NuSil SILICONE TECHNOLOGY

Creative Partners in a Material World

Optical Silicones for use in Harsh Operating Environments

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LIGHTSPAN

Optical Polymers, Gels, and Thermosets for Index Matching Applications

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Abstract

The optics industry widely uses silicones for various fiber optic cable potting applications and light emitting diode protection. Optics manufacturers know traditional silicone elastomers, gels, thixotropic gels, and fluids not only perform extremely well in high temperature applications, but also offer refractive index matching so that silicones can transmit light with admirable efficiency. However, because environmental conditions may affect a material's performance over time, one must also consider the conditions the device operates in to ensure long-term reliability. External environments may include exposure to a combination of UV light and temperature, while other environments may expose devices to hydrocarbon based fuels. This paper will delve into the chemistry of silicones and functional groups that lend themselves to properties such as temperature, fuel, and radiation resistance to show why silicone is the material of choice for optic applications under normally harmful forms of exposure. Data will be presented to examine silicone's performance in these environments.

Discussion

Industry Background

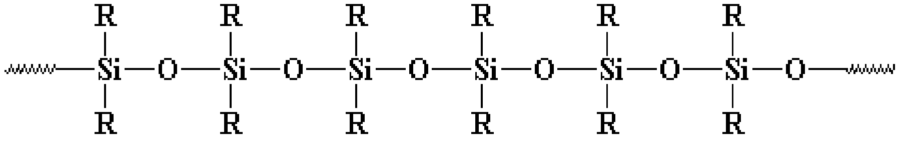
The production of electronics and sensors used in harsh environments is expected to be an $887 million dollar market by 2008. Today's electronics and sensors encounter a variety of harsh environments, including: extremes in temperature or pressure, chemical aggressiveness, acceleration/deceleration, radiation, cyclic operation and shock. Devices employed in such environments must endure these harsh conditions, enabling them to perform their functions over time. A brief list of current optical sensing technology and developing applications is listed below:

- Vision sensors for industrial applications that include the identification and measurement of production outputs, verify accurate assembly, and guide production equipment.
- Weather satellites employ the use of optical sensors technologies that continuously expose their position-sensors to sunlight or radiation. These sensors operate under extremely high temperatures in order to sense the satellite is in its proper position.
- The Department of Energy's National Energy Technology Laboratory is developing novel sensors able to withstand high temperatures and harsh environments. These microsensors will be used in fuel cell, turbines, gasification, and combustion systems.
- NASA's Marshall Space Flight Center utilizes the Advanced Video Guidance Sensor in conjunction with a computer program for the autonomous rendezvous of a spacecraft with a target satellite.

- NASA is investigating hybrid Peizoelectric/fiber optic sensors for aerospace, aeronautical and automotive applications.

Polymer Chemistry

The term “Silicone” is actually a misnomer. Normally the suffix ‘-one’ delineates a substance has a double bonded atom of oxygen in its backbone. Scientists initially believed that silicone materials contained double bonded oxygen, hence the use of ‘silicone.’ However, silicones are really inorganic polymers, having no carbon atoms in the backbone, and therefore should be named ‘Polysiloxanes.’ The diagram below shows their typical structure:



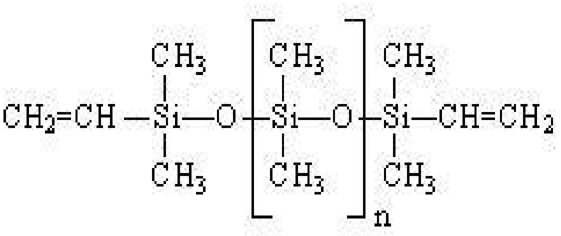
$$\sim-\underset{R}{\overset{R}{\mathrm{Si}}}-\mathrm{O}-\underset{R}{\overset{R}{\mathrm{Si}}}-\mathrm{O}-\underset{R}{\overset{R}{\mathrm{Si}}}-\mathrm{O}-\underset{R}{\overset{R}{\mathrm{Si}}}-\mathrm{O}-\underset{R}{\overset{R}{\mathrm{Si}}}-\mathrm{O}-\underset{R}{\overset{R}{\mathrm{Si}}}-\mathrm{O}-\sim$$

[1]

R=CH_3, phenyl (aromatic carbon ring), $F_3CCH_2CH_2$, $CHCH_2$

This polymeric structure allows polysiloxanes to be used in a wide array of applications because it allows different types of polysiloxanes groups to be incorporated. 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. Different types of silicones, or polysiloxanes, and their property advantages include:

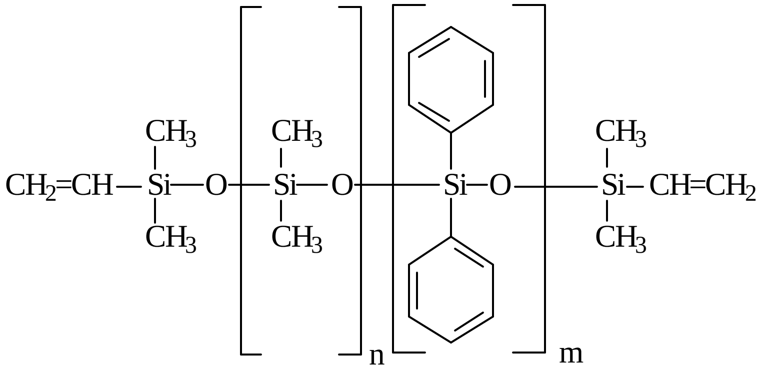
Dimethyl silicones, or dimethylpolysiloxanes, are the most common silicone polymers used industrially. These types of polymers are typically the most cost effective to produce and generally yield good physical properties in silicone elastomers and gels. The polymer pictured below contains vinyl endgroups that participate in a platinum catalyzed addition reaction (see section on *Cure Chemistry* for more information).



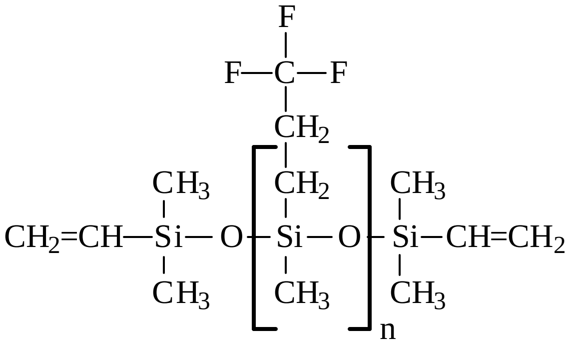
$$CH_2{=}CH-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-\mathrm{O}-\left[\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-\mathrm{O}\right]_n-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}-CH{=}CH_2$$

For optics purposes, all dimethylpolysiloxanes have a refractive index of 1.40, 25°C at 598nm.

Methyl phenyl silicone systems contain diphenyldimethylpolysiloxane co-polymers. The phenyl functionality boosts the refractive index of the polymers from 1.40 upwards to 1.60. There are limitations, the steric hinderance of the large phenyl groups prohibit significantly high concentrations of diphenyl units on the polymer chain. Silicone polymers with diphenyl functionality with refractive index of 1.43 to 1.46 are useful in bio-optic applications (e.g., intraocular lenses) in creating a thin lens. The diagram below shows a typical structure for a methyl phenyl silicone:



Fluorosilicones are based on trifluoropropyl methyl polysiloxane polymers and historically are used for applications that require fuel or hydrocarbon resistance. The trifluoropropyl group contributes a slight polarity to the polymer, resulting in swell resistance to gasoline and jet fuels. For optic applications, the refractive index is 1.38 at 25°C at 598nm. While some fluorosilicones contain 100% trifluoropropylmethylpolysiloxane repeating units, other systems contain a combination of the fluorosiloxane units and dimethyl units to form a co-polymer. Adjusting the amount of trifluoropropyl methyl siloxane units in the polymerization phase provides optimal performance in specific applications. The diagram below shows a typical structure for a fluorosilicone copolymer:



$$CH_2{=}CH{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\left[\underset{CH_3}{\overset{CF_3CH_2CH_2}{Si}}{-}O\right]_n{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}CH{=}CH_2$$

Material Composition

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 optic applications. Some silicone material compositions and their typical applications include:

Silicone Fluids are non-reactive and reactive silicone polymers formulated with dimethyl, methylphenyl, diphenyl, or trifluoropropylmethyl constituent groups, with refractive index ranging from 1.38 to 1.60. 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 20,000cP (like honey). Fluids are typically used to fill air gaps in high temperature lens assemblies in order to displace dust, permit cooling action or reduce interfacial reflections. Fluids can also be used to fill lenses or microchannel waveguides because of the small thermo-optic coefficient of -2 to 5 x 10^{-4}/ºC. Optical fluids can be used as the working medium in bubble-action optical switches or attenuators.

Silicone Thixotropic Gels are comprised of an optical fluid immobilized in a nanoparticle powder. These gels have no curing characteristics and by nature they are thixotropic and do not have well-defined viscosities. At rest they are mechanically stable and will not migrate. Due to the index matching limitations of the nanoparticle powder, these materials are available at 1.46 to 1.59 refractive indices only. Their primary use is for improving the return loss in a single mode mechanical fiber splice.

Silicone Curing Gels 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 – 10,000cP. Depending on the functionality of the polymer, optical index matching can be formulated from 1.38-1.57. For HBLED applications this allows for the optimal light to come out of the die while protecting it from dust, moisture, vibration and changes in temperature. The yield strength of the gel is low enough to permit wire bonds to slice through during thermally induced micromotion without risking wire bond failure. Steps need to be taken to manufacture these materials with minimal outgassing and low ionic species. Other applications besides encapsulating HBLEDs include potting of packaged modules such as transponders, transceivers and detector arrays.

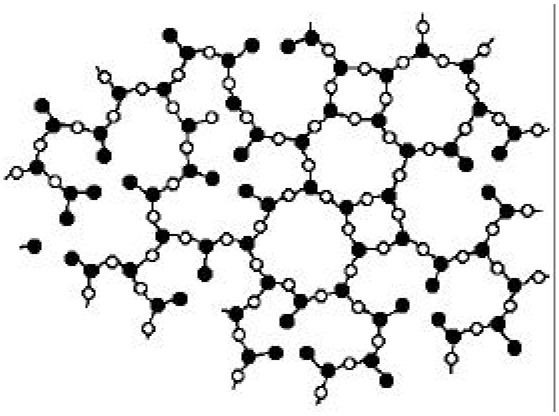
Silicone Thermosets fall into two categories, moldable elastomers and adhesives. Like the Gels, these two-part systems contain reactive polymers and crosslinkers that cure up to a rubbery type hardness. Most will cure at room temperature, however some need heat to cure. To impart increased physical properties, sometimes these materials have higher viscosities. The moldable materials can be casted or injection molded into optical lenses. They have inherently stronger physical properties than the gels and can work as excellent adhesives in optical applications. Special versions of these can be produced to have extremely low outgassing for electronic and aerospace applications. These also can have the broad refractive index range of 1.38 – 1.57.

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

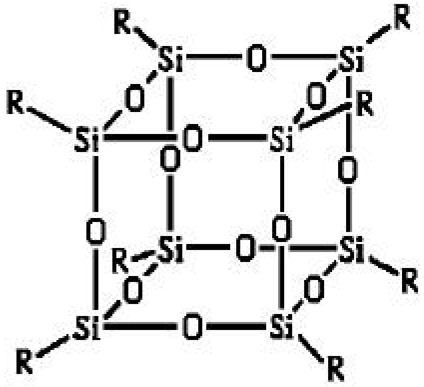
$$R - Si - O_{1.5}$$

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.
Sample Resin Structures:

Amorphous



T_x Cube

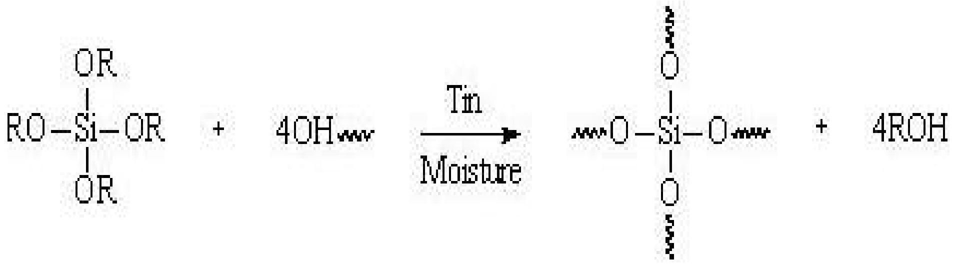


These materials when cured can give very hard durometers, Shore D. The phenyl content can be adjusted providing refractive index from 1.40-1.57.

Cure Chemistry

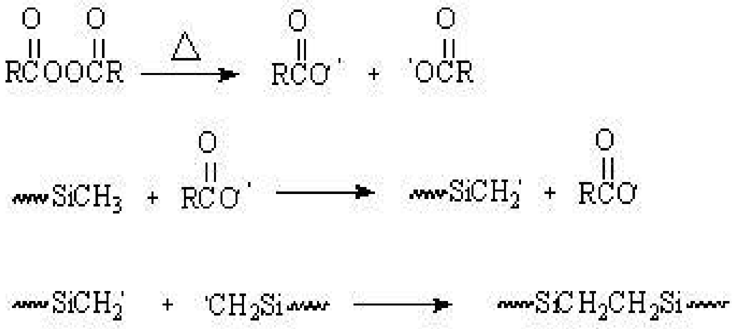
When a manufacturer in the optics industry chooses a material for a specific application, material properties aren’t the only deciding factor. That manufacturer also has to examine how the material is used. Inconvenience in production or material by-products can make a chosen material ineffective for a specific application. Silicones, however, can be designed around various cure chemistries to accommodate different production needs. Silicone systems can cure by platinum catalyzed addition cured systems, tin condensation cure systems, peroxide cure systems, or oxime cure systems. Some of the oldest cure chemistry used with silicones utilizes an acetoxy tin condensation cure system, such as used in household bathroom caulk. These systems yield a vinegar-like smell (acetic acid), a byproduct of the reaction. For various reasons as described below, platinum systems are the most appropriate for optics applications.

Tin condensation systems involve hydroxyl functional polymers and alkoxy-functional crosslinking compounds. The alkoxy functional crosslinker first undergoes a hydrolysis step and is left with a hydroxyl group. This hydroxyl group then participates in a condensation reaction with another hydroxyl group attached to the polymer. The reaction can proceed without the assistance of the tin catalyst, but the presence of the catalyst boosts the rate of reaction. The reaction mechanism is pictured below:



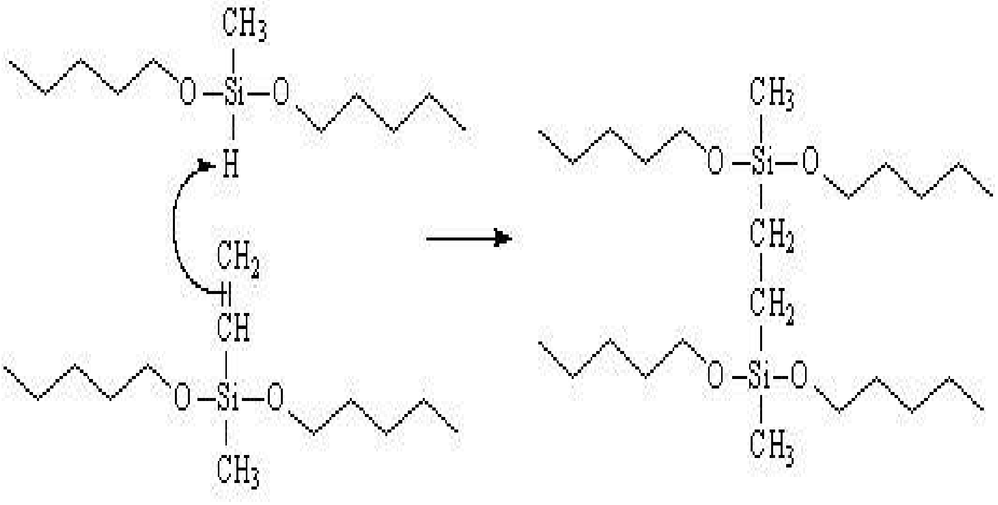
The main disadvantages of condensation systems are the leaving group, shrinkage and long cure time, as several days are often required for to completely cure an elastomer.

Peroxide catalyzed systems, have a reaction mechanism that involves a peroxide catalyst and either methyl groups or vinyl functional groups. The peroxide catalysts create free radical species of the methyl and vinyl that can then form covalent bonds. Pictured below is the reaction mechanism involving a peroxide catalysis of two methyl groups:



Disadvantages include a lengthy post-curing step at high temperatures in order to remove the reaction's byproducts. Other disadvantages include the possibility of the catalyst interacting with active agents.

Platinum catalyzed silicones utilize a platinum complex to participate in a reaction between a hydride functional siloxane polymer and a vinyl functional siloxane polymer. The result is an ethyl bridge between the two polymers. The reaction mechanism is pictured below:



Platinum systems are often cured quickly with heat, but can be formulated to cure at low temperatures or room temperature if necessary. The advantages of these systems include a faster cure and no volatile byproducts. The possibility of inhibiting the cure is the main disadvantage of platinum systems. Inhibition is defined as either temporarily or permanently preventing the system from curing. Some types of inhibitors are purposefully added to these systems to control the rate of cure. However, contact with tin, sulfur, and some amine containing compounds may permanently inhibit the cure. Compounds that inhibit the cure can be identified easily by attempting to cure a platinum catalyzed system in contact with the compound, as inhibition results in uncatalyzed regions of elastomer systems or inconsistency in cure over time.

Typical Testing For Optical Materials

Index Matching

Optical sensing devices operate most efficiently when photons can pass freely through the optics of the device. For this reason, components used in the assembly of the optics should have similar refractive indexes. The refractive index of silicone that can be effective in harsh operating environments can range from 1.38 to 1.60. We describe some of the testing methods to characterize silicones for optical applications.

Refractive Index, the measurement of the speed of light traveling through a transparent material. It is measured at 589 nanometer (nm) wavelength (a.k.a. “the Sodium D line”, or “nD”) with a refractometer using the method of the American Society for Testing and Materials’ ASTM D-1218 at a fixed temperature of 25.0ºC. As previously mentioned, silicones have a refractive index range of 1.38-1.60.

Refractive Index of Common Substances

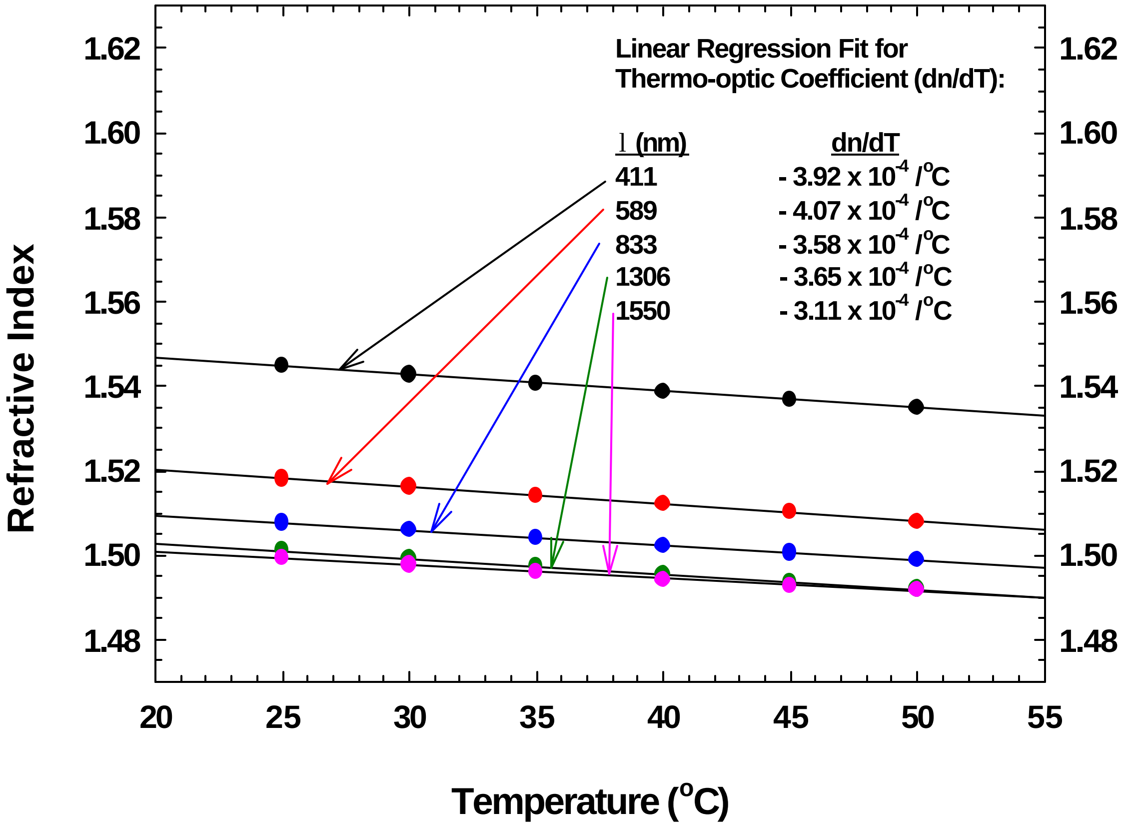
Substrate	Acronym	Tradenames	nD
Water			1.34
Polytetrafluoroethylene	PTFE	Teflon®	1.34
Magnesium Fluoride	MgF2		1.38
Fused quartz			1.46
Acrylate	PMMA	PLexiglass®	1.49
Cyclic Olefin	COC	Topas®	1.53
Polycarbonate	PC	Lexan®	1.59
Aluminum Oxide	Sapphire,ruby		1.76

Refractive index versus change in temperature, is conducted at 25ºC to 50ºC in 5-degree steps. Data is reported as shown in the graph below, and the least squares linear regression fit to the data for the thermo-optic coefficient (in units of dn/dT) is also calculated and provided on the chart.

Refractive Index vs. Temperature, 5 l's

Lightspan Encapsulation Gel

LS-3252, Lot# 20423-0417

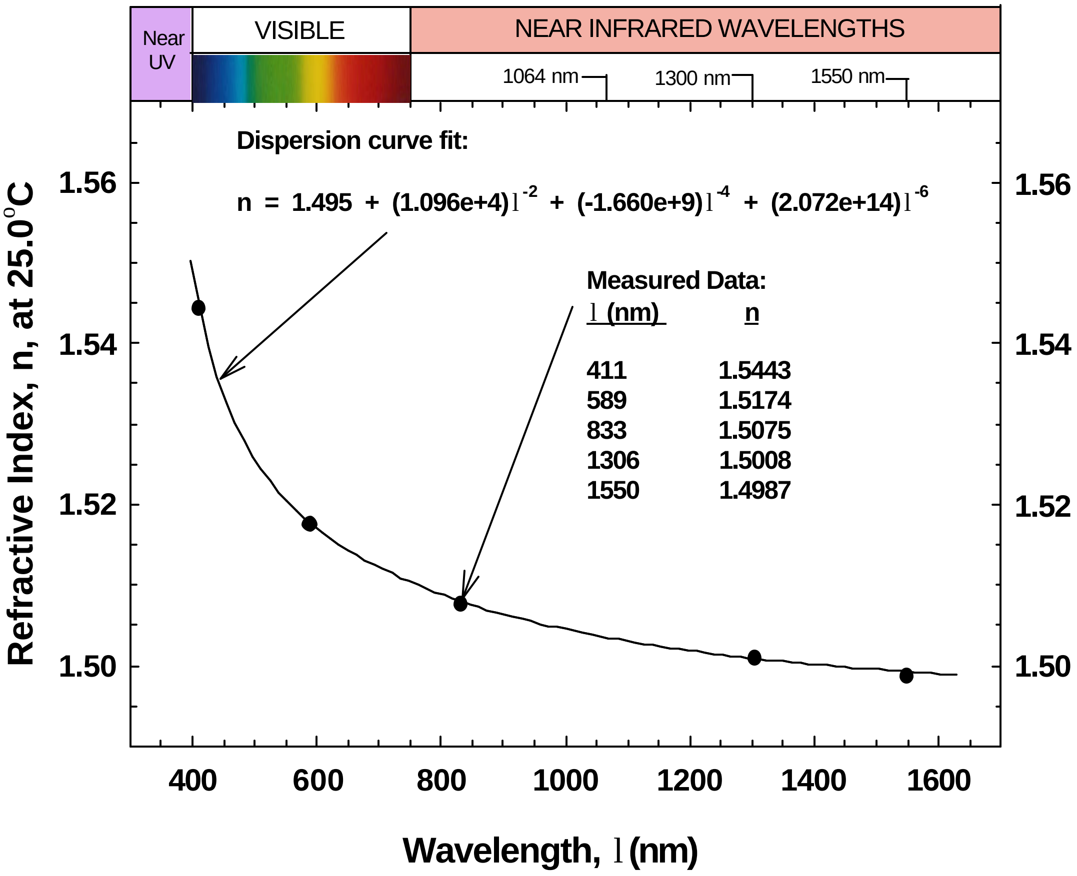


Refractive Index versus change in Wavelength, data are measured at 411nm, 589nm, 833nm, 1306nm and 1550nm at 25.0ºC and presented as shown in the graph below. Coefficients are also printed on the plot for a Sellmeier dispersion curve fit.

Refractive Index vs. Wavelength (25^{o}C)

Lightspan Encapsulation Gel

LS-3252, Lot# 11031-0313



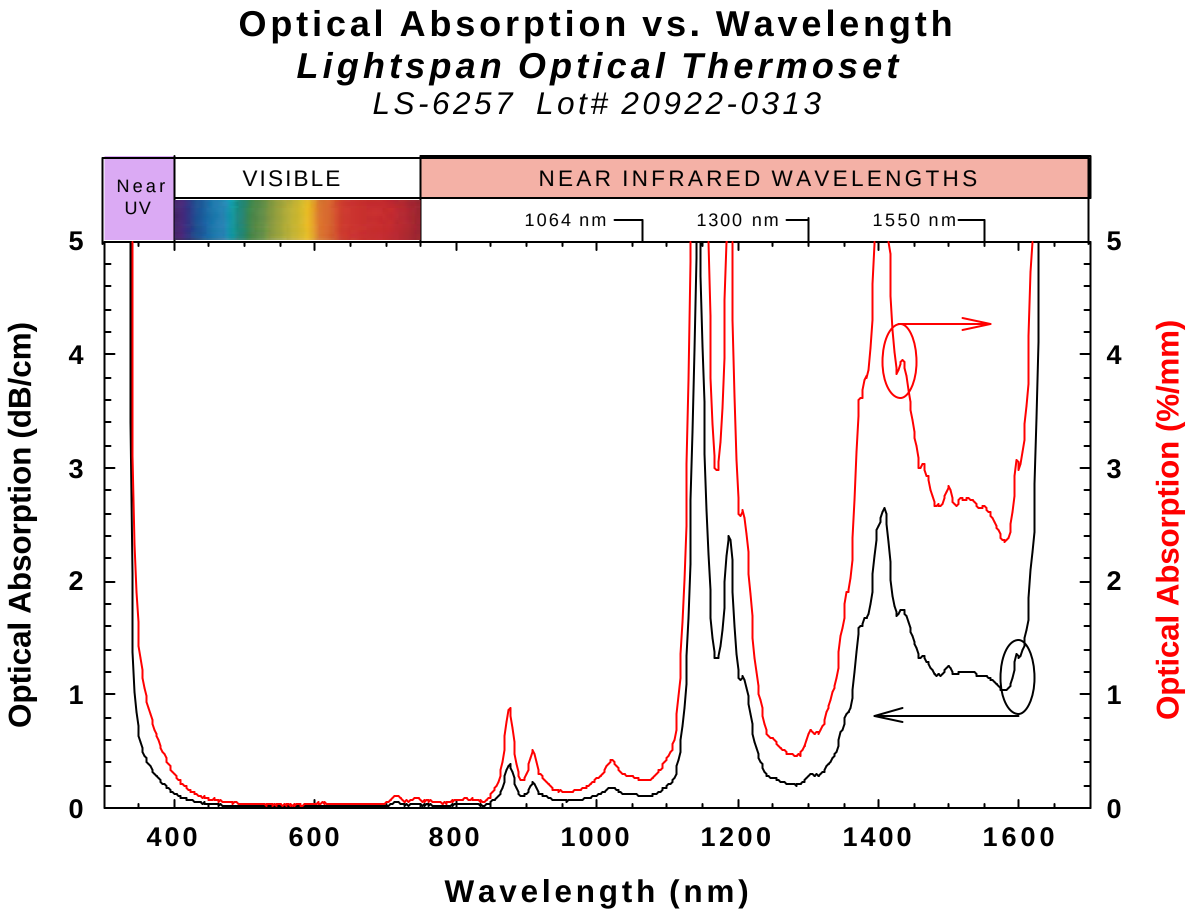
Dispersion curve fit:

$$n = 1.495 + (1.096e{+}4)\lambda^{-2} + (-1.660e{+}9)\lambda^{-4} + (2.072e{+}14)\lambda^{-6}$$

Measured Data:

λ (nm)	n
411	1.5443
589	1.5174
833	1.5075
1306	1.5008
1550	1.4987

Optical Absorption versus change in Wavelength, is measured across the wavelength range of 300nm to 1700nm, with 2nm resolution, using a spectrophotometer with the sample temperature at 25ºC. The graph is presented below:



Results

The general properties of silicones, by product type, are described briefly above. For our purposes, we will present and discuss data that relates specific properties of silicones that are useful in harsh operating environments. While the stability of the siloxane bond bodes well for silicone material performance in a diverse range of operating conditions, we have chosen to focus on three types of environments that can adversely affect materials in a sensor assembly; extreme temperatures, exposure to fuels, and radiation exposure.

Extreme Temperatures

Extreme temperatures can cause outgassing of volatile components with temperatures ranging from -115ºC to 260ºC. In closed electronic and opto-electronic systems, volatile components can contaminate sensitive components. Smaller electronic packages with higher voltage requirements can produce excessive heat, and any components containing volatile chemical species can outgas under these conditions. Electronic systems can contain a variety of components at various operating temperatures. Cooler components behave like a cold soda can on a warm humid day, as they can become a conduit onto which these volatile components re-condense.

Traditionally, applications on satellites and shuttles employ low outgassing materials, as these applications encounter extraterrestrial environments that cause outgassing. These environments typically undergo extreme temperature cycling in a vacuum. The ASTM test method E595 provides a standard for testing all silicone materials for extraterrestrial use. Total Mass Loss (TML) and Collected Volatile Condensable Material (CVCM) testing can be useful in screening low outgassing materials from other materials. NASA has set current limits of Total Mass Loss not to exceed 1.0% and Collected Volatile Condensable Materials not to exceed 0.1%. The materials listed below demonstrate the physical similarities between low outgassing silicone materials and other silicone materials:

Clear Encapsulants:	CV-2500	R-2615
Refractive Index @ 25ºC	1.41	1.41
Durometer, Type A	45	45
Tensile Strength	900psi	1100psi
Elongation	150%	100%
Volume Resistivity	$1x10^{15}$	$1x10^{15}$
Collected Volatile Condensable Material	0.01%	0.80%
Total Mass Loss	0.05%	0.25%

High Temperature Clear Encapsulants:	CV16-2500	R-2655
Refractive Index @ 25ºC	1.43	1.43
Durometer, Type A	40	40
Tensile Strength	500psi	800psi
Elongation	100%	125%
Collected Volatile Condensable Material	0.01%	0.87%
Total Mass Loss	0.05%	2.03%

Another factor to consider is the coefficient of thermal expansion or CTE in electronic packages. Silicone materials typically have large CTE values compared to filled and unfilled epoxies. This large CTE, combined with and related to low modulus values, creates an environment where low stress is imparted on mismatched CTE components. This low stress results in fewer component fractures over large temperature ranges.

Radiation

Applications that are exposed to radiation, such as weather sensors, can adversely affect the materials used. Silicone materials are affected as well by radiation but these effects can be minimized with adjustments to the type of polymer used. Radiation can create free radical groups on polymers within the elastomeric matrix. These free radicals readily form linkages to other polymers creating a higher crosslink density. A higher crosslink density in silicone systems generally translates to higher durometer or hardness, higher modulus and lower elongation. As briefly described above, higher modulus values can create stress in temperature cycling applications where CTE mismatches are observed. While the increase in modulus from radiation exposure may still be lower than epoxies, certain silicone chemistries can be effective in resistance to radiation. Several sources point to phenyl based silicones as having greater stability than standard polysiloxane systems. Walter Noll states, “resistance increases with increasing content of phenyl groups, copolymers with diphenylsiloxane units and methylphenylsiloxane units have proved particularly suitable”. In potting applications where elongation is not a significant factor, like electric wire and cable, electrical properties are “little affected by radiation” Handbook pg 16. The table below demonstrates the radiation resistance of phenyl containing silicone rubbers (PMQ) compared to dimethyl silicone rubbers (VMQ).

Radiation Resistance Silicone Rubber

	VMQ		PMQ	
Dosage (Rads)	Elongation (%)	Tensile (psi)	Elongation (%)	Tensile (psi)
None	200	1200	600	1200
5×10^6	130	1000	450	1100
5×10^7	50	900	225	900
5×10^8	20	600	75	850

Fuel Resistance

When we refer to fuel resistance, we are specifically citing the resistance of silicones to swell when put in contact with hydrocarbon based fuels and fluids. While silicone materials do not undergo structural breakdown when exposed to hydrocarbon-based compounds, some systems expand several times their original size and could create problems in lens and other potting applications. Fluorosilicones, with the chemistry described above, perform effectively in a fuel and fluid environment by retaining geometry and resisting absorption of hydrocarbons. The table below lists one fuel (JP 5) and two hydraulic fluids (Hydrol and Skydrol) common to the aerospace industry. The table also lists the percentage of trifluoropropylmethylsiloxane units used in the polymer of the elastomer system tested. The results are listed as the percent swell after exposure:

	JP5	Hydrol	Skydrol
20 Mole %	28% Swell	43% Swell	4 % Swell
50 Mole %	6% Swell	28% Swell	3% Swell
100 Mole %	16% Swell	5% Swell	6% Swell

The table demonstrates that different fluorosilicone compositions perform optimally in different systems and we point out that more trifluoropropylmethylsiloxane units are not always better.

Conclusion

Silicone elastomers, gels, thixotropic gels, and fluids not only perform extremely well in high temperature applications, but also offer refractive index matching so that silicones can transmit light with admirable efficiency. The examples of emerging and existing sensor technology provided the basis on which optics engineers must also consider the conditions the device operates in to ensure long-term reliability. External environments may include exposure to a combination of UV light and temperature, while other environments may expose devices to radiation and hydrocarbon based fuels. This paper demonstrated that the chemistry of silicones and functional groups that lend themselves to properties such as fuel and radiation resistance show why silicone is the material of choice for optic applications under normally harmful forms of exposure.

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