSITY, 25 °C [mPa·s]
NANOPOL® A 710	50	n-butylacetate	20
NANOPOL® A 720	50	1-methoxy-2-propanol acetate	20

[1] no specification

- Significantly improved tear resistance, fracture toughness and modulus
- Highly filled, transparent adhesives can be formulated based on various reactive resins
- Uncritical solvents for easy processing

PROPERTY IMPROVEMENTS

The products are highly transparent and do not show any sedimentation. Due to the compatibility of the solvents they can be blended with many different reactive resins. Then the solvent is removed by evaporation. This way customer-specific resins or formulations can be modified with nanosilica and the adhesive performance can be improved accordingly (mechanical properties, toughness, fatigue).

TOUGHENING EPOXY ADHESIVES WITH COPOLYMERS BASED ON REACTIVE LIQUID RUBBERS

ALBIPOX®

- Improved impact resistance over a wide temperature range
- Damage-tolerant systems; improved fatigue performance
- Improved inter-adhesion to metals, minerals and oily substrates
- Green tack for PSA performance and thermal postcure

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 green tack of epoxy adhesives 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 thermodimensional 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. Figure 4 shows the lap shear and T-peel improvements of a one part, heat curing epoxy adhesive. ►►►

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

Figure 4
improvement of adhesive properties using reactive copolymers.

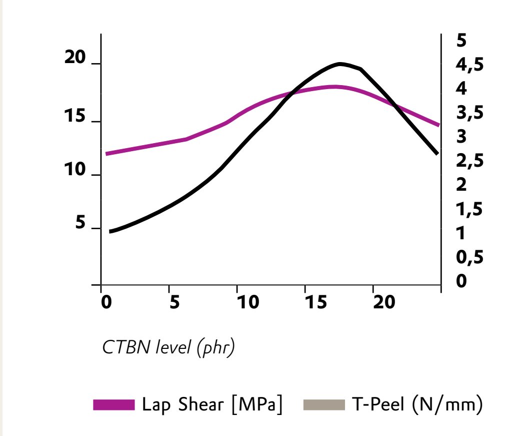


Figure 6
mechanisms of rubber toughening according to Kinloch et al., J. Mat. Sci 27, 2763-2769 (1992)

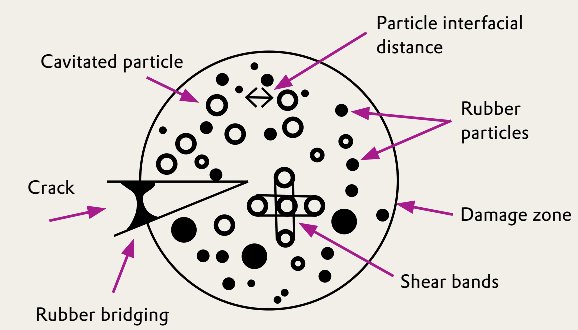
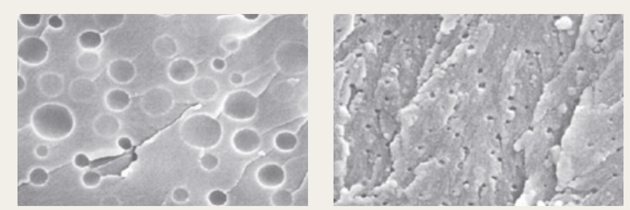


Figure 5
scanning electron microscope image of rubber-modified epoxy resin adhesive



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

►►► Optimum properties are found at approx. 15% reactive liquid rubber (CTBN) which corresponds to around 30% copolymer addition (e.g. ALBIPOX® 2000).

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. In addition to the significantly increased impact resistance, an improved adhesion to metallic substrates (e.g. oil-treated steel, aluminum alloys) as well as to mineral substrates is achieved. Hence the use of copolymers based on reactive liquid rubbers is standard in structural adhesives today; especially for automotive and aerospace adhesives. 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 5 shows the uniformly distributed rubber particles in the epoxy matrix (mechanism see also Fig. 6).

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), which equals approx 30 wt% ALBIPOX®. The amount of hardener is adjusted to the altered epoxy equivalent weight of the new resin mixture. An adjustement 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. If the viscosity of the ALBIPOX® grade selected is too high for handling in production, we recommend to preheat to 70 – 80 °C.

TOUGHENING EPOXY ADHESIVES WITH CORE-SHELL RUBBERS

ALBIDUR®

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.

ALBIDUR® products are miscible with all epoxy resins in any ratio. ALBIDUR® EP 2240 A is suitable for 2 part, RT curing epoxy adhesives as well as for 1 part, heat curing adhesives. There are no limitations in hardeners used. ALBIDUR® EP 5340 A is designed for anhydride cure or UV initiated, cationic curing adhesives.

Another advantage of ALBIDUR® products is the chemical structure of the very thin shell, which is different from the typical acrylic shell of other core-shell materials. No separate Tg of the shell can be measured - and it does not soften at elevated temperatures, thus the adhesive performance is given even at high temperatures.

Compared to copolymers based on reactive liquid rubbers, dosages for optimal adhesive performance are lower, typically 3 – 5 wt% silicone rubber (corresponds to a replacement of 7.5 – 12.5 wt% epoxy resin by e.g. ALBIDUR® EP 2240 A). Of course the epoxy equivalent weight of the blend needs to be recalculated and the amount of hardener needs to be adapted accordingly.

- 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

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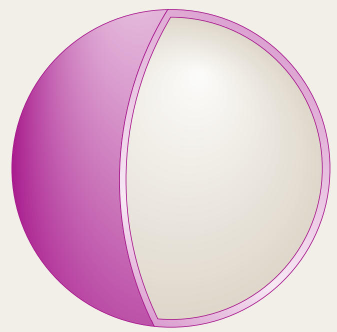
▶▶▶

Figure 8
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
ALBIDUR® EP 5340 A	40	EEC	230	4,000

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

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. 8). The toughening mechanisms are the same as for copolymers based on reactive liquid rubbers, 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.

PERFORMANCE ADDITIVES FOR STRUCTURAL EPOXY AND POLYURETHANE ADHESIVES

TEGOPREN®, TEGOMER®, TEGO® Antifoam

PROPERTY AND PROCESSING IMPROVEMENTS
By using small amounts of these additives in adhesive formulations (typically 0.1–0.8%) the adhesive properties can be increased significantly.

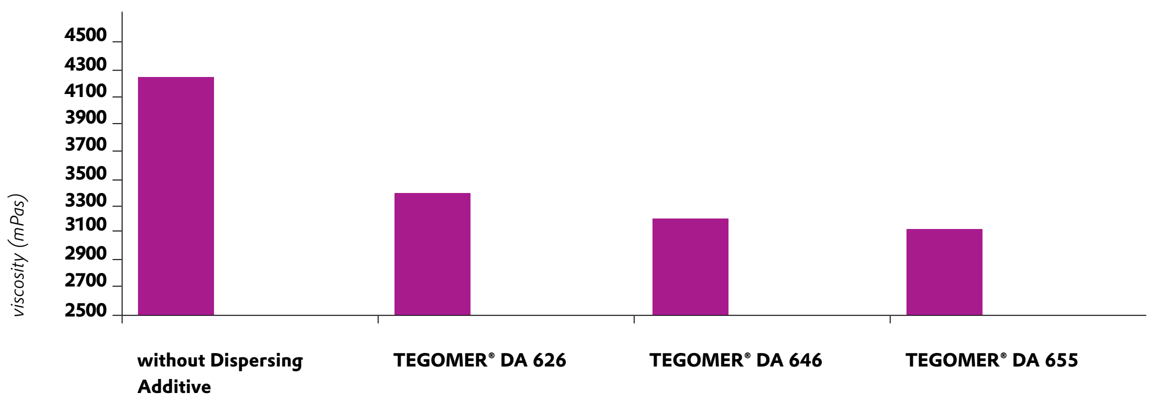
The use of deaerator reduces the amount of bubbles or pores upon cure, hence providing much better mechanical performance of the adhesive. Most important, the dispersing agents do improve the wetting and distribution of fillers, pigments and flame retardants, thus enhancing adhesive performance tremendously. Achieving a uniform particle distribution within the adhesive provides further increased strength, modulus and toughness, regardless of the test method used to document adhesive performance.

Improved wetting of mineral fillers of course improves the rheology of adhesives as well; which is especially important for automated adhesive application. Even very cheap, low quality fillers can be used in adhesive formulations still achieving an excellent rheology profile.

DISPERSING AGENTS
Dispersing of a variety of fillers or glass fibers is a demanding requirement ▶▶▶

- Prevention of air bubble formation, especially upon cure
- Improved filler and flame retardant dispersion, reduced sedimentation
- Improved wetting of polar substrates

Figure 9 viscosity in 1K PU Adhesive



Resulting viscosity of 1K PU replacing 10% of plasticizer by 10% dispersant

▸▸▸ in filled adhesive formulations to balance mechanical properties, cost and special properties such as flame retardancy. TEGOMER®/ TEGOPREN® dispersing agents allow to increase significantly the loading level of inorganic fillers or lower the viscosity of formulations for better handling and applicability of the adhesive.

DISPERSANTS OFFER SEVERAL BENEFITS:

Better distribution of fillers or flame retardants, therefore improved adhesive performance

- Higher filler loading for a better cost-efficiency combined with enhanced mechanical properties
- Prevention of settlement of high density-materials in low viscosity adhesives

INCREASE ADHESIVE PERFORMANCE

Conventional adhesives for automotive and aerospace applications are toughened to provide the required performance. Unfortunately most tougheners, like reactive liquid rubbers, core-shell particles of generation 1 and 2 or thermoplastic modifiers do lower strength, modulus and the glass transition temperature of structural adhesives. Using a specially designed organosilicone as single modification or in combination with standard tougheners, the toughness can be increased further without a loss in Tg due to the epoxy functionality of the molecule.

Impact modified adhesives are used to create a hard and tough bonding as used e.g. in automotive industry to gain a crash-stable adhesive connection. Normally special reactive rubber particles are used as impact modifiers. The problem is that these rubber particles can lower the glass transition temperature of the formulations. This may be important, because typically adhesives with the highest glass transition temperature have the best heat resistance and show due to that the best tensile properties at elevated temperatures.

FIGURE 10
floating roller peel test specimen

Product overview

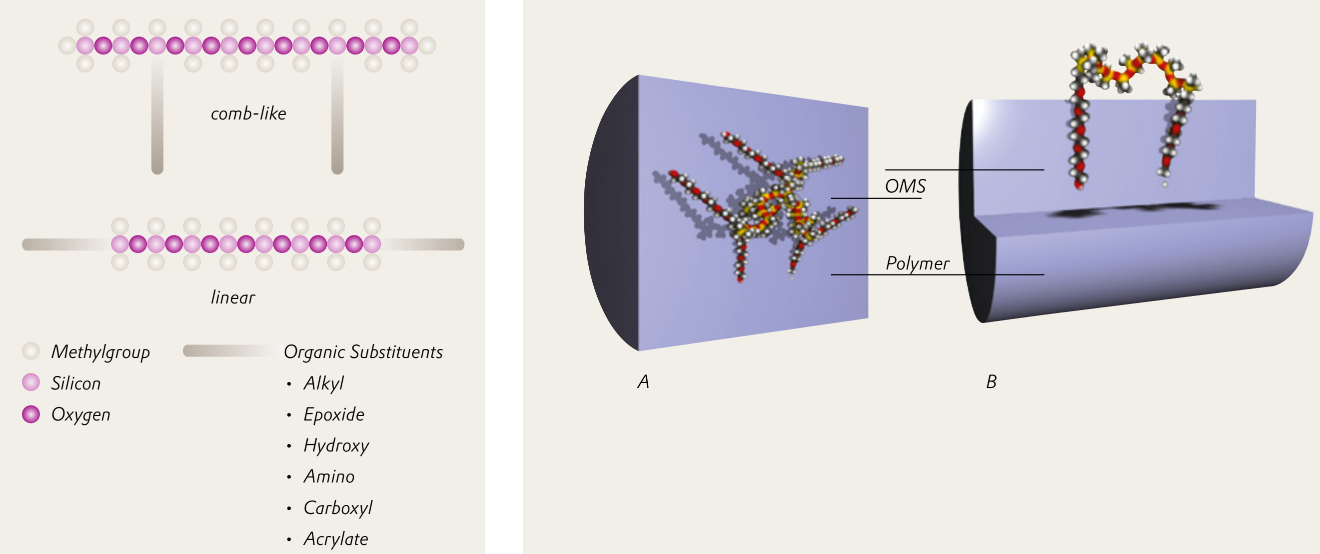
Technical data [1]

PRODUCT NAME	CHEMICAL COMPOSITION	
TEGOMER® DA 626	Polymeric structure	Dispersing agent, deaerator
TEGOMER® DA 646	Polyether structure	Dispersing agent
TEGOPREN® 6875	Organo-modified siloxane	Dispersing agent, anti-settlement
TEGO® Antifoam D 2340, TEGO® Antifoam D 2345	Polymer solution	Deaerator

[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 11 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 11 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
schematic illustration of the structure of an OMS and its interaction with a polymer



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