

11. Silicones in the Electronics Industries

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Before 1943, planes could maintain high altitudes for only a few minutes before ignition losses due to moisture condensing in the engines. A simple thickened PDMS grease was the solution and an early example of the excellent dielectric properties of silicones. This application also illustrates key properties of silicones in the electronic industries like hydrophobicity and high dielectric breakdown (keeping moisture away and avoiding loss of high voltage/low current signals), as well as their resistance to low or high temperatures, which allow use in harsh and critical environments [1].

Today, despite a higher cost to acquire, the number of applications involving silicones continues to increase, in some instances driven by Moore’s law (chip complexity doubling approximately every two years), but also by tighter specifications. The presence of more and smaller components (e.g., sometimes thousands in today’s cars) requires resistance to higher temperatures to ensure reliability and to avoid increasing the probability of failure.

Again, different silicones are used, and it is a combination of their properties that makes them perform well in various electronic and market applications (see Table 1).

Table 1. Markets for Silicones and their Key Properties in Electronic Applications

Silicone Product group	Electronics Major Markets <i>(V = markets where silicone products are used)</i>					
	Automotive	Consumer	Computer	Telecom- munication	Industrial	Medical
Lithography	V	V	V	V	V	V
Wafer Level Dielectric Layers	V	V	V	V	V	V
Wafer Level Passivation Layers	V	V	V	V	V	V
Die Encapsulants	V	V	V	V	V	V
Non-Conductive Die Adhesives	V	V	V	V	V	V
Conductive Die Adhesives	V	V	V	V	V	V
Lid Seal Adhesives	V	V	V	V	V	V
Electrically Conductive Materials	V	V	V	V		V
Gels	V			V	V	V
Conformal Coatings	V	V		V	V	V
Encapsulants	V			V	V	
Adhesives	V			V		
Sealants	V			V	V	
Foams				V		
Electromagnetic Shielding Materials	V			V		V
Primers	V	V	V	V	V	V
Cleaning Fluids	V	V	V	V	V	V
Thermally Conductive Gels	V				V	
Thermally Conductive Encapsulants	V				V	
Thermally Conductive Adhesives	V					
Thermally Conductive Phase Change Materials	V		V			
Thermally Conductive Fabricated Pads and Films	V	V	V	V	V	V
Thermally Conductive Greases / Compounds			V			

Silicone Product group	Physical Properties												
	(■ = key property for the product in the application in which silicones and organics have similar properties; ▲ = key property for the product in the application in which silicones perform generally better than organics												
	Dielectric Constant	Dielectric Loss	High Electrical Resistance	Ion Purity	Dielectric Strength	Degradation Temperature (5)	Transition Temperature Tg and Tm (1)	Water Absorption	Flexibility	Surface Energy (2)	Optical Transparency and UV Stability	Environmental Friendliness and Inertness	Adhesion
Lithography	■	■	■	■			▲	▲	▲	▲ (4)	▲		
Wafer Level Dielectric Layers	■	■	■	■			▲	▲	▲	▲	▲		
Wafer Level Passivation Layers	■	■	■	■			▲	▲	▲	▲	▲		
Die Encapsulants	■	■	■	■		▲	▲	▲	▲		▲ (3)		
Non-Conductive Die Adhesives	■	■	■	■		▲	▲	▲	▲			■	▲
Conductive Die Adhesives						▲	▲	▲	▲			■	▲
Lid Seal Adhesives	■	■	■	■				▲	▲				▲
Electrically Conductive Materials						▲	▲	▲	▲			■	▲
Gels	■	■	■	■		▲	▲	▲	▲	▲	▲		
Conformal Coatings	■	■	■			■	▲	▲		▲	▲ (3)	▲	▲
Encapsulants	■	■	■	■	■	▲	▲	▲	▲	▲	▲ (3)		▲
Adhesives						▲	▲	▲	▲				▲
Sealants						▲							▲
Foams	■	■				▲	▲		▲			▲	
Electromagnetic Shielding Materials						▲		▲					
Primers						▲				▲			▲
Cleaning Fluids				■				▲		▲		▲	
Thermally Conductive Gels			■			▲	▲	▲	▲	▲			
Thermally Conductive Encapsulants			■	■	■	▲	▲	▲	▲	▲			▲
Thermally Conductive Adhesives			■	■	■	▲	▲	▲	▲	▲			▲
Thermally Conductive Phase Change Materials			■	■	■			▲		▲			
Thermally Conductive Fabricated Pads and Films			■			▲	▲	▲	▲			■	
Thermally Conductive Greases / Compounds			■	■	■	▲	▲	▲	▲	▲			

- (1) Low Tg and Tm impacts the influence of temperature on key properties like dielectric properties
 (2) Surface energy impacts the wetting behaviour of the material
 (3) Relevant in optoelectronic applications
 (4) Tunable wetting properties
 (5) Degradation temperature impacts service temperature

The Relationship of Structural Properties in Electronic Applications

The Si-O-Si bond angle in a silicone polymer can vary between 105° and 180° [2], and the rotation is essentially free [3] around these bonds. As a result, the chains are very flexible and occupy a rather large volume, resulting in a high free volume in the material. Consequently, silicones exhibit a very low glass transition temperature ($T_g \approx -125^\circ\text{C}$). Low intermolecular interactions account for the low melting temperature ($T_m \approx -50^\circ\text{C}$) of silicone materials.

Once cross-linked, silicones are soft elastomers with hardness in the Shore A range if reinforced, or much softer in the absence of reinforcing filler and even gel-like if only partially cross-linked. In many applications, this “softness” allows relief of stress induced by temperature changes as thermal dilatation mismatches. Silicone gels are compliant, self healing and outstanding for protecting thin wire-bonding from thermal shocks, vibration and

corrosion. The response of their elastic and storage modulus is linear over a wide range of temperature and frequency.

Dynamic mechanical analysis has been carried out at various temperatures on a standard PDMS gel. The reduced shear storage and loss modulus and $\tan \delta$ are displayed against the reduced frequency for temperature ranging from -40°C to 100°C on Figure 1a and Figure 1b. The Arrhenius plot of the horizontal shift factor a_T can be seen on Figure 1c [4], showing a perfect fit with the Williams-Landel-Ferry (WLF) equation [5]. In that respect, silicone gels are exhibiting model behavior and could be used to study further fundamentals of cross-linked polymer mechanics. Other silicone materials also follow the WLF model as can be seen on the Arrhenius plot in Figure 1d, which compares the behavior of a silicone gel, a silicone elastomer and a silicone resin [4].

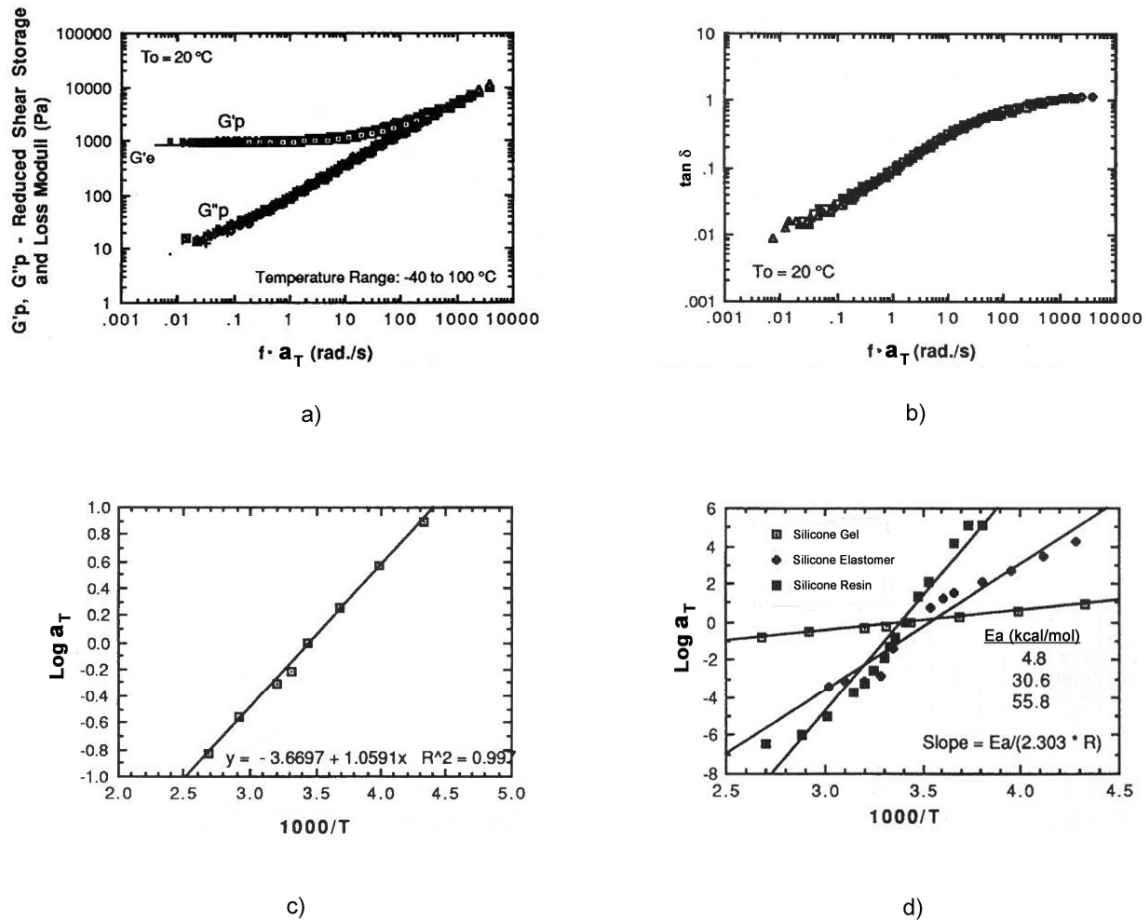


Figure 1. Dynamic mechanical analysis (DMA) shows: a) reduced shear storage and loss modulus of a standard silicone gel as a function of the reduced frequency at -40°C to 100°C ; b) $\tan \delta$ of the gel as a function of the reduced frequency temperature range from -40°C to 100°C ; c) Arrhenius plot of the horizontal shift factor for the gel; d) Arrhenius plot of the horizontal shift for a silicone gel, a silicone elastomer and a silicone resin.

The service temperatures of silicones can be extended by replacing some methyl groups by phenyl groups on the siloxane backbone. The random inclusion of different groups along the chain hinders natural ordering and crystallization. As a result, the T_m is either lowered or eliminated. The presence of phenyl groups also improves high temperature stability.

Electrical Properties of Silicones

Despite strongly polarized Si-O bonds, silicone polymers are nonpolar, as the Me side groups prevent Si-O dipoles from approaching each other too closely. As a result, the intermolecular forces are weak and mainly composed of London-van der Waals interactions that decrease with the square of the distance between molecules. Due to this ambivalent character of the PDMS polymer chain, the polarizability of the molecule accounts for a relatively high dielectric constant of silicones in comparison to a nonpolar polymer like polyethylene (see Table 2). As expected, silicone copolymers in which Me groups have been substituted with more polarizable groups are not better either.

Table 2. Dielectric Properties of Various Polymers [6]

Polymer	Dielectric constant at 100 Hz	Dissipation factor at 100 Hz	Dielectric strength at 60 Hz	Volume resistivity <i>ohm.cm</i>	Tg K
High density polyethylene	2.30	0.00011	811	$2.2 \cdot 10^{16}$	148
Cis-polyisoprene	2.26	0.0094	577	$7.1 \cdot 10^{16}$	210
Poly methylmethacrylate	3.03	0.057	608	$1.2 \cdot 10^{16}$	382
Poly dimethyl siloxane (Me ₂ SiO) _n	2.86	0.00025	552	$5.3 \cdot 10^{14}$	150
Poly diphenyl dimethyl siloxane (φ ₂ SiO) _{5.5} (Me ₂ SiO) _{94.6}	2.90	0.00041	661	$9.8 \cdot 10^{14}$	151
Poly phenylmethyl dimethyl siloxane (φMeSiO) _{7.5} (Me ₂ SiO) _{92.5}	2.87	0.00010	661	$3.0 \cdot 10^{14}$	149
Poly phenyl methyl dimethyl siloxane (φMeSiO) ₃₀ (Me ₂ SiO) ₇₀	2.99	0.00024	720	$4.4 \cdot 10^{14}$	176
Poly trifluoropropyl methyl siloxane [(CF ₃ CH ₂ CH ₂)MeSiO] _n	6.85	0.109	342	$2.7 \cdot 10^{11}$	199
Viton [®] fluoroelastomer	8.55	0.0403	351	$4.1 \cdot 10^{11}$	255

The dielectric constant of PDMS increases with the degree of polymerization (DP) of the siloxane backbone before quickly reaching a plateau value (see Figure 2) [7]. This effect is related to the siloxane-to-methyl-groups ratio, which quickly increases, particularly in the shortest DP polymer. At higher DP, adding one more unit has little impact on the permittivity of the media, which explains the plateau region.

In most organic polymers, the strong attractions between polymer chains diminish as the temperature increases, so many dependent properties change significantly. For silicones, the intermolecular forces are low and do not change much with temperature. Consequently, viscosity, mechanical properties, dielectric properties and many physical properties are little affected over a wide range of temperatures. Electrical properties like dielectric constant and the dissipation factor are also little affected over a wide range of frequencies [8-9-10].

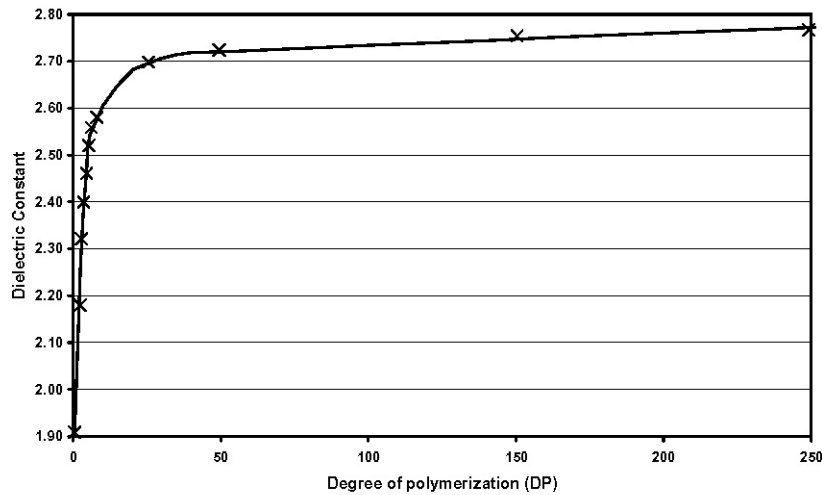


Figure 2. Influence of degree of polymerization on the dielectric constant of polydimethylsiloxanes, measured at 1000 Hz at 23 °C.

The volume resistivity of silicones is marginally lower than organic materials; ion concentration tends to be low in PDMS and dependent only on the presence of impurities like residual traces of polymerization catalysts or other impurities due to presence of reinforcing fillers. However, ion mobility is favored because of the high free volume in PDMS [6].

Although not entirely related to volume resistivity, dielectric strength is also influenced by the presence of material impurities [6-7-8-9-10-11]. For a given matrix, the path for dielectric breakdown follows the weakest path as far as resistivity is concerned. Here again, the high free volume of silicone-based materials lowers their dielectric strength in comparison to organic materials.

The dielectric properties of silicones are good, but not exceptional in comparison with organics. The success of silicone-based products is certainly related more to their stability over a wide range of temperature, humidity and frequency.

Water Absorption

Although often overlooked, water absorption is a key property for products used in electronics, as absorbed water reduces dielectric properties and can contribute to corrosion. Yet, in many electronics applications where silicones are used, it is too simplistic to think that because of their hydrophobicity and water repellency, silicones provide better device protection against corrosion than organics.

Corrosion occurs if reactants like oxygen, water and ions are simultaneously present at the interface. Silicone materials are very permeable to gases and therefore cannot limit oxygen or water vapor from reaching a metal interface. However, ions surrounded by several layers of water molecules are poorly soluble in PDMS and, being large clusters, they have a very low coefficient of diffusion in any polymer matrix. Absorbed water molecules in the protective layer are like stones across the river for ions: they use these favorable “water” paths to migrate across the layer at a much greater rate of diffusion [12]. Because of their high

permeability, silicones will uptake water quickly compared to epoxies. Yet at saturation level, water content in silicones is ten times lower than in epoxies (see Figure 3) [13]. This is the main reason why silicones are so effective when used as corrosion protective materials. An additional benefit in electronics is that when temperature increases suddenly, water diffuses easily from silicones compared to organics and without local pressure build-up (“popcorning” issue).

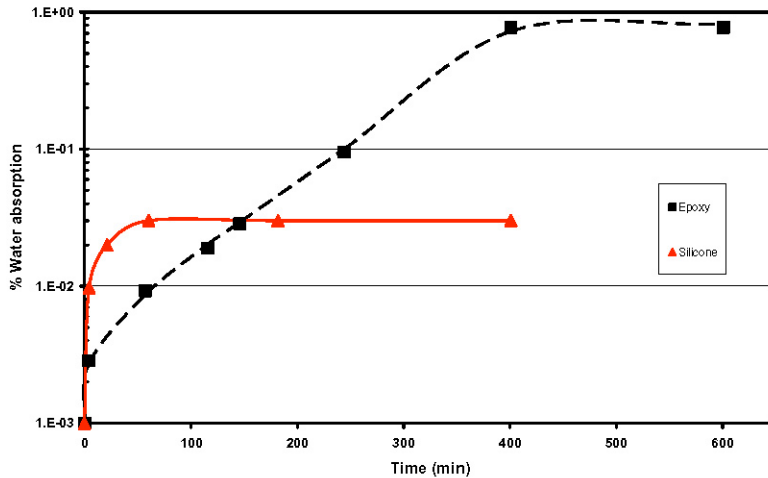


Figure 3. Water absorption of PDMS vs. epoxy in electronic products.

Thermal Conductivity

With trends toward miniaturization and higher power electronics, heat dissipation and protection at component interfaces is becoming more critical. Silicone thermal conductivity is rather low if compared to metals (see Table 3). However, it is about ten times better than air, which is most often responsible for poor heat conduction at metal-metal or metal-plastic interfaces.

Table 3. Thermal Conductivities of Various Materials

Material	Thermal conductivity (W/m.K)
Silver	417.3
Copper	393.7
Silicone, thermally conductive (PDMS + silver filler)	0.7 - 8.0
Silicone (PDMS)	0.2
Epoxy	0.2
Air	0.03

Because of low surface tension [14], PDMS has an enormous advantage that is not demonstrated by its intrinsic heat conductivity if compared to organics. PDMS allows good surface wetting, and so displaces air at interfaces, reducing heat resistance between components. This in particular has driven the penetration of silicones in electronics thermal management applications.

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