Moisture permeability of silicone systems - part 1

Water vapor transmission rate as influenced by durometer, silica, and organic-siloxane group

Why is Moisture Permeability Important?

Many applications, both Engineering and Healthcare related, have an interest in how a silicone will protect or transmit water. For electronics, water is responsible for corrosion of electronic components, fogging and in some cases can cause side reactions that produce unwanted chemicals such as ammonia1. In healthcare applications, many times the opposite is true where the silicone needs to be permeable to act as a membrane allowing water to be transmitted to surrounding tissue as in the case of wound care dressings, external prosthetic devices, and contact lenses. There are other special cases where water will effect the performance of a added filler. In Light Emitting Diodes (LEDs), phosphors added to the silicone encapsulant to make white light may absorb moisture over time, which could alter the light output of the LED. In either case, having a better understanding of the relative differences of WVTR between standard silicone formulations can help immensely with the appropriate silicone selection.

What influences the rate of Moisture Permeability?

Several factors influence moisture permeability rates in polymeric materials. There is a complex relationship between diffusion and solubility of moisture through silicone material. Permeability rates depend on material thickness and environmental factors such as temperature, % Relative Humidity, and pressure. The silicone's chemical characteristics and bulk physical properties influence the rate moisture is absorbed onto the material's surface, dissolved through the material, and desorbed as it exits where:

$P = S \cdot D$
P = Permeability, S = Solubility Coefficient,
D = Diffusion Coefficient

Multiple types of silicones are commercially available for specific applications where the chemical and physical characteristics are essential for optimal performance. These characteristics can influence the water permeability rate as well. Silicones by nature of the long bond lengths have a much larger free volume compared to carbon based polymer system2 and have alternating silicon and oxygen atoms in the bond structure which makes the bulk silicone more polar than carbon based polymeric systems. Silicones are mainly thermosets where once crosslinked (a..k.a. cured) they have strong bonds between the discrete siloxane units that were liquid in the uncured state. Cured silicone matrices have a molecular architecture and crosslink density dictated by the molecular weight of siloxane units, organic groups present on siloxane units and fillers used for mechanical reinforcement or other unique properties such as to make electrically or thermally conductive.

All of these factors affect the free volume through which water vapor (or other gases) can be transported as well as the chemical solubility of water through the system. Silicones that contain functional fillers can greatly reduce the free volume of water through the bulk silicone by acting as an internal barrier within the cured silicone matrix. Another factor that influences the solubility and absorption/desorption rates of water (or gases) through the silicone is the chemical composition where silicones typically will contain specific amounts of methyl, phenyl, or fluoro functional groups to change properties such as refractive index, thermal stability and chemical resistance as needed.

Silicone Composition
Silicone polymers are synthesized with repeating siloxane units (R_2SiO). The R-substituent groups control the chemical and physical properties of the silicone polymer.

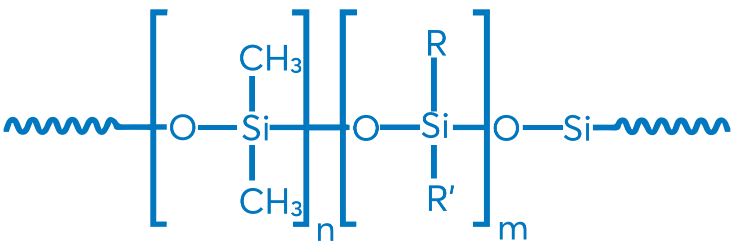
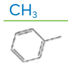
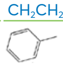


TABLE 1: Characteristics of Silicone Polymer Chemical Composition

R	R'	Properties
CH_3	CH_3	Also known as Polydimethylsiloxane, "PDMS" and "dimethyl" or "Me2". Main component of many standard silicones since the 1960's. Refractive Index (RI) is 1.40-1.41
CH_3	$CH_2CH_2F_3$	"Also known as Fluoro Silicones and are resistant to hydrocarbon solvents and fuels. 100% Fluoro indicates all monomeric units are the same. RI is < 1.40"
 Phenyl	 Phenyl	Phenyl groups have many functions including increasing thermal stability and chemical resistance. They are also known to increase the Refractive Index, the

When only silicone polymers are crosslinked together, the cured material is referred to as a "gel" and has minimal tensile and tear strength properties. Gels are soft and have very low modulus. Silicone polymers can be reinforced with fillers such as fumed silica and/or silicone resins. These reinforcing fillers increase the elastic properties of cured silicone.

CASE STUDY OBJECTIVE

The purpose of this Case Study was to determine if there is a relationship between Water Vapor Transmission Rates (WVTR) of selected silicones to assist with product selection when moisture permeability is of interest for the specific application. Based on historical data and other literature references, common material properties affecting permeability are backbone chemistry, durometer (crosslink density), and fillers. Samples were chosen based on these assumptions.

MATERIALS AND TESTING

There are many variables within each formulation, but incorporating them into the data analysis is beyond the scope of this study. The samples chosen where based on their bulk properties and how they where either vastly different or similar to each other.

Backbone Chemistry: Three gels with drastically different backbone chemistry. The selected gels do not contain fillers and are similar in hardness. Note that silicones are named in reference to the Refractive Index at 589 nm. Also note that phenyl content increases with increasing RI where 1.57 > 1.54 > 1.51 > 1.46 > 1.43

Durometer versus Filler: Two PDMS (Me2) based silicone elastomers with similar durometer were tested. One contains silica and the other is resin reinforced (contains no filler). Comparing these two materials should indicate if durometer or silica is the dominate influence for moisture permeability.

All materials were tested by Mocon Testing Service using the Mocon Permatran-W 3/33 Water Vapor Permeability Instrument. All samples were nominal 0.075 in (1.9 mm) thick and rates measured at 40.0°C, 90 % RH and 760.0 mmHg barometric pressure.

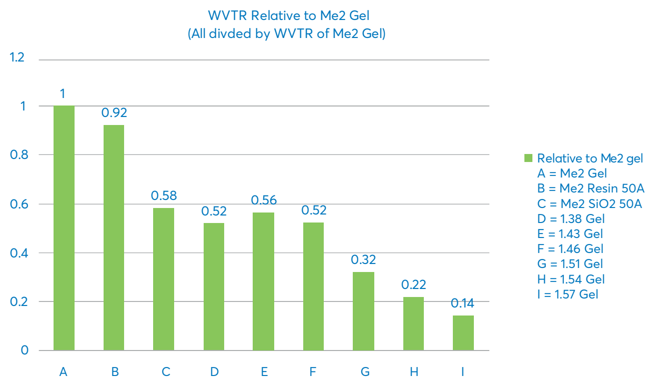
MATERIALS TESTED AND RESULTS:

TABLE 1. Lists the materials and lot numbers tested as well as a brief chemical description

Sample Name	Composition	Hardness	WVTR ($gm/m^2 \cdot day$)	WVTR ($gm/100in^2 \cdot day$)
Me2 Resin 50 A	PDMS polymer and Resin	53 A	62.22	4.01
Me2 w/silica 50 A	PDMS polymer and ~ Fumed silica (~ 30 %)	51 A	39	2.53
Me2 Gel	Crosslinked PDMS, no filler. Refractive index is 1.40"	"0.5 mm Penetration"	67.54	4.36
1.38 Gel	*Crosslinked 100% Fluoro, no filler	13 '00'	34.93	2.25
1.43 Gel	*Crosslinked phenyl polymer, no filler"	4.7 mm Penetration	38.11	2.46
1.46 Gel	*Same as above but %phenyl>1.43	7 '00'	35.4	2.28
1.51 Gel	*Same as above but %phenyl>1.46	12 '00'	21.61	1.39
1.54 Gel	*Same as above but %phenyl>1.51	32 '00'	14.66	0.95
1.57 Gel	*Same as above but %phenyl>1.57	53 '00'	9.46	0.611

(Note that this is a case study only with limited data for analysis .hence the precision and accuracy has not determined at this time. These results are to be used for comparative purposes only and not intended to be used for making Specifications. Please contact NuSil Technology for additional information

GRAPH 1: Analysis of durometer, silica and chemical composition



All WVTR results were normalized relative to the most permeable silicone tested, Me2 Gel.

RESULTS AND CONCLUSION

- **Hardness:** The soft "Me2 Gel" at 0.4 mm hardness versus the significantly harder "Me2 Resin 50A" durometer shows only an 8% drop in permeability therefore hardness does not significantly reduce the WVTR of PDMS systems.
- **Filler:** There was a 34% decrease in permeability between "Me2 Resin 50A" to "Me2 with Silica 50A." The filler appears to reduce the permeability more effectively than durometer alone.
- **Backbone Chemistry:** This case study showed that the R-substituent groups have the greatest influence on WVTR. Polymers with more phenyl groups had the greatest drop of WVTR versus Me2 and Fluoro. The "Me2 Gel" is slightly softer than the "1.57 Gel" and there was an 86% decrease in permeability.

Graph 1 can be used to determine relative differences in moisture permeability rates based on durometer, filler, and R group. If the application demands other testing conditions, these proposed gates could be used to select products that will give the most likely opportunity for success based on the desired conditions.

References:

Lowry, RK.., 2008, Dangerous Gases Within Hermetically Sealed Enclosures, Paper presented atIMAPs Topical Workshop and Tabletop Exhibition on Military, Aerospace, Space and HomelandSecurity: Packaging Issues and Applications (MASH 2008), Maryland, USA.

Robb, W. L. Thin Silicone Membranes – Their Permeation Properties and Some Applications.General Electric Company*, Waterford,N.Y.

Michelle Stevens, Stephen Tuolema and Dan Meyer "Water Vapor Permeation Testing of Ultra-Barriers: Limitations of Current Methods and Advancements Resulting in Increased Sensitivity",Mocon Inc., Minneapolis, MN.

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