Novel Silicone Resin Binder and Compound for Thermally Demanding Applications

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Abstract

This paper deals with a new silicone resin compound that can be cured by addition curing and by peroxide curing, respectively. Curing and post-curing behavior has been investigated and optimized. Numerous trials towards the optimization of the binder-filler combinations have been performed. The resulting material POWERSIL® Resin 710 has been investigated with respect to its mechanical and thermal behavior. The new material exhibits heat class R and can be processed by press molding, pressure gelation, and injection molding.

1. Introduction

Silicone resin binders are used for impregnation, lamination, and coating applications. The main objective of these materials is to show stability against high levels of thermal stress. Electrical motors, mainly for traction applications, as well as mica- and other laminates along with pultruded products represent the key markets for silicone resins. To date, silicone resin compounds for molded parts are not commercially available in adequate quantities to serve the market. Driven by the expected outstanding resistance to thermal stress and UV radiation, a novel, solvent-free, low-viscosity phenyl-methyl-silicone resin binder has been developed and used to create reinforced compounds optimized for the manufacture of parts by press molding and pressure gelation [1]. General information on silicone resins can be found in ref. [2]. This paper deals with the chemical composition and the resulting properties of both binder and cured compounds.

2. Moldable Silicone Resin Parts

Existing silicone resin binders are used to create thermally and UV stable parts. The current standard process for the fabrication of silicone resin-based parts is the machining of semi-finished goods. The mechanical properties of these parts are defined by the lamination of the preliminary products. Direct molding solutions would require suitable mechanical properties of the cured silicone resin compounds. The moldable materials need to conform to the typical processing technologies, such as pressure gelation and injection molding with respect to their respective viscosity and curing behavior. The goal of this work was the development of a new type of silicone resin binder, and establish a method to produce composite materials with the following ideal profile:

- Silicone resin to fabricate molded parts,
- Ready-to-use material (ideally 1-component),
- Long pot life,
- Suitable viscosity,
- Solvent-free,
- Label-free,
- Processable with existing equipment.

Thanks to parallel development work in our resins working group a water-clear, low-viscosity silicone resin binder with a viscosity of approximately 100 mPas has been available for the development of the compound. Like modern liquid-silicone elastomers, the novel material contains highly reactive vinyl groups ($Si-CH=CH_2$), which in the presence of a suitable catalyst and Si-H units form the crosslinking ethylene bridges [$Si-CH_2-CH_2-Si$] *via* the so-called hydrosilylation process. Standard methyl polymer-based additive masterbatches were found to have a negative influence towards the resulting mechanical properties of the cured parts. Therefore, special additives have been developed to result in optimum properties. The curing speed was found to be readily adjustable by using these additives. An example of a DSC graph is shown in (**Figure 1**). The curing enthalpy of a typically filled compound was measured to be about 250 J g^{-1}, which is slightly less than that of a typical epoxy resin (300 – 500) J g^{-1} [3].

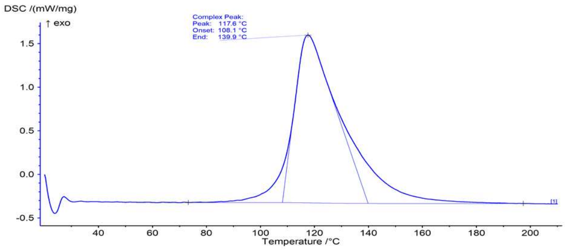

Figure 1 DSC plot of the Pt-catalyzed hydrosilylation of the new silicone resin binder with a temperature rise of 10 K^{-1}

It was found that experimental compounds with the novel binder can be cured rapidly in the presence of peroxides which allows for the formulation of one-component, ready-to-use products.

3. Fillers and Mechanical Properties

The mechanical reinforcement with silica as is typically applied with silicone elastomers does not show satisfactory results. Improved mechanical properties (tensile strength, flexural strength) have been achieved by adding quartz and quartz mixtures. Compounds with a typical binder-filler-ratio of 40:60 show a tensile strength of 20 MPa to 30 MPa. The material did not appear brittle, but the flexural strength was found to remain at a low level with respect to the targeted application.

Optimization of the mechanical properties was achieved by compounding the binder with combinations of fiber- and particle-shaped fillers (**Figure 2**). Using fiber reinforcement yields more consistent material, as opposed to materials with brittle appearance that form without reinforcement. These can be repeatedly deformed to a certain extend.

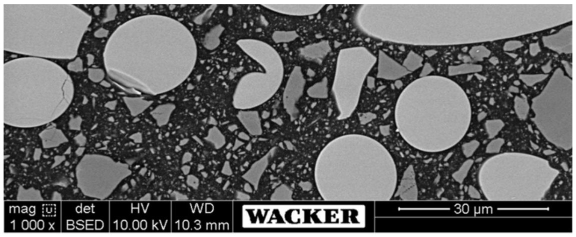

Figure 2 Electron micrograph of silicone resin binder reinforced with glass fibers, quartz, and silica (not visible)

The interphase between the fibers and the binder, in particular the adhesion of fibers in the compound has been found to play an important role to provide a suitable flexural strength (**Figure 3**, **Figure 4**).

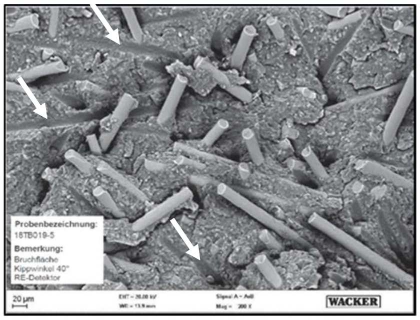

Figure 3 Fractured surface with glass fibers that have been largely broken out of the compound (→)

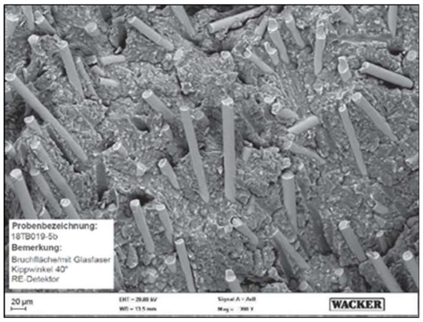

Figure 4 Fractured surface with glass fibers that mostly broke remaining anchored in the compound

Based on numerous trials with mixtures of additives a recipe for further evaluation and testing had been established. This material consists of binder POWERSIL®700, silica, quartz, glass fibers and 2,5-bis-(*tert*-butylperoxo)-2,5 dimethylhexane as peroxide.

Tensile and flexural strength of standardized test specimens with dimensions (80 × 10 × 4) mm^3 have been measured to be 25 Nmm^{-2} and 50 MPa, respectively.

The effect of the fiber reinforcement becomes apparent if specimens are exposed to repeated stress below the fracture threshold (typically 85 N) in a texture analyzer (**Figure 5**).

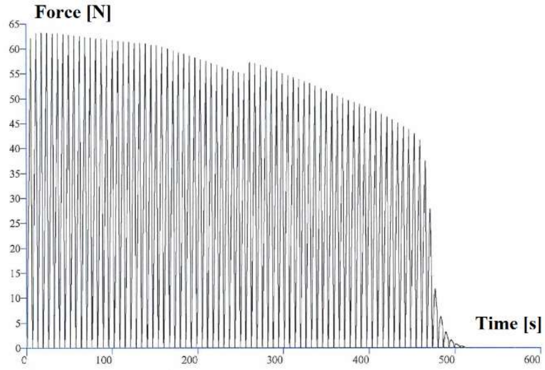

Figure 5 Force-time diagram of repeated slow deformation of a fiber-reinforced silicone resin compound

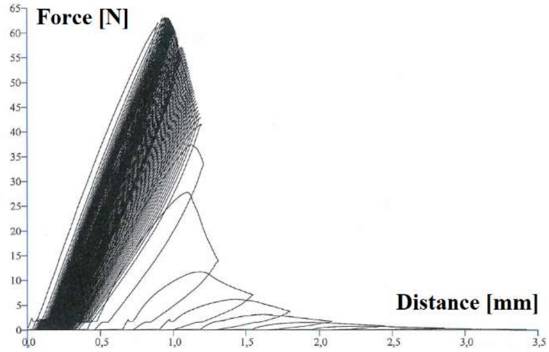

Figure 6 Resulting force-distance diagram of repeated slow deformations of a glass fiber-reinforced silicone resin compound (displacement of the hysteresis curves towards higher distances is caused by a remaining deformation of the specimen during each repeated stress)

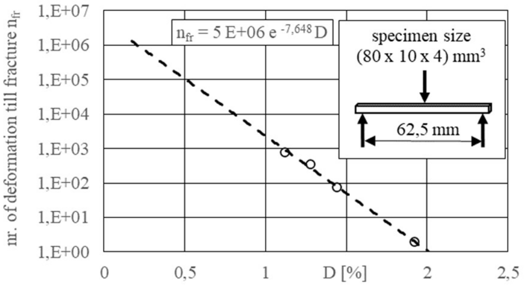

Figure 7 Number of slow deformations to failure; def deformation D [%] is the quotient of the deformation and the support distance

Specimens can be repeatedly deformed to a certain extent without showing immediate fracture. The submitted mechanical power leads to a hysteresis in the force-distance (stress-strain-) diagram as shown. The resulting number of deformations to failure leads to a “life-time-diagram” as shown below (**Figure 7**).

Further investigations are warranted to confirm the applicability of this test, but it may help to further optimize fiber-reinforced compounds to compare the effects of different fiber-shaped reinforcing fillers. The measurement suggests a stability of about 10^5 deformations at a deformation rate of 0,5% or more than 10^6 at 0,1% deformation.

4. Thermal Stability

A key advantage of silicones in comparison to other polymeric materials is their thermal stability. Very typically, a reduction of the tensile strength to 50% of the initial value is used as a reference point when discussing heat stability with potential customers in the field.

For resinous compounds the evaluation is typically done by measuring mass reduction. POWERSIL® 700-based compounds have been evaluated with respect to their thermal stability acc. to ref. [4]. Mass reduction of the binder has been used as an evaluation criterion to determine the thermal index (TI) and the interval to half point (HIC). The 10% threshold for several storage temperatures has been extrapolated from measured data. The resulting thermal long-term diagram is shown above **(Figure 8)**.

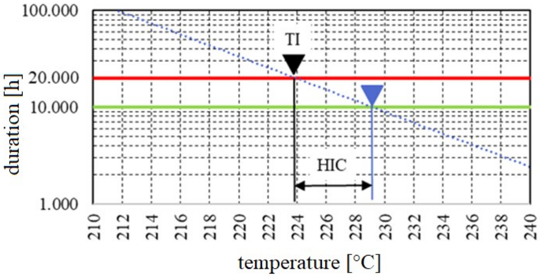

Figure 8 Typical thermal long-term diagram of a compound made from the novel silicone resin binder and suitable mixture of fillers

The thermal index is higher than 220 °C, the interval to half point is about 5K. The material meets the thermal class R acc. to ref. [5], and therefore represents a material with very high thermal stability in comparison to other materials (**Table 1**).

Table 1 Typical thermal classification data for comparison (as sourced from literature)

Thermal class [°C]	Code	Typically used materials
90	Y	Polypropylene
105	A	Phenolic resin
120	E	Paper, Epoxy resin
130	B	Polyester, Epoxy resin
155	F	Aramide
180	H	Polyimide, Glasssilk with silicone elastomer binder
200	N	Polyimide, PTFE
220	R	PTFE, PEEK
250	-	PEEK

5. Further Properties and Molding Trials

Additional advantages of the manufactured silicone-resin-moldings include very high stability against UV exposure, perfect mechanical durability and good processability with existing equipment (pressure gelation, injection molding). Molded parts are easily removable from the mold without release agent.

An overview of the properties of our first commercially available material, POWERSIL® Resin 710, is shown in (

Table 2).

It becomes clear that the new silicone resin compound exhibits a much higher thermal class than that of traditional materials which probably opens the door to novel applications and designs, respectively.

The low viscosity of the material allows for easy processing with existing machines and devices. The glass fiber content may require precautions with respect to the surface hardness of molds and machine components. Molded parts appeared to demold easily without the use of any release agent. Addition of selected color pastes is possible.

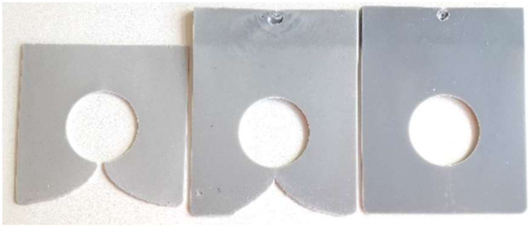

Figure 9 Injection molded plates with a wide upper gate and internal runner (150 × 150 × 2) mm^3

Injection molding trials with POWERSIL® Resin 710 carried out in the technical center of Wacker Chemie AG confirmed observations from press molding trials [6]. In comparison to earlier formulations, the latest materials show the desired mechanical properties without post curing. The material was found rather easy to handle, a good quality part was produced after some experiments using a standard test mold for elastomers **(Figure 9)**. Post-pressure as it is typically applied in a pressure process led to further improvement.

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Table 2 Properties of silicone resin compound POWERSIL Resin 710; Selected literature data of typical epoxy resin compound are shown for comparison.

Property	**Standard**	**Value**	**Value 1)**	**Unit**
Viscosity (at 1 s^{-1})	ISO 53019	330,000		mPas
Viscosity (at 10 s^{-1})	ISO 53019	70,000		mPas
Color		opaque	Reddish brown	
Gel time	ISO 16945	200		s at 160°C
Density	ISO 1183-1	1.57	1,7	g cm^{-3}
Tensile strength	ISO 527	25		N mm^{-2}
Flexural strength	ISO 178	50	80	MPa
Flexural modulus	ISO 178	1,500		MPa
Hardness	ISO 7919-1	90	90	Shore D
Heat class	IEC 60085	220	139	R
Dielectric loss factor (50 Hz)	IEC 60250	0.003	0.008	
Dielectric permittivity (50 Hz)	IEC 60250	3.5	4.2	
Arc resistance	IEC61621	210		s
Flammability	IEC 60695-11-10	V0	V0	
Electrical breakdown strength	DIN EN 60455-2	22	20	kV/mm
CTE	ISO 11359-2	approx. 10×10^{-5}	5×10^{-5}	K^{-1}

1) Data from technical data sheet of material ISO-POX HC 30000 of company ISO-ELEKTRA dated 17.11.2016 (https://www.iso-elektra.de/wp-content/uploads/2017/11/PD_ISO-POX-HC-30000.pdf

6. References

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