EVONIK INDUSTRIES

AEROSIL® fumed silica and SIPERNAT® specialty silica in Silane Terminated Polymers (STP)

Technical Information 1411

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Contents

General information

AEROSIL® fumed silica and SIPERNAT® specialty silica offer enhanced performance in sealant and adhesive formulations. The same performance achieved in long established chemistries are verified in Silane Terminated Polyurethane (STPU) and Silane Terminated Polyether (STPE). Evonik's amorphous, hydrophobic silica improves the rheological property and cured performance of these hybrid, silane terminated systems.

Silane Terminated Polyether and Polyurethane Technology is a fast-growing product technology that is used in formulations for sealant-adhesives on a wide variety of substrates. These polymers also known as Silyl / Silane Modified Polymer (SMP) are primarily one component moisture curing systems. Initially the main benefits of STP/SMP technology focused on environmental as well as human safety. Today, significant performance benefits can be claimed in adhesion, strength, and stability. Progress in polymer design and formulation optimizations allow for applications without need for primer, making installation faster and cost effective.

This Technical Information outlines the process for selecting, handling, and incorporating Evonik's engineered silica based on the requirement of the specific application.

AEROSIL® fumed silica

Evonik manufactures AEROSIL® fumed silica utilizing a flame hydrolysis reaction. Silicon tetrachloride, oxygen and hydrogen are fed continuously through a flame above 1000 °C to produce amorphous silicon dioxide of very high purity. Temperature and dwell time are controlled to affect the primary particle size and aggregate structure.

The primary particles sinter together forming aggregates. Within the silica aggregates the primary particles do not exist in isolated form. They do not form physical boundaries between each other. Downstream processes are employed to render surfaces hydrophobic with a variety of treatment options and mechanical post treatment reduces structure and allows for high fill capability.

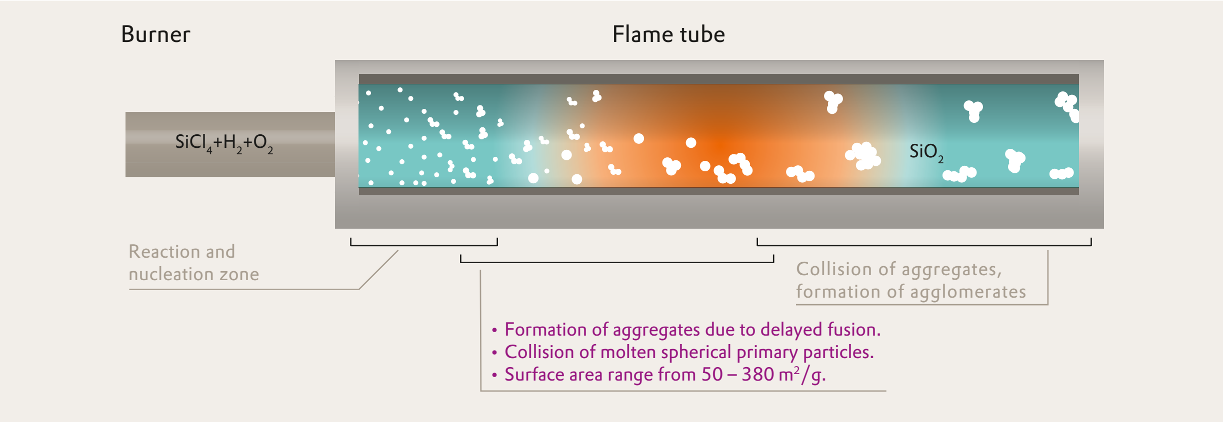
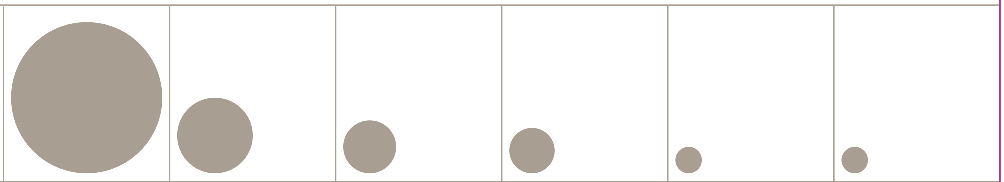


Figure 1 AEROSIL® fumed silica particle growth and formation of aggregates

Down stream processes:
Surface Treatment - Dimethyldichlorosilane, Octamethyltetracyclosiloxane, Hexamethyldisilazane, Octyltrimethoxysilane, Polydimethylsiloxane, etc.
Structure modification - reduced branching, high filler loading, higher tapped density and reinforcement.

The resulting product is of a high purity with a narrow surface area distribution and defined aggregate structure. The average diameters of the strongly bound primary particles theoretically are between 7 and 40 nm according to the standard AEROSIL® fumed silica portfolio, (Figure 2) while the specific surface areas range accordingly between 50 and 380 m^2/g.

Figure 2: Surface area designation



	AEROSIL® OX50	AEROSIL® 90	AEROSIL® 150	AEROSIL® 200	AEROSIL® 300	AEROSIL® 380
BET surface area [m^2/g]	50	90	150	200	300	380

- Most common base type
- Balanced thickening and dispersibility
- Higher surface area gives better transparency
- Lower surface area allows for higher filler loading

Figure 3 is a TEM image showing the complex aggregate structure of fumed silica where the primary particles are completely absorbed as part of the branched aggregate. No physical boundaries exist between the original primary particles.

After manufacturing, the resulting aggregates are rich in surface silanol groups which readily form hydrogen bonds. (Figure 4) The ready interaction through hydrogen bonding of these particles with moisture gives rise to their designation as “hydrophilic (water loving)” silica.

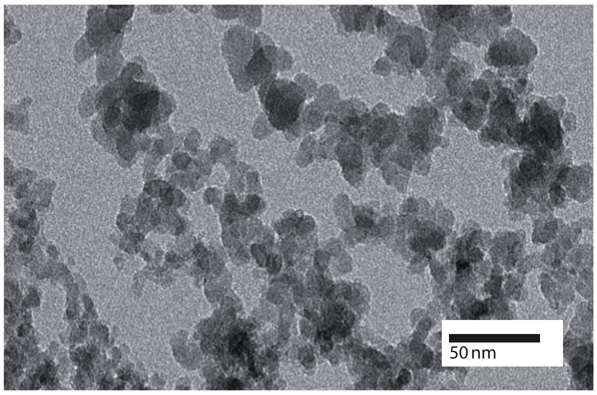


Figure 3 TEM image of AEROSIL® 200

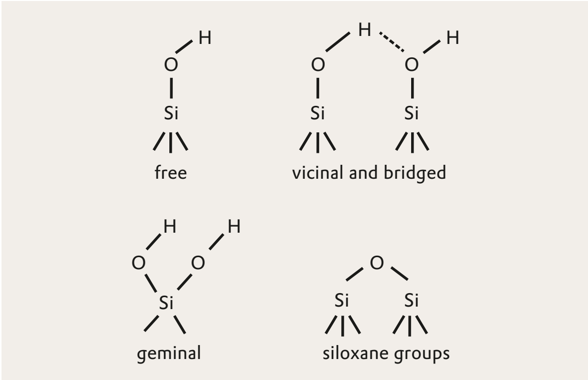
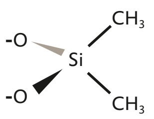
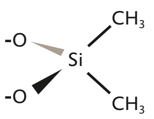
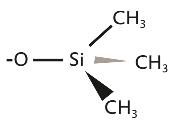
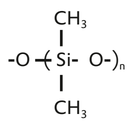
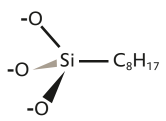


Figure 4 - Surface chemistry

Hydrophilic silica can undergo further derivation in which alkyl and siloxane functionalities are covalently bonded to the surface of the silica. This treatment reduces and or converts surface silanol groups, changing the hydrophobicity of the silica. These treated materials are designated as "hydrophobic (water hating)" silica and have increased rheological performance in polar systems as well as imparting varying levels of hydrophobicity depending on grade selection and loading level.

Figure 5 – AEROSIL® fumed silica grades with chemical treatment

AEROSIL® R 972 AEROSIL® R 974	AEROSIL® R 104 AEROSIL® R 106	AEROSIL® R 812 AEROSIL® R 812 S	AEROSIL® R 202 AEROSIL® R 208	AEROSIL® R 805
				
Dimethyldichlorosilane	Octamethyltetracyclo-siloxane	Hexamethyldisilazane	Polydimethylsiloxane	Octyltrimethoxysilane

SIPERNAT® specialty silica

Trade named SIPERNAT® specialty silica is manufactured by precipitation in an aqueous solution of waterglass and strong acid. The resulting precipitate go through washing, drying and additional mechanical processing to arrive at particles with a variety of surface area, particle size and oil absorption properties. These three parameters support the selection process to meet the application need.

Figure 6 – Specialty silica comparison to fumed silica

SIPERNAT® specialty silica and silicates	AEROSIL® fumed silica
	
Sponge-like structure	Chain-like structure

Properties of specialty Silica:

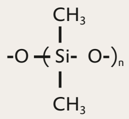
- Surface area – both internal and external –OH (fumed silica only has external –OH)
- No branching – porous sponge like structure
- Low thickening – higher loading possible
- Large particle size – easy to incorporate and disperse
- Residual moisture – LOD typically greater than 5%

Processing SIPERNAT® D 13

The base particle for SIPERNAT® D 13 is precipitated from an aqueous solution, milled and then hydrophobically treated to yield the final, highly hydrophobic material. Despite its high hydrophobicity, there is an available level of moisture that remains internally bound within its high internal structure.

Figure 7 – SIPERNAT® D 13 treatment

SIPERNAT® D 13



Polydimethylsiloxane

Chemical drying using Dynasylan® VTMO and mechanical drying in a forced air oven can be utilized to remove excess moisture to produce stable hybrid sealants and adhesives. This technique is used if filler moisture content negatively affects formulation stability.

Pre-drying of material

SIPERNAT® specialty silica may be mechanically dried by placing in an oven at elevated temperature and dried. The formulator need only dry to a manageable moisture level compliant with their formulation requirements. Care must be taken to minimize exposure of the material post drying to ensure that moisture is not re-absorbed on the surface of the material.

In situ drying

The method for chemical drying involves the stoichiometric calculation of Dynasylan® VTMO to water present in the SIPERNAT® D 13 based on Loss on Drying (LoD) or Karl Fisher titration. The chemical drying becomes the first process step in the sealant mixing procedure. Moisture scavengers, such as Dynasylan® VTMO, is added to the polymer before the silica is incorporated. The batch is heated above 200 °F (93.5 °C) to drive the reaction and evaporate off the evolved methanol from the condensation reaction. The drying time can be one to two hours.

Silane Terminated Polymer systems

Silane Terminated Polymers (STP, also known as silyl-modified polymers, modified-silane polymers, silane modified polymers, etc.) are polymers terminating with a methoxy or ethoxy silane. STPs are often used in solvent-free and isocyanate-free moisture curing sealants and adhesives. Typically the sealant products manufactured with silane modified polymers have good adhesion on a wide range of substrate materials, and have good temperature and UV resistance.

Evonik Polymer ST 48 (STPU polymer) and Kaneka S 303H (STPE Polymer) were used to compare AEROSIL® fumed silica effects in sealant performance.

AEROSIL® fumed silica in adhesives and sealants

AEROSIL® fumed silica must be well dispersed in the resin matrix to ensure optimal rheological and reinforcing support. This process requires high shear energy to break up agglomerates and homogeneously distribute aggregates within the formulation matrix. One of the main performance benefits from proper selection of silica grade is "anti-sag/anti-slump" behavior generally observed after application. This property, supported by the proper choice of grade and loading level allows the adhesive or sealant to quickly recover viscosity after application and remain in place until the curing is complete. This is a critical feature to allow the adhesive or sealant to be applied at precise film thicknesses on vertical / non-horizontal surfaces and gives the confidence to the formulator that it will cure at the same thickness applied.

Hydrophilic and hydrophobic grades of AEROSIL® fumed silica have demonstrated efficacy in numerous fields of application. Pertaining to sealants, the following functions should be highlighted:

- Reinforcing filler
- Thickening and thixotropic agent
- Anti-settling / suspension agent
- Anti-sag / anti-slump agent

Non-polar resin systems

Hydrophilic fumed silica readily forms a three dimensional network through hydrogen bonding which affects rheology and reinforces the sealant. Due to the high temperature, flame process, typically no ionic interaction with the resin system is observed.

Polar and semi-polar resin systems

Fumed silica hydrogen bonding is limited and there is little to no ionic interaction with the resin system. Increased polarity distracts the hydrogen bonding matrix from forming between aggregates and much lower level of the three dimensional network is formed. More polar resins require hydrophobically treated silica to achieve thixotropic behavior as the surface treatment support entanglement and an efficient rheological network is formed.

Cured materials also demonstrate benefits from use of fumed fillers. Polymer matrices reinforced with fumed silica typically manifest gains in tensile strength and longer elongation. The relatively small size of the aggregates does not impact translucence in clear systems. Optimum dispersion is also critical to achieve small aggregate size for least impact to clarity in clear system. Higher surface area technology should also be considered when highest clarity and transparency are desired.

Evonik's engineered silica in STPE resin systems

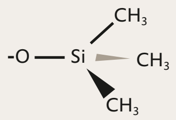
The Silane Terminated Polyether polymer (STPE Polymer also known as MS Polymer™) is used in low viscosity, low modulus applications. These systems are filled to provide strength and reinforcement, and are typically not available in clear systems requiring durability and strength.

AEROSIL® R 8200 is a Structure Modified Fumed Silica which will allow for high loading levels delivering the possibilities of self–leveling and / or a fine tuned rheology to customer requirements.

The hexamethyldisilazane (HMDS) treatment imparts a tri-methyl silyl function to the surface as depicted in Figure 8 and imparts a hydrophobic nature, increasing water resistance of the cured product.

Figure 8 – AEROSIL® R 8200 treatment

AEROSIL® R 8200



Hexamethyldisilazane

AEROSIL® R 8200 undergoes structure modification to reduce the aggregate structure (i.e. low branching aggregates) resulting in higher tapped density and providing faster incorporation with less dusting. This mechanical treatment allows for loading up to 40% in some systems with manageable viscosity in non-pigmented systems where synthetic, amorphous silica is the main filler used for improving reinforcement.

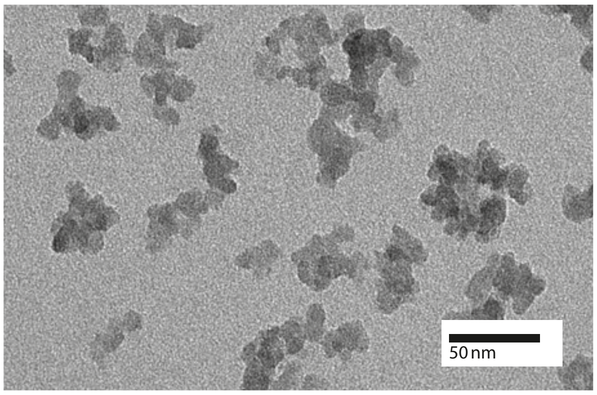


Figure 9 TEM image of structure modified silica

Clarity of the STPE sealant is maintained in two ways, matching refractive index to the resin and providing open reinforcing structures below 400 nanometers in size. Both parameters can be met with AEROSIL® fumed silica. Figure 10 represents the silica impact to clarity seen in STPE polymer systems using AEROSIL® fumed silica.

AEROSIL® R 202	AEROSIL® R 106	AEROSIL® R 812 S	AEROSIL® R 805	Competition (PDMS treated fumed silica)

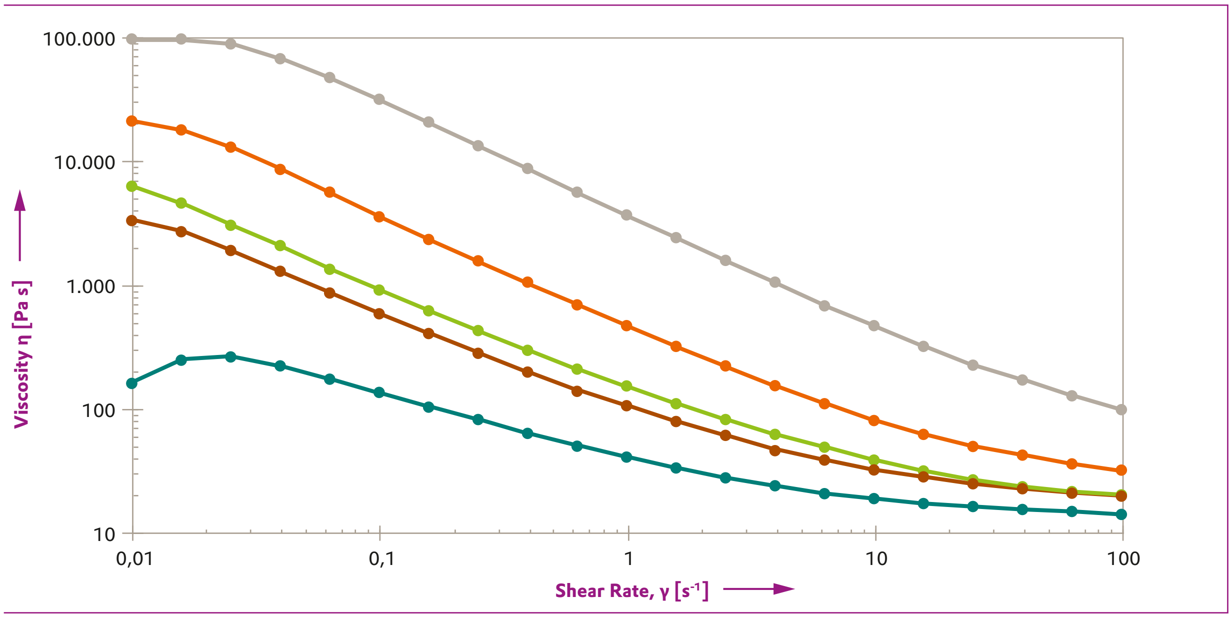
AEROSIL® R 805, AEROSIL® R 812 S and AEROSIL® R 106 are mostly recommended for transparent hybrid products!

Figure 10 – AEROSIL® fumed silica in transparent MS-Sealant

Rheological control in highly filled systems is a primary benefit fumed silica contributes. Whether a highly filled chalk system or high performing clear system, the AEROSIL® portfolio offers fumed silica options to meet formulators needs. AEROSIL® R 202 is the fumed silica of choice in highly filled chalk or talc systems.

AEROSIL® R 8200 is suggested for use as a filler in transparent to translucent (non-pigmented / non-filled), highly reinforced STPE Sealants. Figure 11 shows that structure modified AEROSIL® R 8200 allows for loading up to 40% with manageable rheology.

Figure 11 - AEROSIL® R 8200 rheology contribution



- 5 parts AEROSIL® R 8200 in MS-Sealant
- 10 parts AEROSIL® R 8200 in MS-Sealant
- 20 parts AEROSIL® R 8200 in MS-Sealant
- 40 parts AEROSIL® R 8200 in MS-Sealant
- 5 parts AEROSIL® R 812 S in MS-Sealant

Strength and reinforcement are improved with better resin continuity throughout the filled system. The resin continuity can only be achieved with very small open structures that the structure modified grades possess. Up to 800% increase in sealant strength with no loss in elongation as demonstrated in figures 12 and 13.

Figure 12 - AEROSIL® R 8200 tensile strength

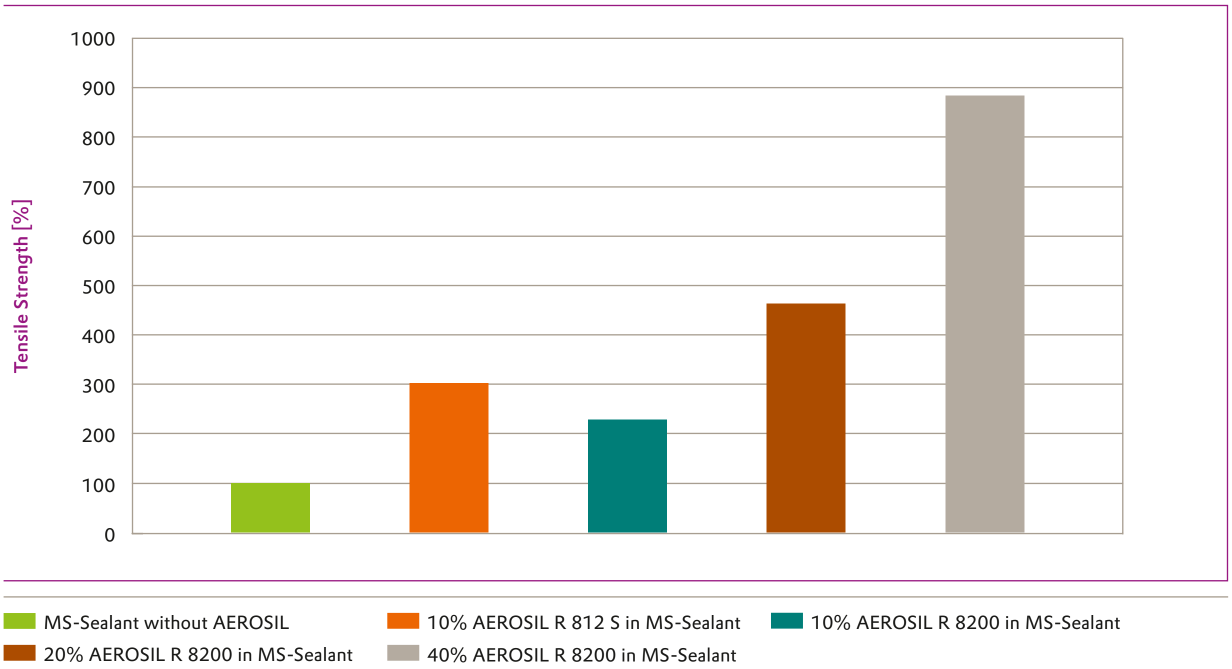
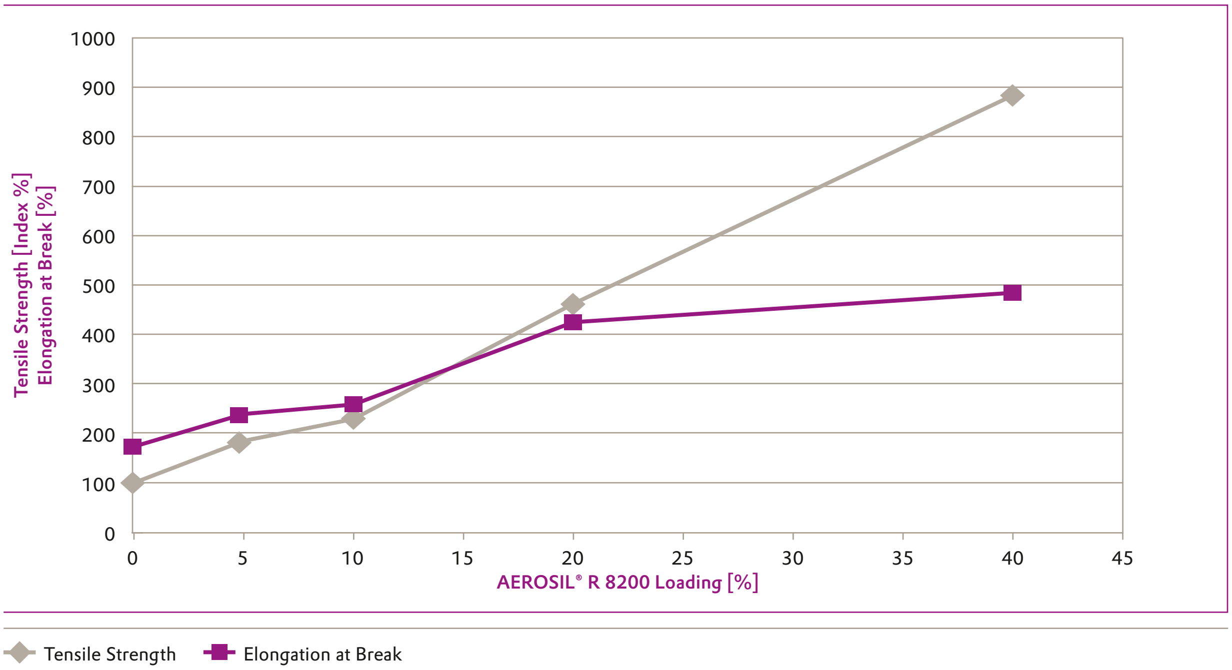


Figure 13 - AEROSIL® R 8200 mechanical performance



Evonik's engineered silica in STPU resin systems

A low modulus sealant is defined as an elastomeric material with a modulus at 100 % elongation of up to 0.4 MPa. This property can be obtained simply by the addition of an appropriate plasticizer. However, being non-reactive and not chemically anchored into the formulation, the plasticizer can have negative effects on properties like the elastic recovery. AEROSIL® fumed silica supports increased modulus in highly plasticized systems by providing reinforcement and improved resin continuity throughout the sealant.

In low modulus STPU sealants, AEROSIL® fumed silica supports:

- Rheology
- Reinforcement
- Clarity
- Durability

To show these attributes, a basic clear STPU test formulation was created to evaluate the relationships between silica and STPU polymer system. The base resin chosen for the experiments was Polymer ST 48 from Evonik. This material is a low modulus moisture reactive prepolymer resin marketed by Evonik to the sealant industry.

Polymer ST 48

Polymer ST 48 is especially recommended for the application as sealant for interior or exterior joints, e.g. expansion or connection joints, interior joints for dry walling, joints at staircases.

Table 1 – Polymer ST properties

Appearance	colorless, transparent
Viscosity	ca. 60,000 mPas
Plasticizer	phthalate
Tensile strength in formulation**	1 N/ mm²
Elongation in formulation**	600%
Modulus 100 % in formulation**	0.3 MPa

Polymer ST 48 offers a good handling viscosity and is therefore easy to apply manually. Formulation surfaces are quickly tack-free after application, which ensures rapid processing and avoids long waiting times. For testing purposes, a basic clear formulation was developed to evaluate the relationships between AEROSIL® fumed silica and Polymer ST 48.

Table 2 – STPU formulation

Components	% by weight
Polymer ST 48	56.7
Plasticizer (e.g. Diisononylphthalate, Jayflex® DINP, EXXON MOBIL)	29.0
Rheological additive (e.g. fumed silica, **AEROSIL®**)	10.0
Dehydration agent (e.g. organofunctional silane, **Dynasylan® VTMO**)	3.0
Adhesion promoter (e.g. organofunctional silane, **Dynasylan® 1146**)	1.0
Crosslinking catalyst (e.g. Dioctyltin dicarboxylate like **Catalyst TD 18**)	0.3

AEROSIL® R 8200 and SIPERNAT® D 13 were substituted into the above formulation at 20% proportionally reducing the concentration of the other ingredients. Due to the lower rheological impact both engineered fillers have, they are typically formulated at higher loading levels for the specific purpose to achieve improved mechanical reinforcing properties.

Catalyst TD 18, due to its low yellowing tendency, is also suited for use in transparent formulations based on silane-terminated polyurethanes (Polymer ST). As Catalyst TD 18 contains no butyltin compounds, it may be used when less hazardous formulations are required.

Silica selection

The performance characteristics associated with each silica choice is summarized in the chart below:

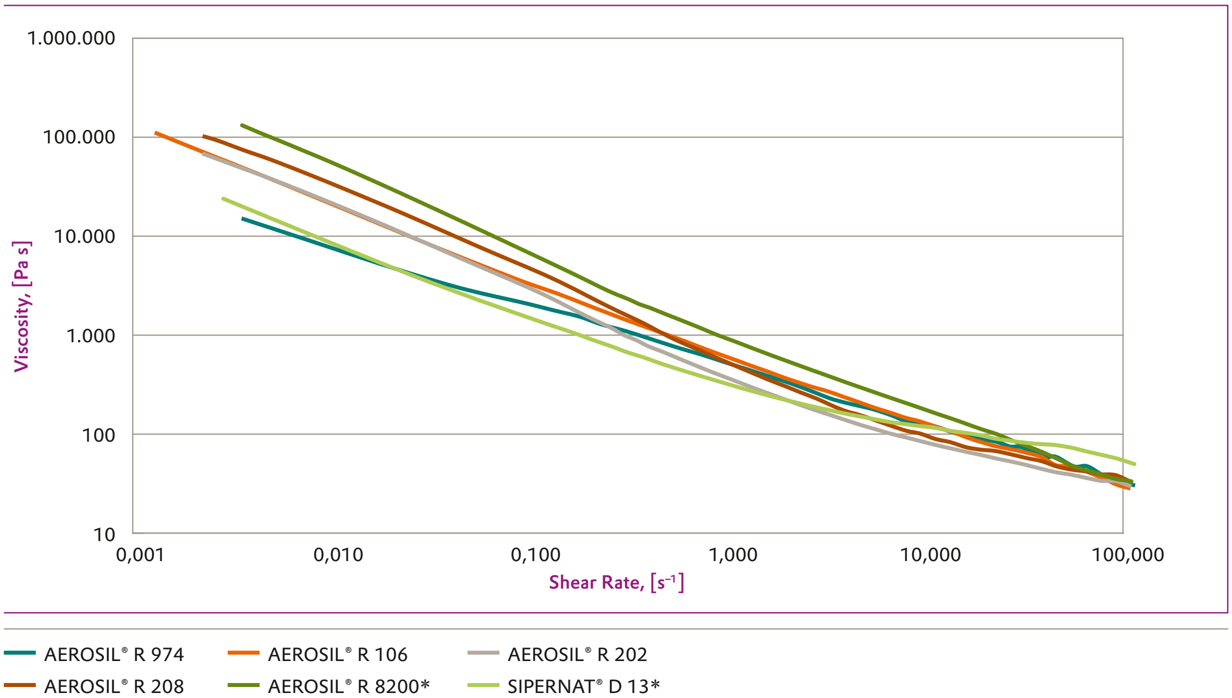
Table 3 – Engineered silica selection by properties

Silica	Performance Characteristic
AEROSIL® R 974	Lower rheology, highest separation syneresis control
AEROSIL® R 106	Medium rheology for clear formulations
AEROSIL® R 202	High rheology
AEROSIL® R 208	Higher rheology
AEROSIL® R 8200	High rheology and reinforcement at high loading
SIPERNAT® D 13	Lowest rheology and high reinforcement at high loading

Figure 14 – Silica effect on clarity in STPU Sealant using Polymer ST® 48

For the preparation of clear STP sealant, proper dispersion of fumed silica is needed to have minimal influence on clarity. As seen above in Figure 14, each drawdown, applied to glass, is 2 mm in thickness. The label placed below the glass plate provides method for comparison of each silica grade and loading. AEROSIL® R 974, R 106 and R 8200 show minimal impact to clarity compared to the polymer without silica. AEROSIL® R 202 appears opaque in the STPU and is a characteristic of most PDMS treated grades. SIPERNAT® D 13 has the most impact on clarity due to the larger particle size and PDMS treatment.

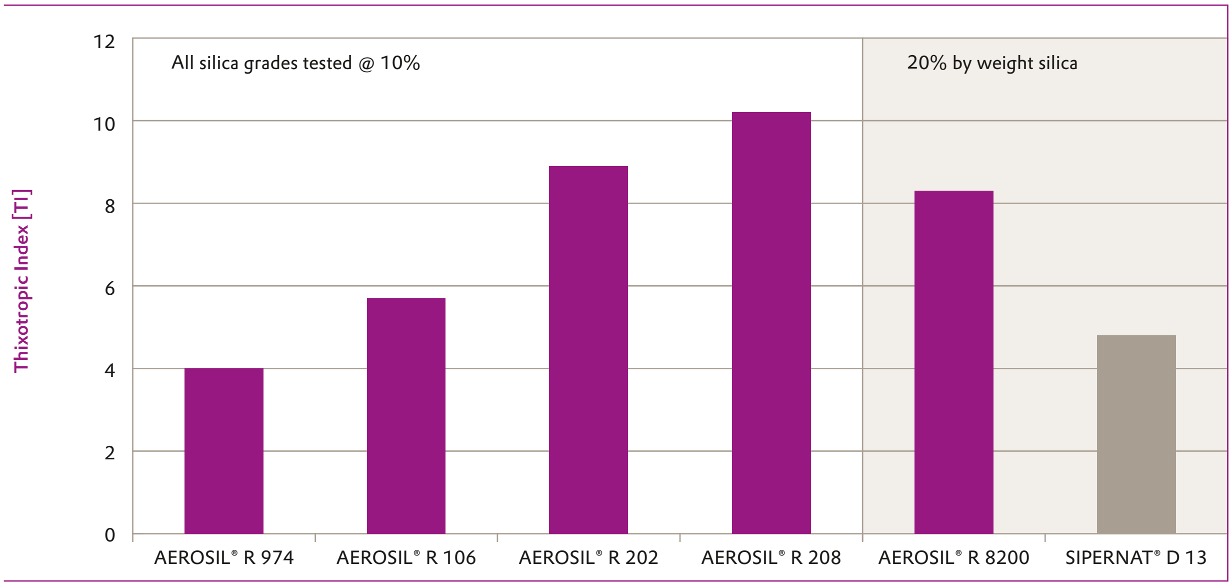
Figure 15 – STPU rheology profiles. 24 Hr. rheology, 25°C, 35mm, 4°CP



*AEROSIL® R 8200 and SIPERNAT® D 13 are loaded to 20% by weight in the total formulation.

AEROSIL® R 208 provides the highest rheological performance at the lowest loading level (10%). AEROSIL® R 8200 shows strong shear thinning rheology at 20% loading compared to the other grades tested at 10%. The characterization explained in Figure 16 where the Thixotropic Index relates to the shear thinning effect of each silica grade. The AEROSIL® R 8200 provides a higher overall viscosity, but a mediocre shear thinning effect. The higher viscosity is an artifact of the higher loading. SIPERNAT® D 13 has the lowest Rheological and shear-thinning contribution as would be expected for this technology. The SIPERNAT® D 13 can be loaded at even higher levels with managed rheological performance. While rheological contribution of both AEROSIL® R 8200 and SIPERNAT® D 13 are lower on a weight addition level to the other grades tested, their effectiveness to support mechanical reinforcing benefits will be demonstrated.

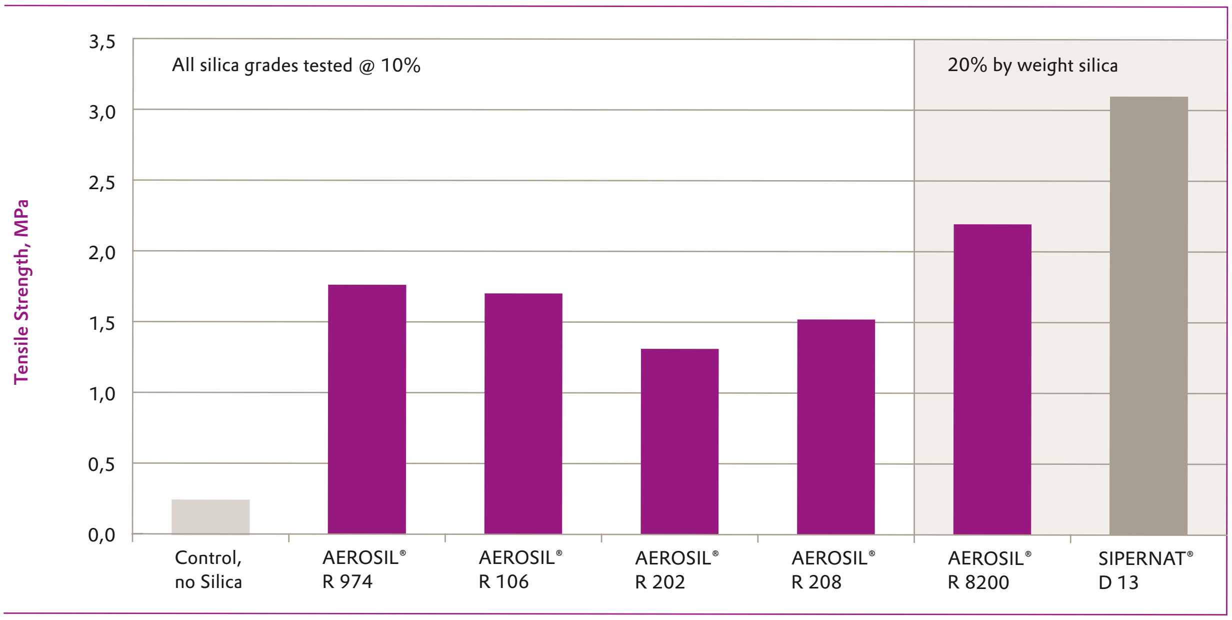
Figure 16 – Thixotropic index in STPU sealant



Mechanical properties

AEROSIL® fumed silica and SIPERNAT® specialty silica significantly improve the mechanical performance of low modulus, highly plasticized STPU Sealants by providing reinforcement with good elasticity. The control in figure 17 and 18 do not contain silica.

Figure 17 – Tensile strength of STPU Sealant



*AEROSIL® R 8200 and SIPERNAT® D 13 were loaded to 20% by weight in the formulation.

The materials presented for consideration increase the tensile strength of the cured material by a minimum of 400% over the strength of the cured resin with no filler. The typical hydrophobic grades of AEROSIL® R 974, AEROSIL® R 106, AEROSIL® R 202 and AEROSIL® R 208 improved the tensile strength by an average of 600% at a loading level of 10%.

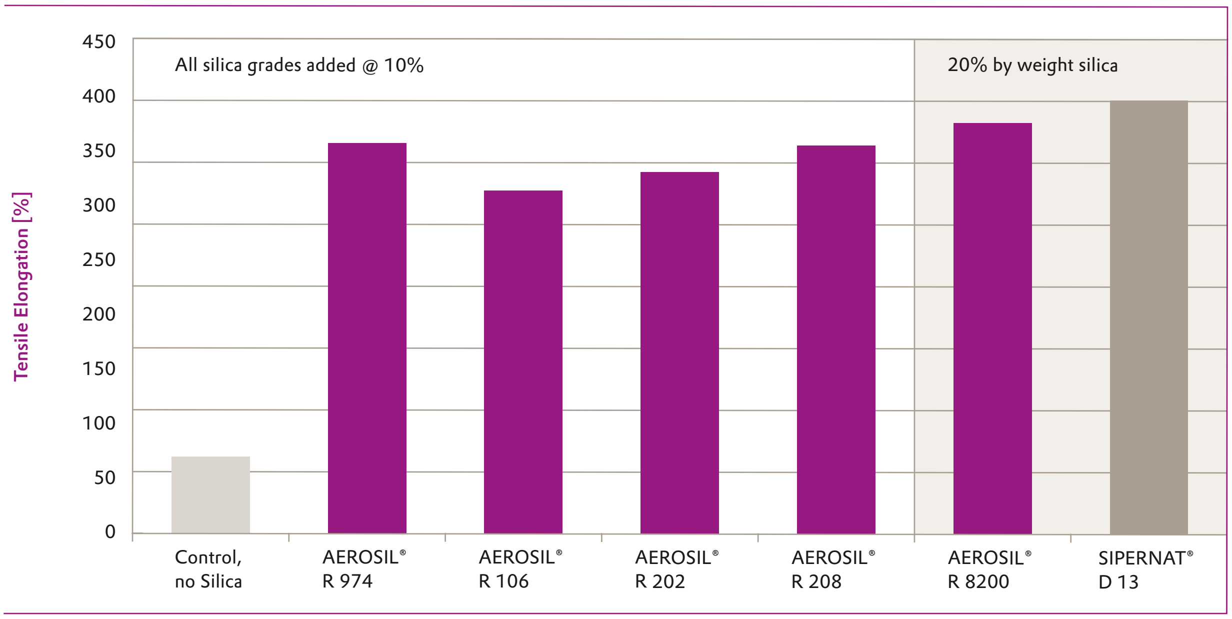
AEROSIL® R 8200 at a loading level of 20%, shows >800% increase.

SIPERNAT® D 13 provided gains in excess of 1000%.

When considering these materials in STPU based systems, the gains reported are only for reference and will vary depending on the resin, pigment and filler system used by the formulator. Results may vary depending on individual formulations.

The increase in tensile strength also results in higher elongation at break for the cured material.

Figure 18 – Elongation of STPU Sealant



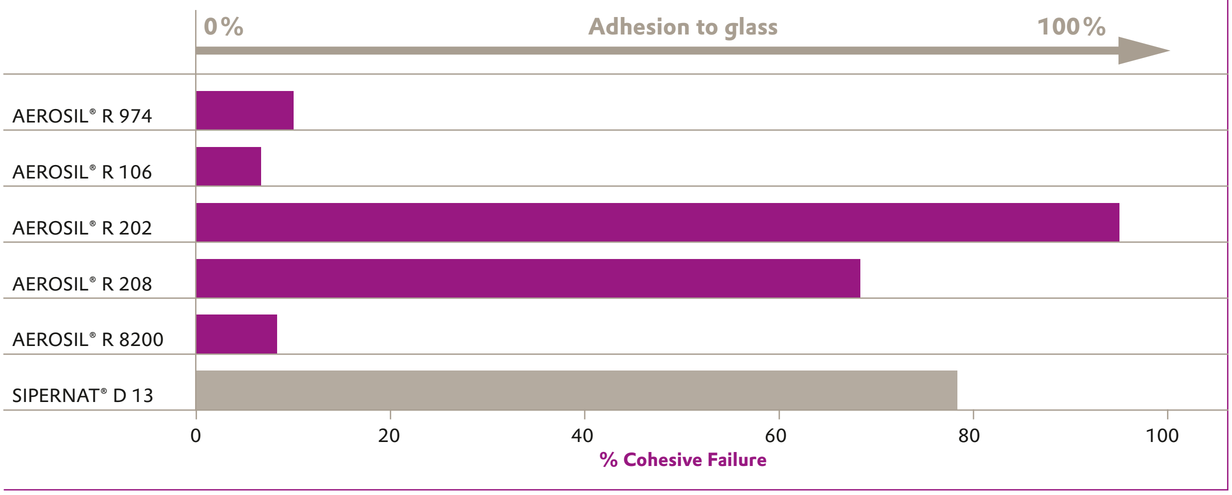
In a highly plasticized system, the sealant elongation can be adversely affected. The AEROSIL® fumed silica and SIPERNAT® specialty silica show considerable increase in elongation. The AEROSIL® fumed silica contribution supports improved elongation through reinforcement and resin continuity through the open structure of the silica.

Adhesion

Primerless adhesion is a benefit offered by STPU resin technology. The Sealant formulations were tested for adhesion to unprimed glass substrates. To lower formulation cost in non-filled / clear systems, often formulators add very high levels of plastiziser. Another effect is that adhesion is often compromised. To improve the adhesion of highly plasticized clear systems, fumed silica is added. The best adhesion to unprimed glass with the highly plasticized sealant is found with PDMS treated silica.

Figure 19 – Adhesion testing of STPU Sealant

Control sample without engineered silica did not adhere to glass due to high level of plasticizer in formulation



Summary

AEROSIL® fumed silica and SIPERNAT ® specialty silica support STP hybrid systems with focus on
- Mechanical Reinforcement
- Rheological control
- Optical Clarity
- Durability
- Adhesion

Results from experiments show that:
- AEROSIL® R 208 provides the highest rheological performance by weight.
- AEROSIL® R 8200 improves mechanical properties of the sealant allowing for high loading and rheological control.
- AEROSIL® R 106 provides good rheological support with minimal influence on light transmission and clarity.
- The PDMS Treated Silica AEROSIL® R 202, R 208 and SIPERNAT® D 13 support adhesion in highly plasticized STPU Resin systems.
- SIPERNAT® D 13 has the lowest rheological impact while supporting very high loading and mechanical performance. SIPERNAT® D 13 must be either chemically or mechanically dried before use in an STP formulation.

Table 4 provides a quick view of AEROSIL® fumed silica and SIPERNAT® D 13 performance attributes.

Table 4 – Performance recommendation

Property	Recommendation
Rheology	**AEROSIL® R 202 and R 208 – PDMS Treated Fumed Silica** for increased slump and sag resistance with excellent shear thinning and thixotropy
Clarity / Transparency	**AEROSIL® R 106 – Octylmethyltetracyclosiloxane Treated Fumed Silica** with high surface area has minimal influence on light transmission and clarity of transparent STP sealants and adhesives.
Reinforcement	**AEROSIL® R 8200 – Structure Modified Fumed Silica** for increased toughness and hardness with managed viscosity. **SIPERNAT® D 13 – PDMS Treated Specialty Silica** for increased toughness, hardness and low viscosity.
Adhesion	**AEROSIL® R 202, R 208, or SIPERNAT® D 13 – PDMS Treated Fumed and Specialty Silica** to support adhesion to unprimed glass.

Literature

- Brochure No. 27, AEROSIL® Fumed Silica for Solvent-Free Epoxy Resins
- Brochure No. 63, AEROSIL® Fumed Silica and SIPERNAT® in Sealants
- Technical Overview AEROSIL® - Fumed Silica
- Polymer ST and TEGOPAC®
- Polymer ST and TEGOPAC®, Product Overview

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