# Material and process innovations with filled silicone elastomers

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## ABSTRACT

Today the technological progress of modern military aircraft design has been greatly influenced by the use of advanced composite materials. These materials permit design of lighter stronger more flexible aircraft yet offers a new set of challenges in design, production and quality. Silicones are excellent materials that can be designed with unique properties that are compatible with emerging aerospace and aircraft designs. Most widely known for their ability to maintain elastomeric properties in extreme conditions, silicones can be incorporated with varying amounts of fillers that can impart properties like electrical and thermal conductivity, static dissipation, and radar absorbing characteristics. However, many important considerations such as processing and weight of the modified silicones must be taken into account when formulating a filled silicone system to achieve the desired properties. This paper will discuss the chemical and physical properties behind incorporating various fillers into silicones and the results that can be achieved with certain fillers.

KEY WORDS: Materials – Silicone; Thermally Conductive; Electrically Conductive

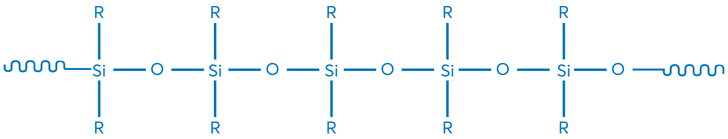
## 1. INTRODUCTION

Silicones can be designed and formulated to have unique physical properties. Different polysiloxanes can provide a variety of excellent properties that can be chosen according to the specific application, temperature stability (-115 to 260°C), fuel resistance, optical clarity (with refractive indexes as high as 1.60), low shrinkage (2 %), and low shear stress (1,2). The potential contamination due to volatile materials coming off of standard silicone at extreme temperatures and high vacuum environments is a serious problem that can cause degradation of expensive operating equipment. Identifying and removing materials species responsible for contamination, verifying material quality, and selecting the proper system for specific applications without compromising the physical properties of the system is critical. Contamination in space, electronics, clean-room, or other high vacuum

applications such as leak detectors and particle accelerators may be avoided or at least significantly reduced by the use of low outgas silicones, known as controlled volatility (CV) silicone materials.

### 1.1 Silicone Polymer Chemistry

Silicones are inorganic polymers, having no carbon atoms in the backbone, and are named polysiloxane polymers. The diagram below shows their typical structure:



R=CH3, C6H5, F3CCH2CH2, CHCH2

The silioxane backbone can be formulated with different types of constituent groups incorporated onto the polymer backbone. Typical constituent groups include dimethyl, methylphenyl, diphenyl, and trifluoropropylmethyl functionality. This polymeric structure allows polysiloxanes to be modified to suit a wide array of applications.

### 1.2 Silicone Material Types.

Silicone materials, with the chemistries described above appear in a wide variety of material compositions. This broad range of material compositions makes silicone a viable option to endless numbers of applications. Some silicone material compositions and their typical applications include:

#### 1.2.1 Silicone Fluids.

Silicone fluids are non-reactive and reactive silicone polymers formulated with dimethyl, methylphenyl, diphenyl, or trifluoropropylmethyl constituent groups. These materials' viscosity depends largely on molecular weight of the polymer and steric hinderance of functional groups on the polymer chain and can range from 100cP (a light oil) to 2,000,000 cP. Silicone fluids are used in hydraulic fluids and damping fluids in extreme environments.

#### 1.2.2 Silicone Curing Gels.

These materials contain reactive silicone polymers and reactive silicone crosslinkers in a two-part system. When mixed together these materials are designed to have a very soft and compliant feel when cured and will stick to substrates without migrating. Viscosities can be adjusted with the molecular weight of the polymers from 200 – 10,000 cP. Gels are typically used in situations where low modulus or self-healing properties are important.

### 1.2.3 Silicone Elastomers

Silicone elastomers fall into two categories, moldable elastomers and adhesives. Like the gels, these two-part systems contain reactive polymers and crosslinkers that cure up to a rubbery type hardness. Elastomers differ from gels in they contain reinforcing fillers, which are described in the section below. Most will cure at room temperature, however some need heat to cure. To impart increased physical properties, sometimes these materials contain high levels of reinforcing fillers and longer polymer chains, resulting in higher viscosities. The moldable materials can be casted or injection molded into various configurations. Elastomer can also be dispersed into solvent systems for use in spraying or dipping applications. Adhesives are low viscosity elastomer systems that incorporate silicone based adhesion promoters.

### 1.2.4 Silicone resins

Silicone resins are also called Polysilsesquioxanes, are highly crosslinked siloxane systems with the empirical formula:

R - Si - O1.5

Both the Polysilsesquioxane and T-resin names can be derived from the empirical formula. The root "sesqui" indicates the one and a half stoichiometry of the oxygen bond to silicon. T-resin indicates the trisubstitution of silicon by oxygen. Silicone resins are also named by the organic, or "R," group. These silicones usually have high modulus and high durometers.

### 1.3 Silicone Polymerization

A silicone polymer is manufactured in several steps. Initially, a silicone polymer is produced via a Ring Opening Polymerization (ROP). The process begins with polyorganosiloxane cyclics reacting with a chain terminating species, or "end blockers," in the presence of an acid or base initiator as shown in Figure 1.

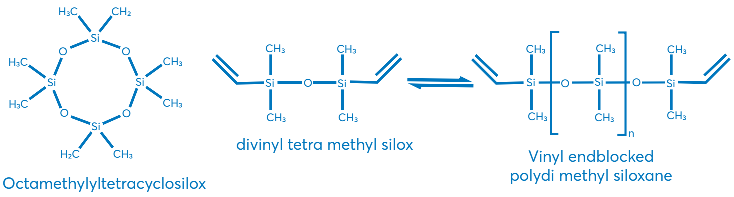


**FIGURE 1:** Basic Ring Opening Polymerization (ROP) reaction for a vinyl terminated polydimethylsiloxane.

The product of this polymerization reaction is a mixture of various molecular weights of cyclics, short chained linear molecules and higher molecular weight polymers where the concentrations of each species is based on its thermodynamic equilibrium. When analyzed using gel permeation chromatography a bimodal distribution with a smaller, low molecular weight peak (representing cyclics and very short chained linears) and a larger peak representing the larger molecular weight polymers is produced as shown in Figure 2. The species represented in the smaller peak and the lower molecular weight portion of the larger peak may readily migrate out of a cured elastomeric matrix if the species lacks the proper reactive groups to tie in. Another scenario involves the short-chained reactive species, which may prove problematic to achieving consistent crosslink density if not controlled.

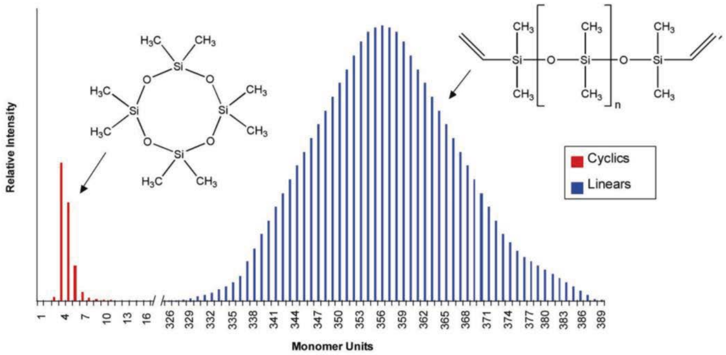


**FIGURE 2:** Molecular weight distribution of final ROP reaction products of PDMS.

### 1.4 Controlled Volatility Materials

A distillation process that removes low molecular weight linears and cyclics from the polymer mixture generates CV grade silicones. The distillation apparatus is typically an evacuated chamber with heated walls and a central cooling finger designed for condensing low molecular weight molecules. Polymer is driven into the heated chamber and wiped onto the chamber walls. This exposes a thin film of the polymer to heat under vacuum conditions. The low molecular weight materials condense on the cold finger and are separated to a collection vessel. Depending on the size of equipment and the ultimate use of the polymer, one to multiple passes through the distillation process can be performed to remove a sufficient amount of low molecular weight species based on the ultimate requirement of polymer.

Advancements in processing techniques and testing methods have produced low contaminating silicones which have ten times lower volatile fraction as required and tested per ASTM E –595 (3). These materials meet the specifications outlined in NASA SPR- 0022A and ESA PSS-014-702, which require a maximum allowable Total Mass Loss (TML) of 1.0% and Collected Volatile Condensable Material (CVCM) of 0.1% (4, 5). Nonetheless, the physical properties achieved by standard silicones are not compromised with low outgassing silicone materials. Several studies have been conducted that compare the low outgas silicones to the standard silicones. These studies demonstrate that low outgas silicones maintain mechanical properties while displaying lower overall contaminates (ionic content and <1.0% weight loss) than standard silicones when exposed to high temperature environments (6,7).

## 2. RESULTS AND DISCUSSION

### 2.1 Silicone Fillers

Many powder fillers are currently added to silicone systems to achieve different properties, see Table 1. Some of the most significant properties that fillers can achieve include strength, thermal and electrical conductivity, thermal stability, and color to the elastomer system. These improvements in the material properties result from molecular level interactions that take place at the interface between the silicone and the surface of the filler.

Reinforcement fillers are the most common fillers added to silicone elastomer systems. They are primarily used to improve mechanical properties. Filler particles reinforce an elastomer by reducing the mobility of the siloxane chains. The bond angles of the silicon-oxygen bonds create large amounts of free volume in silicone elastomers. This free volume associated with the high compressibility found in silicones, bodes well for dispersions of fillers in silicone. The uniform distribution and the particle surface area available to make contact with the siloxane chains have the most influence on the physical properties of a reinforced elastomer. The more free space, the more filler that can be added and the more uniform the dispersion.

Thermally and electrically conductive fillers are referred to as functional fillers. Thermally conductive silicones are designed to dissipate heat generated by an electronic device to the ambient environment. They can be also be formulated as compressible thermal interface gap fillers to provide a thermal path between components. However, filling all air gaps is critical for effective heat transfer. Air trapped between a heat generating device and a heat spreader or heat sink inhibits the effective heat transfer from hot spots to the exterior of the closed system. Factors that inhibit effective thermal transfer are surface concavity, surface roughness, uneven pressure along the interface and uneven distribution along the surface.

| Filler | Properties | Density | Particle size (µm) | Surface Area (m2/g) |
|---|---|---|---|---|
| Fumed Silica | Increase strength | 2-5 lbs/ft3 | 0.011-0.014 | 200-255 |
| Microballoons | Reduce density | 0.16 g/cc | 35-135 | NA |
| Ferro Black, $TiO_2$ | Color | 5.0 g/cc | 1, 0.3 | NA, 9 |
| Boron Nitride | Thermal Conductivity | 2.29 g/cc | 7-10 | 13 |
| Iron oxide red | Thermal stability | 4.1 lbs/ft3 | 3 | NA |
| Diatomaceous Earth | Increase hardness | 352 g/l | 7 | 100-200 |
| Carbon, Silver | Electrical conductivity | 6, 10.4 g/cm3 | 30 nm,30-40 | 254, 10 |

**TABLE 1:** Silicone filler properties..

Electrically conductive additives provide protection against static accumulation and discharge that can damage sensitive electronic components. The static is allowed to dissipate continuously rather than accumulate and discharge rapidly. The electrical conductivity is measured by volume resistivity (  cm) and is used to gage the shielding effectiveness of the material (8). Electrically conductive fillers are typically metal particles (0.1 ohm  cm), metal coated particles (2.0 ohm  cm) or carbon black (4 ohm  cm). It also is important that an electrically conductive silicone maintain its' shape and conductivity under stress (i.e. elongation or compression). These materials typically have high dielectric properties (  500V/mil (0.001 inch) or 20 KV/mm) and low modulus. This provides stress relief during thermal cycling between substrates with different coefficient of Thermal Expansions (CTEs).

### 2. 2. Use-based Considerations

Many considerations must be taken into account when formulating a filled silicone system to achieve the desired properties. The use-based considerations for the engineer are as follows:

### 2.2.1 Loading Level

Targeting the desired physical properties is the first objective to consider. Table 1 demonstrates how variations in similar fillers can greatly alter the properties desired. While functional fillers add specific properties to an elastomer system, the addition of too much filler may adversely affect physical properties like tensile, tear, elongation and adhesion. For instance, increasing the filler loading level causes a rapid increase in viscosity. The plot shown in Figure 3 of the Boron Nitride filler content versus viscosity of an LSR demonstrates this point (9).

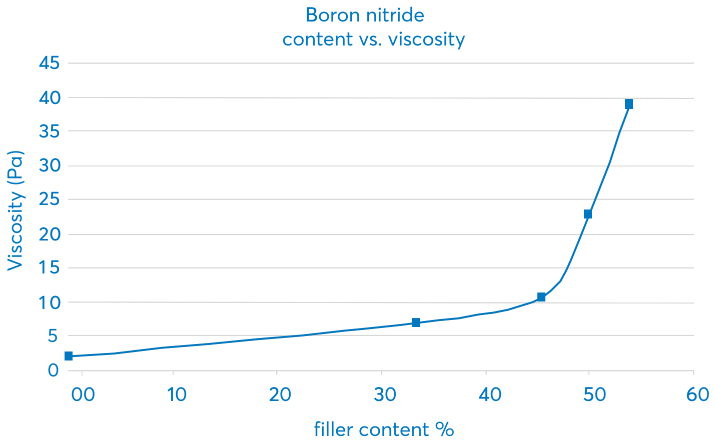


**FIGURE 3:** Dependence of viscosity on filler loading of boron nitride on a silicone polymer(8).

Filler loading levels also directly influences electrical and mechanical properties of conductive silicones (8,10). The material only becomes conductive at the point where the particle network has been formed to create an effective electrical circuit. A rapid drop in volume resistivity demonstrates this point as shown in Figure 4 (11). As the electrical properties improve with increased loading levels, the mechanical properties become compromised. Thus it is critical to find the optimum filler concentration to form an electrical path throughout the material while maintaining the integrity of the material.

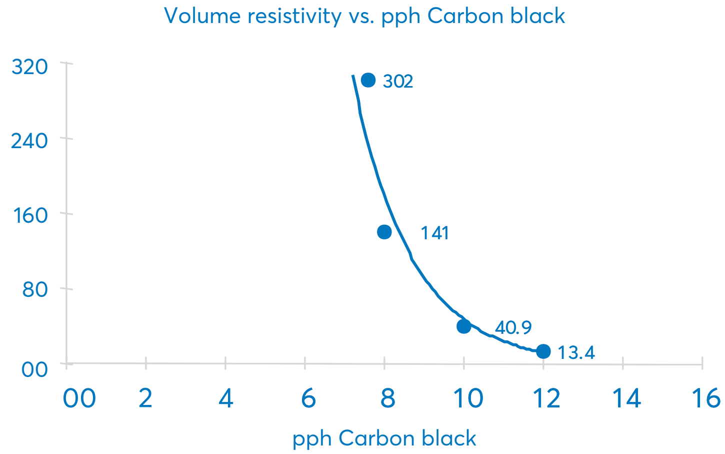


**FIGURE 4:** Dependence of conductivity on filler loading of CarbonBlack in a silicone polymer (9).

### 2.2.2 Homogeneous Mixtures

For fillers to perform their desired function, the ideal displacement of filler will be homogeneous throughout the mixture. Silicone users may choose to incorporate fillers to the suppliedsilicone. Consistency is the key in making a dispersion of any powder. Theideal dispersion process breaks down filler into primary particles of uniformsize and coats the particles with a uniform layer of silicone. Inadequatemixing causes clumping which can lead to accelerated filler settling andunnecessary variability in properties. Uniform mixing is dependent on theshearing capacity of the dispersion equipment, the length of shearingtime, the viscosity of the liquid, and the particle size and density of thepowder.Unlike reinforcing fillers, functional fillers typically are not soluble and havelittle to no reactivity with polysiloxane polymers, and this results inseparation over time. This separation can significantly alter the intendedproperty. For instance, electrical conductivity through silicone elastomersdepends on point-to-point contact of conductive fillers, settling of thosefillers may create an electrically insulating layer between the surface ofthe elastomer and the conductive filler. Air-less mixing can reverse thisseparation, in the uncured state. It is irreversible when the material beginsto cure.

### 2.2.3. Processing

Silicone materials containing a high level of functionalfillers are typically high viscosity products, which can be limiting forapplications like coating but ideal for applications like form-in-placegasketing and groove filling. One option for expanding the use of highviscosity products is the addition of solvents that lower the system viscosityfor coating applications. This allows easier application while providingbetter physical properties. It is important to note that lower viscosity systems fillers separate more rapidly than high viscosity systems.

### 2.2.4 Filler Particle Shape

The filler particle shape has influence on particle packing. Fillers can come in several different shapes. The most common shapes are spherical, flakes and fibers. Spherical particles offer good point-to-point contact, which is critical for good electrical conductivity of silicones. Spherical particles also have the lowest surface area and usually offer the lowest viscosity at similar loading levels of any particle. Flakes on the other hand have better aspect ratios and therefore they have better conductivity with elongation. This is critical for helping with CTE mismatch of silicones. Flake filled silicones however, are higher in viscosity because of the larger surface area as compared to spherical particles. Often, flakes are coated with a surfactant to prevent self-welding during the processing phase. Fibers have the most favorable aspect ratio of all particle shapes and eliminate CTE mismatch problems best. Of all the fillers, fibers have the highest viscosity for similar loading levels with a tendency to segregate during extrusion.

### 2.2.5 Weight

The few metal fillers listed above have a high density and can add to the weight of the material, which can be problematic for aerospace applications. One development strategy may be to add a minimal amount of filler to provide the necessary radar absorbing properties. If the weight does become a problem, microballons may be necessary to reduce the density of the materials.

## 3. CONCLUSION

Silicone materials' properties and adaptability make silicone a candidate for use in a broad range of applications. Incorporating functional fillers offers significant property benefits. Many properties imposed by functional fillers are based on interdependent variables, therefore factors such as loading levels, processing, and weight of modified silicones must be considered. A combination of highly processed silicones free of contaminants and different fillers may provide the best solutions and endless opportunities for improved properties. In summary, the optimal formulation and processes must be well thought-out to maximize filled silicone material performance.

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