NuSil SILICONE TECHNOLOGY

Creative Partners in a Material World

Choosing a Silicone for Joining Technologies

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CHOOSING A SILICONE FOR JOINING TECHNOLOGIES

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ABSTRACT

Engineers and material scientists are constantly looking for a polymeric adhesive that can perform in a broad operating temperature range, maintain chemical stability and offer unique mechanical properties. The dynamic attributes of silicone adhesives, sealants, coatings and encapsulants provide design engineers with a variety of solutions to the complex challenges they face. The advantages of silicone lie in the chemistry of the polymer chain, which can be modified to achieve desired mechanical properties. The different functional groups (R-substituent groups) bonded to the siloxane backbone can affect properties such as hydrocarbon resistance, optical clarity and elasticity. Another benefit of silicone is the ability to incorporate functional fillers that impart unique properties such as electrical conductivity, thermal conductivity, lower density and increased physical properties. These advanced silicones can also be designed as controlled volatility (CV) materials to handle the rigorous demands of aerospace requirements.

Choosing a silicone for your application involves detailed planning and collaboration with a silicone supplier. This article outlines several types of silicones, how they can be modified and customized to suit a specific application, and how to select the appropriate silicone adhesive.

1. INTRODUCTION TO SILICONE

When choosing a silicone adhesive, it is important to consider the attributes necessary for each application. A silicone's polymer can be formulated and processed to posses various targeted physical properties. Depending on an application's requirements, properties — such as temperature stability (-115°C to 260°C), fuel resistance, optical clarity (with refractive indexes ranging from 1.38 to 1.57), low shrinkage (2 %), low out gassing and low shear stress — can be optimized to accommodate specific needs[1, 2]. Silicones can be customized further by adding various fillers to the polymer that affect the silicone's thermal conductivity, electric conductivity and physical strength.

1.1 Silicone Polymer Chemistry. Silicone is comprised of repeating siloxane units, Si-O, with substituent groups attached to the open valences of the silicon atom. Having no carbon in the backbone, these repeating siloxane units are often referred to as a polysiloxane polymer. Furthermore, silicone polymers are also referred to as polyorganosiloxanes when considering the organic substituent groups.

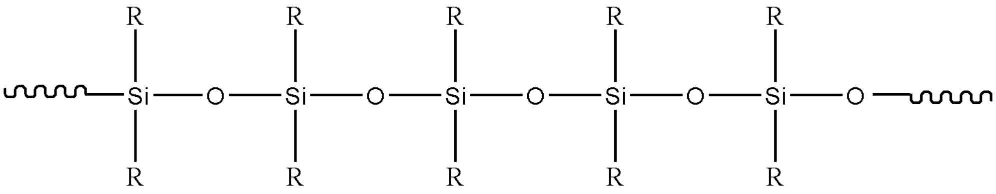

Figure1: Basic structure of Polyorganosiloxane chain

The siloxane backbone can be formulated with varying substituent groups on the polymer backbone. Typical substituent groups include methyl, phenyl and trifluoropropyl. In addition, the siloxane backbone allows the groups to be added in several ways. For example, polymers can either have a combination of different substituent groups, such as a diphenyldimethylpolysiloxane copolymer, or the substituent groups can all be of the same molecule, like a dimethylpolysiloxane polymer. Reasons why one would choose each group include:

1.1.1 Methyl Groups. The most common type of silicone is comprised of polydimethylsiloxane polymers (PDMS). Historically, PDMS silicones offer the best physical properties such as tensile, tear strength and elongation. Methyl groups allow a silicone to be versatile in regards to fillers. PDMS silicones can be found in every form of silicone that is produced; from fluids to high-consistency rubbers (HCR).

1.1.2 Trifluoropropyl Groups. Trifluoropropyl groups can be added to form trifluoropropyl methyl polymers and are typically used for applications that require hydrocarbon resistance. While some fluorosilicones contain 100 mole% trifluoropropylmethyl siloxane polymers, other fluorosilicones are copolymers that contain a combination of trifluoropropylmethyl siloxanes and dimethyl siloxanes. Adjusting the amount of trifluoropropyl methyl siloxanes in the polymerization phase provides optimal performance in specific applications.

1.1.3 Phenyl Groups Phenyl groups can be added to form diphenyldimethylpolysiloxane copolymers. With the addition of phenyl groups, several properties of the silicone are affected. The refractive index (RI) of a silicone can range from 1.43-1.57, depending on the mole% of diphenyl siloxanes included in the copolymer. Also, a decrease in moisture and gas permeability is directly related to the diphenyl siloxane concentration. Furthermore, low levels of phenyl increase the temperature range of a silicone and allow for a lower T_g.

1.2 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 2.

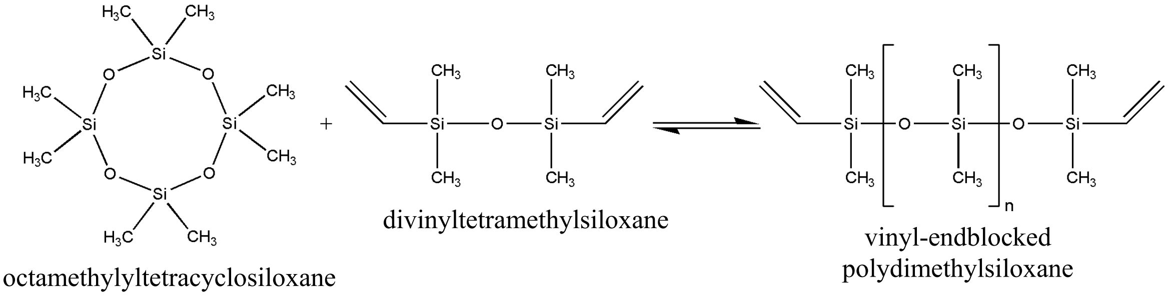

Figure 2: Basic Ring Opening Polymerization (ROP) reaction for a vinyl-terminated polydimethylsiloxane.

The product of this polymerization reaction is a mixture of various molecular weight molecules, including cyclics and linear polymers of varying lengths; concentrations of each species are based on a thermodynamic equilibrium. When analyzed using gel permeation chromatography, a bimodal distribution can be seen. A smaller, low-molecular-weight peak represents cyclics and very short chained polymers can be observed, as well as a larger peak representing the larger molecular weight polymers, as shown in Figure 3.

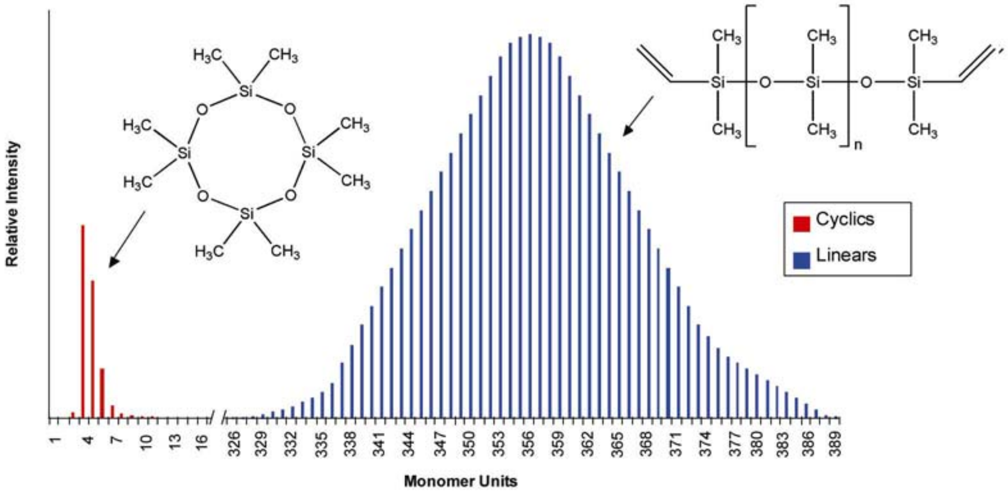

Figure 3: Molecular weight distribution of final ROP reaction products of PDMS.

1.3 Controlled Volatility Materials. To some degree, the species represented in the smaller peak and the lower molecular weight portion of the larger peak of Figure 2 can be problematic in a cured silicone. These lower molecular weight species will migrate out of the cured matrix over time, resulting in contaminants. Therefore, a distillation process that removes low-molecular-weight polymers and cyclics from the polymer mixture is necessary. The apparatus used to achieve this process 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 process 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 the equipment and the ultimate use of the polymer, multiple passes through the distillation process may be required to remove a sufficient amount of lower-molecular-weight species.

For applications that demand measurable, minimal outgassing, controlled volatility (CV) materials have been developed. Primarily for applications that exist in a vacuum, usually extra terrestrial, CV materials are processed to be tested per ASTM E 595[3] and to meet specifications outlined in NASA SP-R-0022A and ESA PSS-014-702, with a maximum allowable Total Mass Loss (TML) of 1% and a Collected Volatile Condensable Material (CVCM) of less than 0.1%[4,5]. With these materials, physical properties remain the same but volatiles are minimized[7]. If the lack of outgassing or volatiles is of the utmost importance, Ultra Low Out gassing (ULO) materials can be processed to exceed the current ASTM E 595 by an order of magnitude, ≤ 0.1% TML and ≤ 0.01% CVCM.

1.4 Silicone Material Types. Silicone exists in many different forms. By functionalizing the silicone polymer or adding fillers, the composition silicone forms changes. This broad range of material compositions makes silicone a viable option for an endless number of applications. Some silicone material compositions and their typical applications include:

1.4.1 Silicone Fluids. Silicone fluids are made of non-reactive polymers. The viscosity of the fluid depends chiefly on the degree of polymerization (DP). As the polymer's chain length increases (higher DP), so too does the viscosity. The viscosity range of a silicone fluid is large, ranging from near water (20 cP) to millions of cP. Silicone fluids are used as lubricants, as well as hydraulic or damping fluids in extreme environments.

1.4.2 Silicone Gels. Silicone gels are made of reactive silicone polymers and reactive silicone cross-linkers in a two-part system. When cured, these gels are designed to have a soft, compliant feel with a range of terminal hardness. Typically, silicone gels are used in situations where low modulus, low stress or self-healing properties are important and posses little to no elastomeric "strength."

1.4.3 Silicone Elastomers. Silicone elastomers fall into two categories: moldable elastomers and adhesives. Like gels, these two-part systems contain reactive polymers and cross-linkers that cure to form a rubber like elastomer. Elastomers differ from gels however in that they contain reinforcing filler, described in the section below. Most will cure at room temperature; however, some require heat to cure. To impart increased physical properties, these materials will often contain high levels of reinforcing fillers and longer polymer chains that result in higher viscosities. The moldable materials can be cast or injected into molds of various configurations. Elastomers can also be dispersed into solvent systems for use in spraying or dipping applications. Adhesives are low-viscosity elastomers systems that incorporate silicone-based adhesion promoters.

1.4.4 Silicone Resins. Silicone resins, also known as polysilsesquioxanes, are highly crosslinked siloxane systems with the empirical formula:

$$R - Si - O_{1.5}$$

The root “sesqui” indicates the one and a half stoichiometry of the oxygen bond to silicon. These silicones usually have a high modulus and high durometer. By adding resin to silicone polymer, it is possible to increase the hardness of the cured material without drastically increasing the viscosity of the uncured silicone.

2. RESULTS AND DISCUSSION

2.1 Silicone Fillers. When compared to organic polymers, bond lengths and particularly bond angles are larger with Silicon-Oxygen (Si-O) bonds than Carbon-Carbon (C-C) bonds. This increased Si-O bond angle creates large amounts of free volume in the polymer chain, allowing for the incorporation of many different types of filler. From reinforcement fillers to functional fillers, silicone can be optimized in many different ways.

Filler	**Properties**	**Density**	**PARTICLE SIZE (μm)**	**Surface Area (m^2/g)**
Fumed Silica	Increase strength	2-5 lbs/ft^3	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/ft^3	3	NA
Diatomaceous Earth	Increase hardness	352 g/l	7	100-200
Carbon, Silver	Electrical conductivity	6, 10.4 g/cm^3	30 nm, 30-40	254, 10

Table 1. Silicone filler properties.

2.1.1 Reinforcement Fillers. Reinforcement fillers are the most common fillers added to a silicone elastomeric system. An example of a common reinforcement filler is silica. Both fumed and precipitated, silica is used to increase mechanical properties such as lap shear, elongation and tear. Primarily, reinforcement fillers are used to improve the mechanical properties of silicone and to increase their ability to survive in harsh environments.

2.1.2 Functional Fillers. Thermally and electrically conductive fillers are referred to as functional fillers. Thermally conductive silicones are designed to be an interface that dissipates heat generated by a component to either a heat sink or the ambient environment. They can also be formulated as compressible thermal interface gap fillers to provide a thermal path when joining multiple components.

Silicone is inherently insulative at approximately 10^{15} Ω·cm. Electrically conductive fillers — ranging from static dissipative (10^4-10^{11}) Ω·cm to conductive <10^4 Ω·cm — can be added to a silicone to impart conductivity. The specific filler used, the particle size, and the distribution and the amount of filler determines the silicone's conductivity. Electrically conductive fillers are typically metal particles (0.1 Ω·cm), metal-coated particles (2.0 Ω·cm) or carbon black (4 Ω·cm). Maintaining conductivity in harsh environments is often challenging when one considers the coefficient of thermal expansion (CTE) of silicone. When joining substrates with conductive silicone, the particle size and shape of the filler play a key role in maintaining conductivity during thermal cycling.

2. 2. Material Considerations. Filler shape and size significantly affect a material's rheology and conductivity. Physically, the amount of filler that can be added is governed by the interaction between the polymer and the filler. However, it is also important to understand that while maximum loading gives the best conductivity, changes to the silicone's physical properties are common as fillers are added to a silicone matrix. The following are changes that should be expected in the physical properties of a material:

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 desired properties. While functional fillers impart specific properties to a silicone system, the addition of too much filler may adversely affect physical properties. For instance, as the filler loading level increases, so does the silicone material's viscosity. The plot shown in Figure 4 demonstrates this point[9].

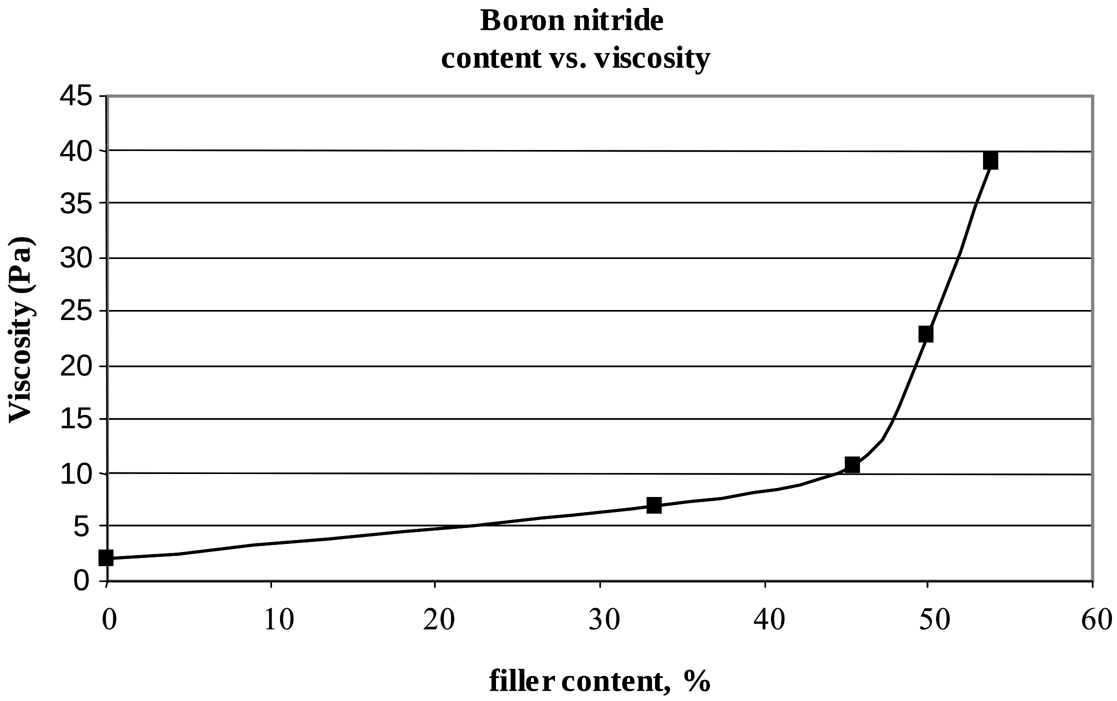

Figure 4. Viscosity dependence on filler loading of boron nitride on a silicone polymer (8).

Filler loading levels also directly influence how conductive a silicone will be[8,10]. For a silicone to become conductive, point-to-point contact of the conductive filler must be present. Depending on the size and shape of the filler, different loading levels are necessary. A rapid drop in volume resistivity demonstrates this point as shown in Figure 5[11].

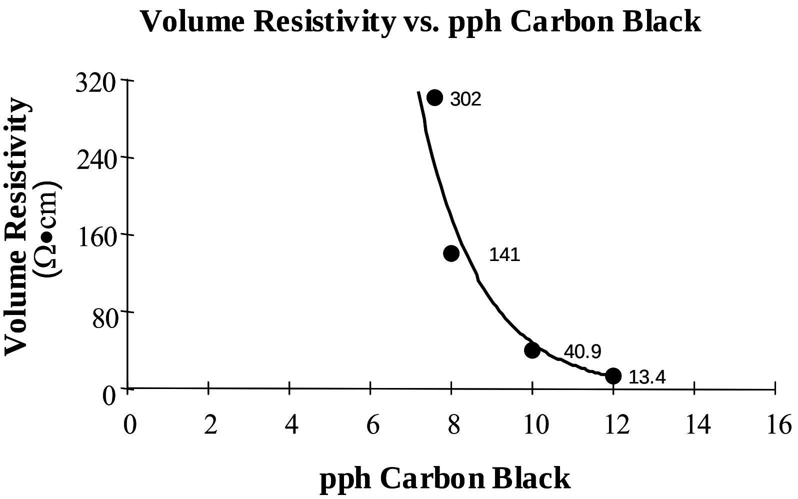

Figure 5. Conductivity dependence on filler loading of CarbonBlack in a silicone polymer[9].

An inverse relationship can be seen, however, between increased loading levels of functional fillers and the silicone's mechanical properties. Thus, it is critical to find the optimum filler concentration to form an electrical path throughout the material, while maintaining the material's integrity.

2.2.2 Homogeneous Mixtures. When considering any filler, functional or reinforcing, a homogeneous mixture is crucial to achieving desired results. Uniform mixing is dependent on the shearing capacity of the mixing equipment, the length of the shearing time, the viscosity of the polymer, and the added filler's particle size and density. Inadequate mixing causes clumping which can lead to accelerated filler settling and unacceptable variability in targeted properties.

Unlike reinforcing fillers, functional fillers typically are not soluble and have little to no reactivity with the silicone polymers, resulting in separation over time. As previously discussed, point-to-point contact of functional fillers is necessary to maintain conductivity because separation can significantly alter the intended property. Before applying the material, proper mixing is vital to ensure a homogeneous distribution.

2.2.3 Filler Particle Shape. To maintain conductivity, point-to-point contact of filler particles is necessary. The three most common shapes for filler particles are spherical, flakes and fibers. Spherical particles offer good point-to-point contact and have the lowest surface area, resulting in the lowest viscosity at similar loading levels of any particle. Flakes, on the other hand, have better aspect ratios and better conductivity with elongation. This is important to cope with the large CTE that silicones pose when exposed to changes in temperature. Flake-filled silicones are higher in viscosity because of the larger surface area 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 mitigate CTE problems the best. Of all the fillers, fibers have the highest viscosity for similar loading levels. In summary, at ambient conditions, achieving point-to-point contact is more dependent on the concentration of the filler than anything else. However, during thermal cycling, the shape of a particle, as described above, becomes just as — if not more — important.

2.2.4 Weight. In some cases, the amount of filler added may be problematic due to the increase in application weight. Particularly in the aerospace or aircraft industry, the weight of an individual component is regulated, and denser fillers such as iron or silver add to that weight. Optimizing loading levels becomes crucial, and a thorough understanding of the requirements of a particular application becomes paramount.

2. 3. Processing Considerations. Due to the material level alterations that occur when adding various fillers, using and processing filled silicone materials must be done carefully. Saturating a silicone polymer with filler may result in a higher conductivity value, but the resulting product will thicken. Because of this, users must consider their processing capabilities, as the resulting material will be paste-like with little to no flow. This is when a good understanding of application requirements is crucial. In this example, if half the conductivity is necessary, then filler levels can be adjusted to make the material easier to process.

Along with adjusting filler levels, alternate silicone forms — like dispersion or film adhesives — should be considered. Dispersions are silicone polymers and fillers suspended in compatible solvents. The result of this is a very low-viscosity product that can be easily sprayed onto a substrate that cures as a silicone elastomer. Different solvents can be considered, including low volatile organic compound (VOC) solvents for locations that have tighter regulations. Film adhesives are sheets of silicone that can be used in a "peel and stick" manner. Film adhesives are also beneficial because the bond line thickness (BLT) is controlled and complex patterns can be dye cut depending on the application. These benefits save time and labor for those applying it. Finally, films can be loaded homogeneously with filler, eliminating the necessity to mix and de-air and the problems of applying the thixotropic material in a liquid-like form.

3. SUMMARY

For engineers looking for a polymeric adhesive to join materials in broad operating temperatures, while maintaining chemical stability and offering unique, tailored properties, silicone is the first choice. Inherently, silicone is biologically inert, electrically and thermally insulative and stable when subjected to various harsh environments. In addition to silicone's innate properties, the ability to optimize it for different applications is particularly beneficial. Reinforcement fillers can be added to increase mechanical properties — such as elongation, tear strength and lap shear — that cured silicones don't get from the polymers alone.

In addition, functional fillers can be added to provide conductivity that silicone doesn't have. Whether a silicone needs to be thermally conductive, electrically conductive or both, fillers are available to provide the necessary characteristics. More than that, the degree of conductivity can be controlled and maintained, even in harsh environments. An understanding of the trade-offs involved when adding functional fillers should be considered when choosing a silicone for a specific application. Unlike reinforcement fillers, functional fillers will decrease mechanical properties of a silicone as loading levels increase. Again, a thorough understanding of application requirements and the silicone forms available for use is crucial when choosing a silicone.

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