AEROSIL® R 8200 for Silicone Rubber

Fumed silica with high reinforcing properties and a particularly low thickening effect

Technical Information 1209

Contents

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1. Introduction

Since the development of the polysiloxane systems by Rochow (1) in the Forties, synthetic silicas have been used as reinforcing fillers by the silicone industry. Fumed silicas in particular, which are produced by the AEROSIL® process, have contributed significantly to the success of silicone rubber.

Hydrophobic products for special applications were also developed along with the classic hydrophilic reinforcing silicas. The surfaces of hydrophilic AEROSIL® are modified with silanes to give these products their hydrophobic behaviour (2,3).

This Technical Information introduces AEROSIL® R 8200, a specially treated silica developed to improve silicone rubber compounding efficiency. In order to meet customer requirements, the silica has been modified by several treatment stages that follow production and hydrophobization steps. This product is characterized by a particularly low thickening effect, while at the same time retaining strong reinforcing properties.

The following chapter describes in detail the physico-chemical characteristics of AEROSIL® R 8200 and its technical application properties in two component room temperature curing silicone rubber (RTV-2), in RTV-1C Silicone Sealants and in liquid silicone rubber (LSR) formulations.

2. Synthetic silicas in silicone rubber

The reinforcing properties of synthetic silicas in polymers have already been extensively reported in various publications (see 2–6). In addition to enhancing the mechanical strength of cured silicone products, silicas often show undesirable thickening properties which, for example, result in the so-called "crepe hardening"effect in Heat Cured Rubber (HCR) applications. Silicone compounds, which have not been cross-linked become hard and rigid within a storage of a few days, so that it is often very difficult or even impossible to process them any further. In RTV systems, the right balance between the thickening and reinforcing effect is crucial. It should be easy and simple to process the unlinked silicone mass, but after cross-linking, the polymer should possess high mechanical strength.

By carrying out a work-intensive in-situ hydrophobization process, the "crepe hardening" effect can be suppressed and the thickening effect of the reinforcing silica adjusted to a desirable level. This is achieved by chemical after-treatment of the silica with hydrophobization agents during the compounding stage. The silanol groups on the silica surface react with organo-functional silicon compounds. This avoids a multi-dimensional network developing via hydrogen bonding. However, the condensation by-products formed during this process must be removed from the compound, since they would otherwise seriously impair the properties of the cured compounds. This necessitates the use of laborious and time consuming techniques. Furthermore, ecological considerations require subsequent treatment steps to clean the exhaust air generated during this process.

For many years, Evonik Industries has been offering hydrophobic silicas, which can significantly shorten the above mentioned in-situ process. For example, AEROSIL® R 972, which is a hydrophobic silica treated with dimethyldichloro silane, was introduced into the market in 1962. Since then, several different silane modified AEROSIL® grades have been developed specifically for silicone rubber applications. AEROSIL® R 104 and R 106 deserve specific mention as well as AEROSIL® R 812 S, which possesses strong hydrophobic properties resulting from its modification with trimethylsilyl groups. Although these treated AEROSIL® grades are clearly effective in the production of peroxide, condensation and additive cross-linked silicone compounds, in contrast to large surface area hydrophilic grades, Evonik offers AEROSIL® R 8200 as a class of silica to fulfil the demands of extremely difficult applications.

3. Production and properties of AEROSIL® R 8200

3.1 Production

AEROSIL® R 8200 is produced by the flame hydrolysis of $SiCl_4$ (7), as with all AEROSIL® grades. Large quantities of hydrogen chloride are generated and are separated from the fumed silica using special techniques. The new aspect of this process is that the silica's surface is specifically modified by an intensive hydrophobization treatment with trimethylsilyl groups and that the silica's thickening effect is reduced to a particularly low level by subsequent treatment processes.

An additional advantage for the user is that this is a continuous production process, ensuring quality fluctuations are reduced to a minimum.

3.2 Physico-chemical properties

AEROSIL® R 8200 , produced by the process described in 3.1, possesses all the advantages of the hydrophobic types of AEROSIL®. Its carbon content, which is a measure of the degree of hydrophobicity, is 2–4 % and is higher than that of other hydrophobic silicas. Only AEROSIL® R 812 S has a similar level of hydrophobicity.

The high tamped density of AEROSIL® R 8200 (approx. 140 g/l) also deserves special mention. It is significantly higher than that of other fumed silicas, which have tamped densities of approx. 50 g/l. When handled correctly, AEROSIL® R 8200 generates considerably less dust during processing. The high tamped density is also an advantage when incorporating the product into polymers as it considerably reduces the addition time. Based on our experiences, this will lead to a marked increase in productivity during the compounding process and to a greater utilization of the equipment. Further details are listed in Table 1.

Table 1
Physico-chemical data of AEROSIL® R 8200 in comparison to AEROSIL® 200, R 974, R 104 and R 812 S.

Properties	AEROSIL® 200	AEROSIL® R 974	AEROSIL® R 104	AEROSIL® R 812 S	AEROSIL® R 8200
Behaviour in water	hydrophilic	hydrophobic			
BET surface area m^2/g	200 ± 25	170 ± 20	150 ± 25	220 ± 25	160 ± 25
Tamped density g/l	ca. 50	ca. 50	ca. 50	ca. 50	ca. 140
Drying loss (2 h at 105 °C) %	≤ 1.5	≤ 0.5	-	≤ 0.5	≤ 0.5
pH-value (4 % suspension)	3.7–4.5	3.4–5.0	≥ 4.0	5.5–9.0	≥ 5.0
Carbon content %	-	0.9–1.5	1.0–2.0	3.0–4.0	2.0–4.0
SiO_2 %	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8
Fe_2O_3 %	≤ 0.003	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01
TiO_2 %	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03	≤ 0.03
HCl %	≤ 0.025	≤ 0.1	≤ 0.02	≤ 0.025	≤ 0.025

4. The influence of AEROSIL® R 8200 in different silicone rubber systems

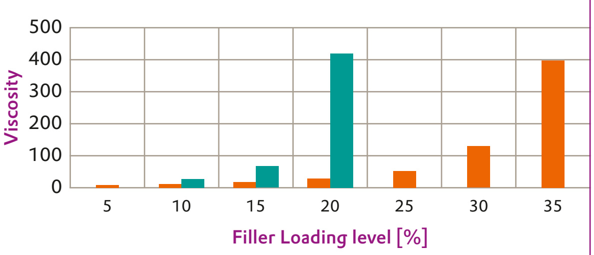
4.1 Properties in two component RTV silicone rubber

Applications for two component systems can be found in areas such as dental technology, monument preservation and in the rapid prototyping of moulded plastic parts, e.g. as used in the automotive industry. The advantage of two component silicone rubber is its easy processing at room temperatures. Its excellent separation effect and precision moulding capability are particularly important characteristics. To achieve this, the low viscosity characteristics of the polymer must not be significantly affected by the filler content which has, at the same time, to impart a high level of mechanical strength to the crosslinked compounds. AEROSIL® R 8200 is the only hydrophobic AEROSIL® grade to satisfy these requirements.

Figure 1 illustrates the viscosity increase relative to the addition levels of the two AEROSIL® grades R 8200 and R 812 S, both of which are modified with trimethylsilyl-groups. Already, at a loading level of 20 %, the viscosity of the AEROSIL® R 812 S filled polymer is 10 times greater than that of the AEROSIL® R 8200 filled formulation. Fumed silicas such as AEROSIL® 200 or 300, which have had no treatment whatsoever, would give a comparative viscosity of several thousand Pascal seconds under these circumstances.

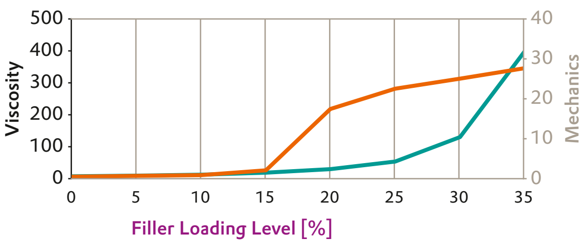
The low thickening effect of AEROSIL® R 8200 enables high addition levels in two component systems, which in turn have a very positive effect on the mechanical properties of the vulcanized compounds.

Figure 1
Relationship between the viscosity of two component RTV silicone formulations and the filler loadings
(AEROSIL® R 8200 , AEROSIL® R 812 S)



Tear resistance increases sharply with addition levels above 15 %. At this concentration level, a so-called "locking effect" is reached. At higher addition levels a continued but more gradual increase becomes apparent (see Figure 2).

Figure 2
Rheological and mechanical properties of a two component RTV formulation containing AEROSIL® R 8200 at different addition levels.



A comparison between the properties of a two component RTV silicone rubber containing AEROSIL® R 8200 as filler with AEROSIL® R 812 S is given in Table 2. Other types of AEROSIL® are not included since they cannot be recommended for two component RTV silicone rubber systems without additional in-situ-hydrophobization because of their pronounced thickening effect.

Table 2
Properties of two component RTV formulations based on AEROSIL® R 8200 and AEROSIL® R 812 S , silica loading 20 %

Properties	Dim.	AEROSIL® R 812 S	AEROSIL® R 8200
Viscosity (after incorporation)	Pa s	209	24
Viscosity (after 7 days)	Pa s	292	33
Shore A, Hardness		40	31
Tensile Strength	N/mm²	4.2	2.6
Elongation at Break	%	430	400
Tear Resistance	N/mm	19	16
Rebound Elasticity	%	58	67
Transparency		40	28

Table 3
Properties of one component RTV silicone sealant compounds containing AEROSIL® R 8200 and AEROSIL® R 812 S in comparison to AEROSIL® 150, AEROSIL® R 972, AEROSIL® R104 and AEROSIL® R 106, the filler loading level being 8%.

Properties	Dim.	AEROSIL® 150	AEROSIL® R 972	AEROSIL® R104	AEROSIL® R 106	AEROSIL® R 812 S	AEROSIL® R 8200
Extrudability	g/min	–	–	–	–	29.3	54.2
Viscosity at D = 10s⁻¹	Pa s	126	98	121	120	57	28
Yield Point	Pa	320	168	217	172	13	< 5
Ease of Dispersion Spots (roughness of a spread surface)	rating*	1.5	2.0	2.0	2.0	1.5	1.5
Shore-A, Hardness		19	17	16	17	13	10
Tensile Strength	N/mm²	1.6	1.5	1.4	1.5	1.1	0.6
Elongation at Break	%	610	660	470	410	890	660
Rebound Elasticity	%	53	49	45	51	53	50
Transparency		27	23	30	31	29	23

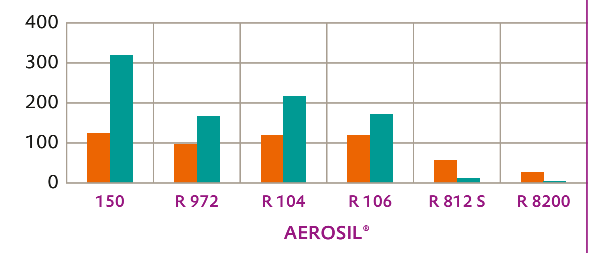
* Grade 1 = excellent Grade 5 = insufficient

4.2 Properties in RTV-1 Silicone Sealants

Because of its extremely low thickening effect, AEROSIL® R 8200 can be used to its full advantage in RTV-1 Silicone Sealants for the production of self-levelling rubbers, e.g. for coating textile based building materials. AEROSIL® R 8200 also displays excellent rheological properties in these formulations compared with other silicas. (see Table 3).

The viscosity and yield points of standard acetate formulations are distinctly lower with AEROSIL® R 8200 as reinforcing filler, than with any other type of AEROSIL® at the same filling level. The mechanical properties of the compounds are of the same order despite the low thickening effect of AEROSIL® R 8200 (see Figure 3).

Figure 3
Comparison between the rheological properties of a one component RTV formulation based on AEROSIL® R 8200 and other types of AEROSIL® (filler content 8%).



By increasing the loading level to 14% or 20%, formulations are obtained with comparable rheological properties to those of commercially available silicone sealant compounds. However, they also have the added advantage of high mechanical strength after the cross-linking process is complete (see Table 4).

Table 4
The relationship between the properties of a one component RTV formulation containing AEROSIL® R 8200 and the filler loading level

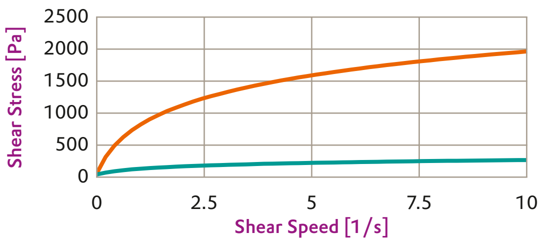
Properties	Dim.	Filler Loading Level %		
		8	14	20
Extrudability	g/min	58.0	45.0	28.0
Viscosity at D=10s⁻¹	Pa s	38	68	129
Yield Point	Pa	8	45	237
Ease of Dispersion (roughness of a spread surface)	rating	1.0	2.0	2.0
Shore-A, Hardness		13	17	22
Tensile Strength	N/mm²	0.7	2.2	3.6
Elongation at Break	%	450	980	860
Tear Resistance	N/mm	2	4	16
Rebound Elasticity	%	51	46	41
Transparency		24	23	24

4.3 Properties in liquid silicone rubber (LSR)

AEROSIL® R 8200 can also be used as reinforcing silica in those formulations where the thickening effect of hydrophilic silcas is generally far too high. Either hydrophobic types of AEROSIL® are used or the manufacturer has to employ an additional elaborate in-situ-hydrophobization process at the compounding stage. Intensive shearing is also necessary to break down the silica structure in the compound. Because of its unique production method, AEROSIL® R 8200 is also able to show its characteristic very low thickening effect in LSR polymers. The behaviour of AEROSIL® R 8200 was compared to that of

AEROSIL® R 812 S , using flow curves. These curves give an impressive demonstration of the rheological advantages of AEROSIL® R 8200 over AEROSIL® R 812 S and, therefore, over other hydrophobic AEROSIL® types (see Figure 4).

Figure 4
Comparison between the flow of viscosity of a LSR formulation containing AEROSIL® R 8200 and one containing AEROSIL® R 812 S .



Further detailed information concerning rheological, mechanical and optical properties of AEROSIL® R 8200 and R 812 S can be found in our TI 1253 (8)

5. Experimental Part

5. 1 RTV-2C silicone rubber, condensation-crosslinking

The RTV-2C silicone formulation was prepared with the aid of a high-speed mixer. The dispersion time is 5 minutes at 3000 rpm. The crosslinker (3 % based on the total formulation) is subsequently added.

58 %	of Silicone Polymer (C18/Momentive Performance Materials)
19 %	of Silicone Oil (M100/Momentive Performance Materials)
20 %	of Fumed Silica (AEROSIL® R 8200/ Evonik Industries AG)
3%	of Crosslinker (C5/Momentive Performance Materials)

5.2 RTV-1C Silicone sealant

Silicone polymer, silicone oil, crosslinker and coupling agent are homogenized for 1 minute in a high-speed planetary mixer.
The silica is subsequently stirred in stages and dispersed for 5 minutes under reduced pressure (100 rpm stirrer, 2000 rpm high-speed mixer). After addition of the catalyst the mixture is dispersed for a further 5 minutes under reduced pressure.

62.4 %	of Silicone Polymer (Polymer OH 50/ Evonik Hanse GmbH)
24.6 %	of Silicone Oil (Siliconöl M1000/ Momentive Performance Materials)
4.0 %	of Crosslinker (Crosslinker AC 10; Evonik Hanse GmbH)
1.0 %	of Coupling Agent (Dynasylan® BDAC/ Evonik Industries AG)
0.01 %	of Catalyst (dibutyltin diacetate/ TIB Chemicals)
8.0 %	of Fumed Silica (AEROSIL® 150/ Evonik Industries AG)

5.3 Liquid Silicone Rubber formulation

The LSR formulations were produced using a laboratory dissolver. The following components were thoroughly dispersed. The dispersion time of the silica in silicone polymer is 30 minutes at 2000 rpm.

75.9 %	of Silicone Polymer (Polymer VS 10.000/ Evonik Hanse GmbH)
19.0 %	of Fumed Silica (AEROSIL® R 812 S or AEROSIL® R 8200 / Evonik Industries AG)
3.3 %	of Inhibitor (2 % 1-Ethinyl-1-cyclohexanol in Polymer VS 10.000 / Aldrich)
1.7 %	of Crosslinker (Crosslinker 100 / Evonik Hanse GmbH)
0.1%	of Pt-Catatyst (PT-VTS-C / Umicore)

All tests were carried out according to the appropriate DIN, ISO or ASTM standards.

6 Literature

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