

Silicone Rubber in Extreme Environments

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Neil Armstrong's "One small step..." is remarkable as silicone's most famous step as well. Did you know that Neil's boot had a silicone rubber sole for thermal protection?



Photo 1. Neil Armstrong's "First step":
Photo: NASA, July 20, 1969

That "out of this world" example of silicone's reliable performance under challenging conditions illustrates its temperature range as an elastomer. Silicones thrive on challenges, including exposure to extreme heat, extreme cold, harsh chemicals, sterilization, rain, snow, salt spray, ultraviolet radiation, ozone, and acid rain, to name a few. Silicones have unique properties that enable them to thrive in harsh environments:

- Silicones resist oxidative deterioration (normal aging) for decades on end.
- They are stable over a wide range of temperatures, from -100 to 300°C (about -150 to 575°F) and resistant to thermal shock and remain flexible and compliant.
- Silicones resist moisture, pressure, salt spray, mechanical fluids, and UV light.
- They have stable electrical resistance properties, even with high frequency alternating current.
- Silicones have inherent flame resistance and produce low toxicity smoke.
- And finally, silicones are broken down by microbial decomposition in land-fill for low bio-residuals.

For "down to earth" examples, silicones have true advantages in many applications. For example, for **gaskets and seals**, the materials of choice for performance must:

- Perform reliably in extreme conditions of temperature, pressure, or chemical exposure.
- Maintain flexibility, resiliency, and the ability to transmit mechanical sealing force at both high and low temperatures.
- Be low cost and have easy processing for efficient and lean manufacturing.

Silicone Rubber, the elastomer that does these things so well is not some "hard to come by" exotic polymer. It is easily obtainable and is the fastest growing segment of elastomers. Dow Corning Corporation has led the effort in development of silicone materials for over 60 years and makes these products widely available across the globe.

SILICONE ELASOTMER CHEMISTRY AND PROPERTIES

Silicone Rubber is a semi-inorganic system (known as polysiloxane) constructed of repeating units of oxygen and silicon. While oxygen and silicon are the first and second most abundant elements on earth, conversion to polysiloxane is energy intensive and does not occur naturally. Polysiloxane was first synthesized in the 1940's. The semi-inorganic nature of this polymer provides useful properties that differ widely from organic analogs. Table 1 shows comparisons of the various chemical structural properties between carbon and silicon based linkages.

Rotational energy	Si—O	polydimethylsiloxane	~ 0 kJ/mol
	C—C	polystyrene	13,8 kJ/mol
	C—C	polytetrafluoroethylene	19,7 kJ/mol
Bond energy	Si—O	444 kJ/mol	
	Si—C	314 kJ/mol	
	C—C	356 kJ/mol	
Interatomic distance	Si—O	hexamethyldisiloxane	0,163 nm
	C—O	dimethyl ether	0,142 nm
	C—C	propane	0,154 nm
Bond angle	Si—O—Si	hexamethyldisiloxane	130°
	Si—O—Si	organosiloxane	105° to 180°
	C—C—C	propane	112°
	C—O—C	dimethyl ether	111°

Table 1. Chemical Property of Silicon and Carbon Bonds Table from "Silicon and Silicones"

Siloxane chemistry provides a highly flexible backbone with large bond angles, extended bond lengths, and free rotation. These characteristics impart a helix polymeric structure. The structure is further enhanced by attaching organic units to pendant sites along the chain. Polydimethyl-siloxane (Schematically shown in figure 1) is one such outcome. Electrochemical behavior is apolar having a polar Silicon-Oxygen (-Si-O-) backbone yet covered with non-polar pendant methyl (CH₃-) groups. The polymer then exhibits unique family behavior giving rise to low intermolecular interaction and surface energy. Polydimethyl-siloxane then can be made to very high molecular weight yet it will not become plastic due to the apolar arrangement. High permeation and extreme hydrophobicity are examples of this unique behavior.

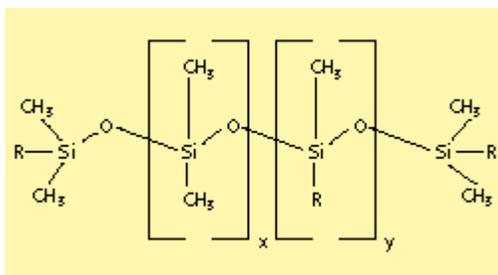


Figure 1. Chemical structure of typical silicone elastomers

Silicone elastomers are of the general structure depicted in Figure 1, where R represents -OH, -CH₃, or an aryl group. The degree of polymerization (DP) is the sum of subscripts x and y. In silicone rubber elastomers, the DP is typically in the range of 500 to 10,000, thus, the molecular weight ranges from 25,000 to 500,000. R/ represents the pendant functionality of the polymer where cross-linking takes place, which is usually a vinyl group and most commonly ethenyl (vinyl) (CH₂=CH-). The ratio of y/x gives the relative reactivity index (functionality) of the polymer expressed in mole percent.

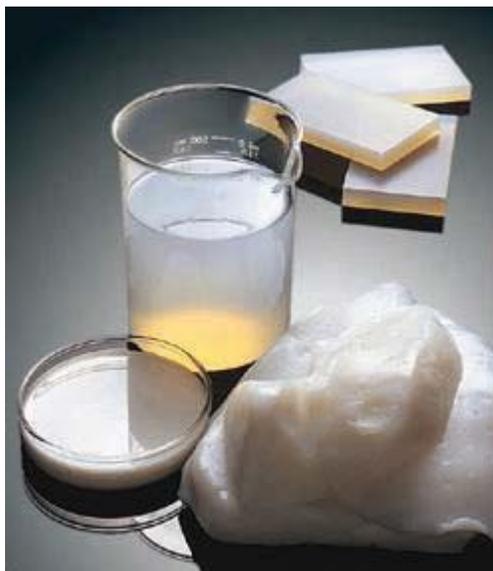


Photo 2. Silicone rubbers and polymer additives: Photo: Dow Corning Corp.

Polymer variations exist that extend the useful range of this polymer. Tetrafluoropropyl and Phenyl chemistry replaces methyl groups along the chain. Phenylsilicone, so named from phenyl addition, imparts extreme low temperature performance by disruption of polymer crystallization by steric hindrance. Fluorosilicone, so named from tetrafluoropropyl addition, improves resistance to fuels and organic oils by creating a more polar arrangement.

The polymer is cured in a number of ways but two methods are applicable in heat resistant elastomers. As hinted at previously, vinyl functionality provides cross-link sites for peroxide free radical addition or catalyzed addition reaction. Addition cure (Hydrosilation) is accomplished with catalytic platinum acids, hydridesiloxane cross-linking and inhibited with polar organic alcohols. Cross-link density in either case is controlled by the vinyl-methyl to dimethyl mole fraction (y/x) and location of vinyl-methyl functionality.

Reinforcing Fillers add strength to the polymer. Silicas are used primarily; amorphous or precipitated in the range of particle sizes of 5 to 20 nm in diameter are most common. The reinforcement that occurs is the result of interaction between the polymer and the filler. These interactions are controlled by pacification of the silica through the addition of silanol-end blocked polydimethyl siloxane oligomers (Silicone Plasticizers) or via a capping reaction using reactive silanes or silazanes.

Conclusion:

Silicone elastomers provide real advantages in Sealing Applications considering that they:

- Have a wider operating temperature range than organic elastomers.
- Can be tailored via custom compounding to meet extreme or extended heat resistance requirements.
- Withstand many flexing cycles over a wide temperature range.

- Retain their natural flexibility and continue to perform at low temperatures that would cause organic elastomers to become brittle.
- Resist compression set at both high and low temperatures.
- Maintain their properties longer than organic elastomers at higher temperatures.
- Additionally, fluorosilicone elastomers resist aggressive oils, fuels, and other fluids that would quickly degrade most organic elastomers.