# 12. Silicones for Photonics

J.V. Jr. DeGroot, Dow Corning Corporation, Midland MI (USA)

As the photonics market develops, there is a continuing need to bring costs down. For opto-electronics, polymer-based components and structures are being considered because they are inherently easier to process than glass-based materials. Polymers can be batch processed by spin coating or stamping, but also processed continuously via printing or extrusion. In addition, this processing can take place at ambient temperatures and pressures. A variety of polymer systems have been investigated in photonics with varying degrees of success.

Light transmission through polymers can be limited by electronic transitions in the UV-visible region or by vibrational absorptions in the near-IR or IR, including overtones. These sources of loss are specific to each polymer. Intrinsic light losses tend to be higher with polymers than with glass-based materials. Under high flux, polymer degradation can occur: organics will yellow because of the heat generated, and they can also degrade because of photo-initiated oxidation. Despite these shortcomings, polymers are considered to take advantages of their inherent benefits. These benefits include ease of processing (resulting in lower-cost production) and also some material-specific functionality like high thermo-optic coefficient (see discussion below). Optical applications are considered, despite the higher intrinsic light loss generally associated with polymers, because the loss is not as critical for short-length (e.g., less than one meter) applications such as passive waveguides for communications between circuit boards, between integrated chips or even for lenses for light emitting diodes (LED).

In addition to their excellent thermal stability, mechanical properties and ease of processing, silicones are highly transparent to radiation in the visible range all the way down to UV. Silicones also have good transmission at selected near-IR wavelengths [1]. Very low levels of Rayleigh scattering can be achieved with silicones. Therefore, silicone-based polymers possess a set of properties making them suitable for waveguide applications, as well as for lenses and encapsulants through which light must travel.

**Necessary Properties for Photonics Applications**

For waveguide applications, critical material attributes are [2]:

- Low dielectric constant, and this usually also implies low refractive index
- Transparency with negligible light loss due to UV-visible electronic or IR vibration absorptions
- Homogeneity to minimize scattering
- Low intrinsic birefringence, and in most applications, low stress-induced birefringence
- Satisfactory thermophysical properties for the desired application

The most common silicone polymers are linear PDMS based on $Me_2SiO_{2/2}$ or D units with refractive indices approximately 1.40 - 1.42. More complex as well as more rigid structures can be engineered by including T or Q units. Some methyl groups along the chain can be substituted with phenyl groups to increase the refractive index to approx. 1.55 or with trifluoropropyl groups to reduce the refractive index below 1.40.

In the following section, important characteristics including dielectric properties, thermophysical properties and absorption characteristics will be developed and highlighted with examples.

*Dielectric Properties.* A low dielectric constant is desired because it minimizes light absorption by the material. The absorption and complex dielectric constants are linked through the Kramers-Kronig relations. Silicones in general have low dielectric constants when compared to other optically transparent plastics. The dielectric constant depends on the overall modulus of the system, state of cure, and overall system composition (i.e., type of polymers, cross-linkers and additives used). For PDMS with viscosities between 10 to 60,000 cSt, the dielectric constant ranges from 2.72 to 2.75 when measured from 100 to 10,000 Hz at 25 ºC [3]. The dielectric constant for PDMS also varies with temperature: at 800 Hz, it measures 2.8 and 2.3 for 20 ºC and 200 ºC respectively [4]. For a polymethylphenyl siloxane, the dielectric constant has been measured at 2.98 at 25 ºC and independent of frequency from 100 to 1,000,000 Hz [5]. By comparison, polymethylmethacrylate (PMMA) has dielectric properties that range from 3.6 at 50 Hz, 3.0 at 1000 Hz, and 2.6 at 1,000,000 Hz when measured at 25 ºC [6], and polycarbonate (PC) has a dielectric constant of 3.02 at 1000 Hz [7]. Because of the lower dielectric sensitivity to frequency, siloxane polymers in general have lower levels of dispersion than common organic polymers.

*Thermophysical Properties.* Siloxane polymers are not prone to yellowing, and if care is taken to remove catalyst impurities, they have very good thermal stability. The inclusion of phenyl groups leads to polymers that are stable for short durations at 300 ºC under nitrogen or air (see Figure 1) [8]. Many siloxanes have continuous temperatures specified at 150 ºC or above. For comparison, the continuous use temperature for PMMA is < 90 ºC and for PC is 121 °C [7].

Waveguides made from silicones maintain their shape without cold flow because the materials are cross-linked. Because the $T_g$ of PDMS is very low, stress birefringence remains low at most temperatures. The stress-optical coefficient for PDMS is 1.35 x $10^{-10}$ $m^2$/N at 20 ºC and 632.8 nm [9]. For polymethylphenyl siloxane, the coefficient is reported to be slightly higher at 5.73 x $10^{-9}$ $m^2$/N [10].

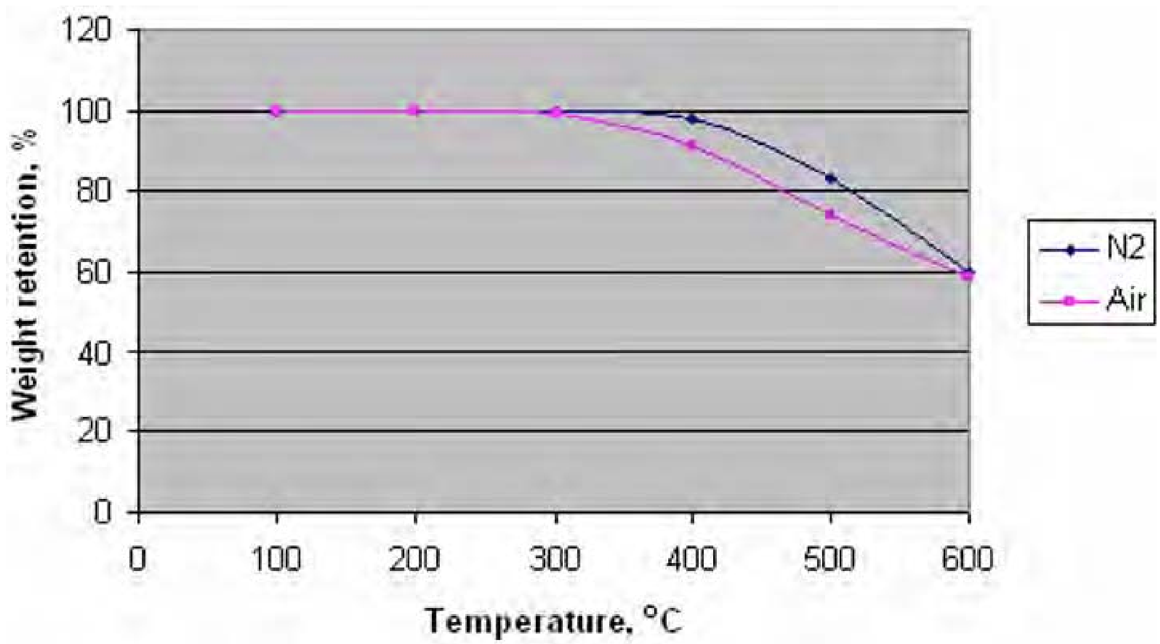


**Figure 1.** ***Thermal gravimetric analysis of a poly methylphenyl dimethyl siloxane copolymer under nitrogen or air under a temperature ramp rate for the testing of 10 ºC/min.***

The thermo-optic coefficient (change of the refractive index vs. temperature), dn/dT, for siloxanes varies from $-1.5 \times 10^{-4}$ to $-5 \times 10^{-4}$, depending on composition and cross-linking density [2]. The capability to tune dn/dT can be of use in some applications like thermally controlled variable optical attenuators and athermalizing planar light circuit components. For PMMA, dn/dT = $-1.1 \times 10^{-4}$ below $T_g$, which is approximately 105 ºC [11].

*Phonon and Absorption Characteristics.* Methyl siloxanes do not show characteristic absorption bands in the UV or visible spectrum, while methylphenyl copolymers have characteristic absorptions at 270, 264 and 250 nm. Both have many absorption bands in the NIR region (see Table 1) [1].

**Table 1. Light Loss Characteristics of Silicone Polymers or Copolymers at Various Wavelengths**

| ***Silicone Polymer or Copolymer*** | ***Loss at Specific Wavelength** dB/cm* | | | | | |
|---|---|---|---|---|---|---|
| | *1550 nm* | *1310 nm* | *850 nm* | *633 nm* | *400 nm* | *300 nm* |
| Dimethyl | 0.67 | 0.14 | < 0.01 | < 0.01 | 0.03 | 0.09 |
| Dimethyl methylphenyl | 0.66 | 0.28 | 0.03 | 0.03 | 0.04 | 0.24 |
| Methylphenyl | 0.62 | 0.35 | < 0.01 | < 0.01 | < 0.01 | 0.55 |
| Trifluoropropyl methyl - 1 | 0.54 | 0.16 | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| Trifluoropropyl methyl - 2 | 0.35 | 0.07 | 0.12 | 0.22 | 0.64 | 1.36 |
| Phenyl resin - 1 | 0.49 | 0.41 | 0.01 | 0.02 | 0.06 | 2.39 |
| Phenyl resin - 2 | 0.39 | | 0.03 | 0.05 | 0.11 | 2.94 |

Phenyl groups or trifluoropropyl groups can be added to reduce the absorptions in the 1500-1560 nm wavelength regions. However, the phenyl can have a negative impact on the absorptions at 1100, 1280-1320 nm. Despite these trade-offs, silicones are capable of excellent loss properties in the datacom wavelengths and certainly are adequate for short-range applications in the wavelength bands of interest for telecom (see Figure 2).

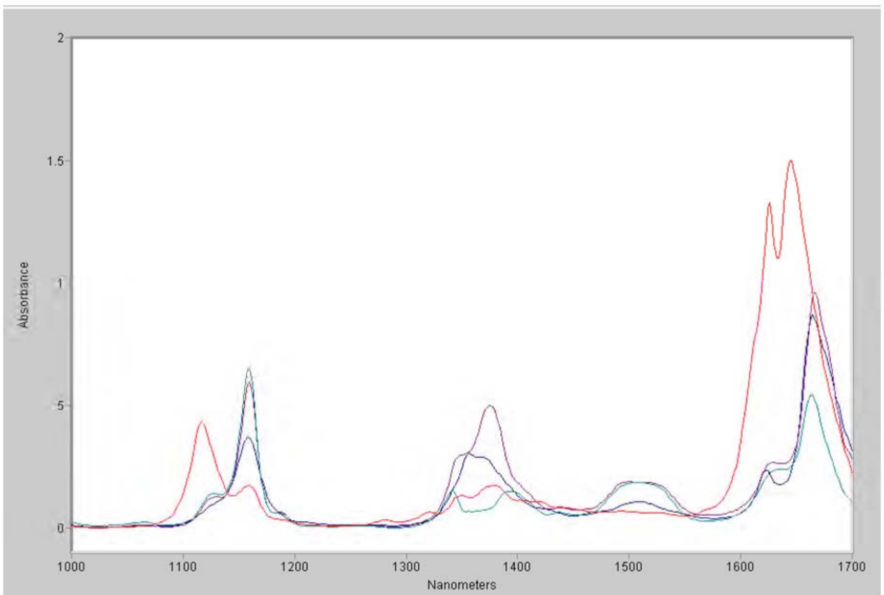


**Figure 2.** ***NIR absorption spectra of a PDMS polymer (in teal) and shifts in absorption when different substituents are added. In general, decreased absorbance at 1160 nm and 1500 nm and increasing absorbance at ~ 1630 nm results from increasing the phenyl content of the system (in red-resin and in purple-polymer). The addition of trifluoropropyl groups reduces absorption around 1160 and 1500 nm (in blue).***

In summary, silicones possess an interesting set of properties for photonic applications when compared to organic polymers. Silicones display high-temperature stability, which makes them compatible with solder reflow processing or in "under-the-hood" high-temperature applications, and they can be processed at room temperature. Silicones also have the optical characteristics necessary to enable them to function in waveguides with acceptable losses at telecom wavelengths and with very low losses over data-communications wavelengths.

## References

[1] Lipp, E. D.; Smith, A. L. Infrared, Raman, Near-Infrared, and Ultraviolet Spectroscopy. In *The Analytical Chemistry of Silicones*, Smith, A. L., Ed. Volume 112 in Chemical Analysis, Wiley-Interscience: New York, 1991; 305-345.
[2] Norris, A. et al. High Reliability of Silicone Materials for Use as Polymer Waveguides, *Proc. SPIE Linear and Nonlinear Optics of Organic Materials III*, Kuzyk, M.; Eich, M.; Norwood, R., Eds., Vol. 212, SPIE, 2003; 76-82
[3] *Dow Corning 200 Fluid, Information about Dow Corning 200 Fluid*, Form No.22-931A-90, 22-926D- 93, 22-927B-90, 22-928E-94, 22-929A-90, 22-930A-90.
[4] Noll, W. *Chemistry and Technology of Silicone*, Chapter 6, Academic Press: New York, 1968.
[5] *Table of Dielectric Materials*, Laboratory for Insulation Research, MIT, Cambridge, Massachusetts, 1953; 67.
[6] Wood, L. A. Physical Constants of Different Rubbers. *Polymer Handbook, 3rd ed*., Brandrup, J.; Immergut, E. H., Eds., Wiley: New York, 1989; V7-V13
[7] Rodriquez, F. *Principles of Polymer Systems, 3rd ed.*, Hemisphere Publishing Corp.: New York, 1989; 589-594.
[8] DeGroot, J. V. et al. Highly transparent silicone materials, Proc. SPIE Linear and Nonlinear Optics of Organic Materials IV, Norwood, R.; Eich, M., Kuzyk, M., Eds. Vol. 5517, SPIE, 2004; 116-123.
[9] van Krevelen, D.W. *Properties of Polymers*, *3rd ed*., Elsevier: Amsterdam, 1997; 304.
[10] Lorente, M. A. et al., *Macromolecules*, 1985, *18*, 2663.
[11] Wunderlich, W. Physical Constants for Poly(methyl methacrylate). *Polymer Handbook, 3rd ed.*, Brandrup, J. and Immergut, E. H., Eds., Wiley: New York, 1989; pp V77-V80.

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