Silicones for high reliability and yield in electronic applications

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INTRODUCTION

Silicones have been used for decades in electronics, aerospace and other applications wherein harsh environments with temperature extremes are common. These siloxane-based polymeric systems are unique polymers compared to standard organic-based materials due to their atomic composition. The low modulus of their crosslinked networks allows them to absorb stresses during thermal cycling as well as to resist degradation at continuous operating temperatures up to 250°C and greater. Silicones have low glass transition temperatures (Tg) ranging from approximately -115° C to -60°C which keep their elastomeric systems flexible in cold environments and when experiencing vibration. Thermally conductive silicones provide protection to sensitive electronic components and systems. The silicone matrix is an essential polymer compatible with a variety of fillers due to its unique chemistry, making silicones excellent materials for use as the binder for a variety of thermally conductive fillers where high level loadings can be achieved without dramatically increasing the shear stress.

As electronics are becoming smaller, thinner, vertically stacked and require more power, silicone becomes more desirable to increase reliability. The history and prolific success of silicone speaks to its capacity for reliability. Silicone is typically non-hazardous in its "neat" state once cured and complies with the restricted levels of the regulated chemicals listed in the ROHS and WEEE directives. In medical devices, silicones have proven they can be manufactured to have very high purity for robustness in high-risk applications. Quantifiably, and most relevant for electronics applications, silicones can be processed to have low D4/D5 (< 50 ppm) content as well as to comply with 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%1,2. This reduces risk of fogging, delamination and other failure-inducing occurrences which volatile species of impure material can cause. Silicones for electronics can also be optimized to exhibit high purity with regard to ionic content < 20 ppm of Na, K and Cl, and their permeability to moisture, a most brutal contaminant, can be adjusted as needed for a given electronic device. Because water is detrimental to many components, extremely low Water Vapor Transmission Rates (WVTR) are often imperative of encapsulating materials. Understanding the opportunities and limitations of silicone allows the formulator or engineer to choose the best options available for maximum performance and protection of components in the harsh environments of electronic applications.

SILICONE IN ELECTRONICS

For their ability to withstand exposure to high temperatures such as in lead-free solder reflow and for longer durations when compared to other polymeric materials, silicone encapsulants are used to protect the components against shock, vibration, moisture, dust, chemicals and other environmental hazards3. Although naturally insulating with dielectric strengths typically greater than 400 V/mil (15.6 kV/mm), dielectric constant at ~2.5 and volume resistivityat 1X1012 ohm-cm, silicone can be made to be conductive when needed. For instance, as the processing capability of semiconductor devices increases and chip size decreases to more compact electronic modules, the need for thermal management increases. Even with a heat sink directly in contact with a chip, heat may not transfer efficiently if the mating surfaces are at all rough or irregular.

To enhance the thermal contact between the heat sink and the die, Thermal Interface Materials (TIM) are utilized between the two surfaces. Under mechanical pressure, the soft TIMs conform to the microscopic surface contours of the adjacent solid surfaces and increase the microscopic area of contact between them. The thermal conductivity of the material then assists to reduce the temperature drop across this contact. Lead-free solder reflow temperatures of > 260°C and high heat created during operation (> 100 °C) cause greater temperature extremes during the thermal cycling in the electronic package. Stress within the electronic assembly will increase when it is comprised of a myriad of materials with various Coefficients of Friction (CTE). This stress induces metal fatigue in the solder and can cause cracking of the solder joint. An adhesive or encapsulant in the gap between the printed circuit board and chip helps minimize the shear stress by mechanically coupling the board to the die and restricting the relative lateral motion. This coupling reduces the stress on the solder joints and converts the in-plane stress to a bending stress.

The electronic packaging industry has used epoxy adhesives and encapsulants for years as thermal management materials such as TIMs and underfills4 for their strong adhesion and low CTEs. Silicones may have high CTE relative to the organic-based

thermosets, but compared to epoxies, silicones have very low modulus. This helps absorb stress incurred from thermal cycling when in hybrid devices, reducing to little or no significance the high CTE they may possess relative to organic thermosets such as epoxies.

Specific Property	Epoxy (C-C-C)	Silicone (Si-O-Si)
Bond Lengths (nm)	0.154	0.164
Bond Angles	109o	130 -150o
*Tg (oC)	> 80	< - 60
*CTE (ppm/oC)	45 - 100	120 - 1000
G' Storage Modulus (Epoxy (85A)	2300 MPa	X
G' Storage Modulus (Silicone 50A)	X	1.3 MPa
G' Storage Modulus (Silicone Gel)	X	0.002 MPa

TABLE 1: Molecular and Property comparison of silicone versus epoxy

Historically, silicone greases have been popular thermal management components for electronic applications since they are easy to use and impart minimal stress. These materials are excellent in applications involving flat surfaces or in which risk of shear stress is high. However, greases are mobile and can "pump out" of the device after extensive thermal cycling. This complication can be preemptively combated by crosslinking the silicone covalently. This links all the polymers together into a three-dimensional network, forming an elastomer and greatly sidestepping creep and mobility. The more bonds created between vinyl and hydride, the higher the crosslink density of the silicone and, generally speaking, the greater the hardness of the elastomer. Theoretically, the resulting tradeoff is an increase in modulus, but this can be avoided with a platinum addition cure silicone material. Addition cure silicones are optimized to contain specific amounts of hydrides on the crosslinker and vinyls on the polymer network. These react in the siloxane system to form a three-dimensional network in which there is no generation of small molecules (Figure 2) and generally less than 2% shrinkage. In addition to minimal shrinkage and no cure by-products, platinum addition cure chemistry eases processing with a 24-hour room temperature vulcanizing (RTV) time that can be accelerated with heat.

MODIFYING SILICONES: HIGH RELIABILITY FROM CONDUCTIVITY TO PERMEABILITY

From cure chemistry options to customized performance levels, the unique, sought-after advantages of silicone are due to its atomic structure, which lends silicone to unrivaled formulation flexibility. Silicones are unique polymers in that they have inorganic and organic characteristics which make them easily adaptable. The backbone of the polymer is composed primarily of repeating silicon and oxygen atoms, collectively known as polysiloxanes. Compared to epoxies and other organic-based rubbers with Carbon-Carbon (C-C) bonds, the Si-O bonds of silicones provide larger bond angles[5] and thereby, freer rotation. These bond angles yield large amounts of free volume, leaving space for design or, more specifically, for managing the amount and type of substituent group and filler that go into a silicone system. The silicon-oxygen backbone allows for the varying of organic (R and R') groups on the polymer chain, and due to its slight polarity evident in its ability to wet out a variety of surfaces, it also allows for the incorporation of fillers. These opportunities for design enable adjustments in silicone's physical and mechanical properties, such as viscosity and permeability, and fillers even enable new properties, such as conductivity, to be imparted to the given silicone material.

Typical substituent groups include methyl, phenyl and trifluoropropyl. The most common type of silicone is comprised of polydimethylsiloxane polymers[6] (PDMS) from dimethyl groups, which facilitate strong physical properties such as tensile, tear strength and elongation. Chemically, these are the most accommodating to the incorporation of fillers into the silicone formulation. Trifluoropropyl (fluoro) or phenyl groups are often added in varying degrees to form trifluoropropyl methyl polymers or diphenyldimethylpolysiloxane polymers, respectively. Phenyl groups can manipulate the refractive index (RI) of a silicone system, as well as its glass transition temperature (Tg) and permeability to moisture and gases. Fluoro-containing silicone products, also known as fluorosilicones, are often used for applications that require hydrocarbon resistance. Compared to dimethyl silicones, fluorosilicones generally exhibit lower elastomeric properties—a tradeoff for their resistance to fuel and organic solids. Table 2 provides some details on the chemical

structures and typical manifestations in material performance of methyl and phenyl inclusion in a silicone formulation.

R	R'	Properties
$-CH_3$ Methyl	$-CH_3$ Methyl	Standard Refractive Index = 1.40 Standard polymer Legacy material
$-CH_3$ Methyl	-H Hydride	React with vinyl groups to form covalent crosslinks Polymers known as "crosslinkers"
$-CH_3$ Methyl"	$-CH{=}CH_2$ Vinyl	Reacts with hydride groups to form covalent crosslinks with crosslinker
$-CH_3$ Methyl	$F\text{-}\overset{F}{\underset{F}{C}}\text{-}H_2CH_2\text{-}$	Refractive Index < 1.40 Hydrocarbon solvent resistance (Fuels and oils) Available as co-polymers up to 100% F
Phenyl	Phenyl	Refractive Index > 1.43 Increase temperature stability Reduces gas permeability Increase refractive index up to 1.54 commercially Phenyl concentration limited

TABLE 2: Common organic groups used to modify siloxane chemical performance

Beyond alteration of substituent groups on the polymer chain, electrically and thermally conductive fillers are common design steps in formulating silicones for electronic applications. Frequently used fillers in silicones for thermal management include boron nitride for imparting thermal conductivity and silver for thermal and/or electrical conductivity.

The conductivity of silicone elastomers is largely dependent upon point-to-point contact of conductive fillers; hence, the loading levels are typically greater than 50% (w/w). Thermally conductive fillers are typically non-reinforcing, unlike silica and resins, and their filler particle shape and size influence particle packing as well as viscosity. Thermally conductive fillers are available as metals or ceramic-based materials and come in several different shapes. Spherical particles such as those in silver give consistent, strong point-to-point contact, critical for the silicone to maintain the level of electrical conductivity for which it was designed and selected for use. Flakes or platelet-shaped particles like those of boron nitride have better aspect ratios (length versus height) and therefore facilitate conductivity with elongation. This is critical for helping with CTE mismatch of silicones. Flake-filled silicones do tend to be higher in viscosity because of the larger surface area as compared to spherical particles, and often they are coated with a surfactant to prevent self-welding during the processing phase.

Generally, with increasing filler content comes a corresponding increase in durometer followed by a decrease in elongation and tensile strength. Specifically, the hard inorganic filler particles have a higher durometer than the soft organic polymer chains, meaning their inclusion decreases the concentration of polymer chains resulting in an increase in the product's durometer. More than elastomers, which possess relatively high mechanical properties to begin with, silicone gels offer significant relief from the tradeoffs that often accompany filler incorporation. In contrast to elastomers, they are characterized by low modulus and low viscosity ranging from 100 to 20, 000 cPs, and the large free volume of gels once crosslinked allows >70% (w/w) of inorganic fillers to be added into the silicone matrix. Traditionally, the uniquely large free of gels has been utilized with the incorporation of phenyl to produce encapsulating materials with high RIs for use in optoelectronics applications. Gels are compliant as well as resilient, with a unique viscoelastic softness that enables them to more closely encapsulate components than higher viscosity elastomers, as well as to absorb stress and protect the electronic device for longer time periods than thermal greases.

Study on the Permeability of Conductive and Non-conductive Silicone Formulations

When it comes to electronic systems, silicone gels and other forms have repeatedly proven their worth and reliability as components for protection with regard to thermal management. Where low permeability to moisture is required, silicone's inherently high permeability to various gases and vapors may appear to demote it in the material selection process when in competition with epoxies. However, the aforementioned properties intrinsic to silicone often give this material an edge over epoxies, and like silicone's conductivity, its permeability can be adjusted as needed.

A recent study evaluated silicone formulations for permeability to moisture. Silicone gels with varying backbone chemistry were compared to higher crosslink density PDMS silicones with and without filler, or containing only resin for reinforcement. The fillers evaluated were silver (Ag) or boron nitride (BN) filler. Water Vapor Transmission Rates (WVTR) were measured at 40.0°C, 90%

Relative Humidity and 760 mmHg barometric pressure. The results of this study indicate that fillers as well as organic groups can reduce the permeability of silicone materials. It is shown that the ability to guard components from moisture can come from the same source as high RI or conductivity. Figure 1 depicts the WTVRs of the silicone systems featured relative to the most permeable silicone tested, a basic dimethyl (Me2) gel with a normalized moisture permeability rate of 1.

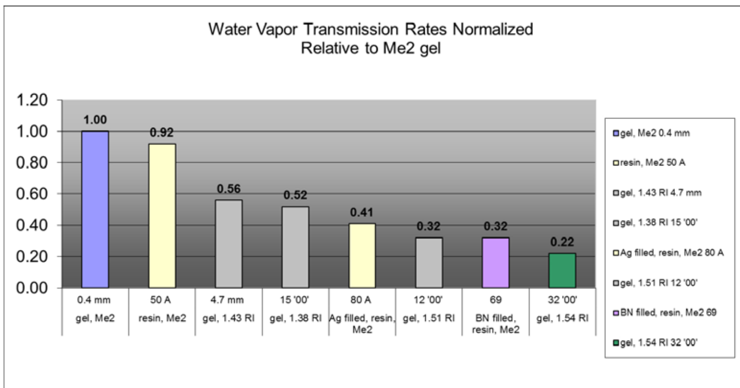

Figure 1. Relative Permeability Rates of Various Silicone Formulations. Durometer and penetration values are listed.

With regard to the filled PDMS silicones, it was observed that the type of filler used has more influence on the WVTR than the filler loading level does. For example, the silver sphere filled product contains nearly two times the amount of filler that the boron nitride filled product contains, yet it has a WVTR almost 10% higher than the BN filler. This difference is attributed to the shape of the fillers. The conclusion is that compared to the spherical shape of the silver particles, the platelet structures of the BN filler particles can better align in one axis (Z axis) due to higher aspect ratio that forms a non-permeable barrier, thereby decreasing the WVTR more significantly than the silver filler.

CONCLUSION

The significant decrease in permeability for high RI and conductive silicones reinforces their viability for component protection. Due to their particularly versatile chemistry, silicone gels especially demonstrate ideal suitability for use in thermal management and similar electronic applications.

In general, thanks to high adaptability, silicone lends itself to optimization for varying levels of conductivity, permeability, and other properties as needed. When maximized, silicone's material performance is unrivaled in the high reliability and yield it brings to electronic systems.

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