Moisture permeability of silicone systems - part 2

Guidelines for choosing a silicone based on water vapor transmission rates for barrier applications

CASE STUDY OBJECTIVE

The purpose of this Case Study is to further clarify the relationship between Water Vapor Transmission Rates (WVTR) and select silicones. This study will assist with product selection when moisture permeability is of interest for specific applications.

In Case Study 1, researchers conducted preliminary results and assessed that radical substituents (R Groups) bonded to the polymer chain have the greatest influence on Water Vapor Transmission Rates. Phenyl groups were found to have a greater drop in WVTR than methyl or fluoro. The data collected also pointed researchers towards the conclusion that filler and durometer affect the WVTR – but not as significantly as the R groups affect them.

In Case Study 2, additional testing was performed. Researchers had a broader range of data to analyze. Similar to Case Study 1, researchers confirmed that the R groups present on the backbone chain are the most influential factors when determining permeability. However, the scope of Case Study 2 also includes an analysis of how various fillers and durometers influence WVTR.

Why is moisture permeability important?

Many applications, both Engineering and Healthcare related, have an interest in how a silicone protects or transmits 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 ammonia.1 In healthcare applications, where water is beneficial when 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 special cases where water will affect the performance of the added filler. For example, in Light Emitting Diodes (LEDs) the phosphors added to the silicone encapsulant to make white light may absorb moisture over time, thus altering the light output of the LED. In any case, having a better understanding of the relative differences of WVTR between standard silicone formulations can help immensely with the appropriate silicone selection.

Variables affecting water vapor transmission rates of silicones

By nature of their long intramolecular bond lengths, flexible backbones and weak intermolecular forces, silicones have a much larger free volume compared to carbon based polymer systems.2 The bonds between alternating silicon and oxygen atoms make the silicone network more polar than carbon based polymeric systems. Cured silicone matrices have a molecular architecture and crosslink density dictated by the molecular weight of siloxane units, organic groups present on siloxane units (See Figure 1) and fillers used for mechanical reinforcement or other unique properties.

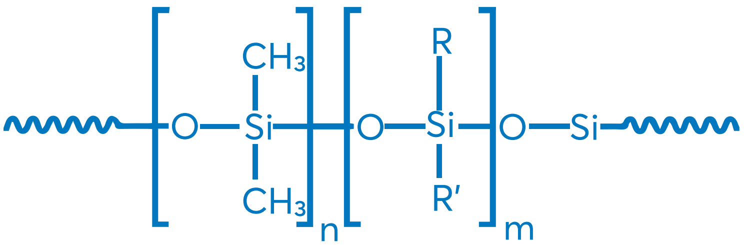

FIGURE 1. Characteristics of silicone polymer chemical composition

Different types of fillers are currently used to achieve high elastomeric properties or to make silicones electrically or thermally conductive. Other properties that can be achieved through adding fillers are: color, durometer, lower density, and thermal stability (See Table 1). These improvements in the material properties result from the molecular level interactions that take place at the interface between silicone and the surface of the filler.3 Whether filler is added for mechanical reinforcement or as a functional filler engineers must take the filler loading level, weight, particle size and shape into consideration because those factors can heavily influence the WVTR.

TABLE 1. List of possible functional fillers commonly used in silicone

Properties	Filler	Density	Particle Size	Surface Area
Increase Strength	Fumed Silica	2-5 lbs/ft^3	0.011-0.014	**200-255**
Reduce Density	Microballoons	0.16 g/cc	35-135	NA
Color	Ferro Black, TIO_2	5.0 g/cc	1, 0.3	NA, **9**
Thermal Conductivity	Boron Nitride	2.29 g/cc	7-10	**13**
Thermal Stability	Iron Oxide	4.1 lbs/ft^3	3	NA
Increase Hardness	Diatomaceous Earth	352 g/l	7	**100-200**
Electrical Conductivity	Carbon, Silver	6, 10.4 g/cm^3	30 nm, 30-40	**254, 10**

The permeability of silicones can also be altered by varying the polymer's crosslink density, which can be controlled by adjusting the amount of hydrogen on a polymer chain. In platinum addition cured silicones, crosslink density is controlled by vinyl and hydride content as well as its location. More bonds are created between two chains with more hydrogen present – giving a higher crosslink density (See Figure 2).

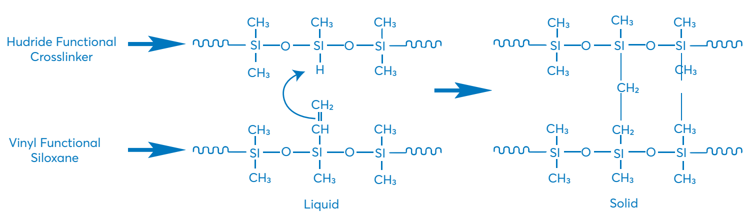

FIGURE 2. Crosslink Reaction

As discussed in Case Study 1, the organic R groups are another variable in the chemical composition where silicones typically contain specific amounts of methyl, phenyl, or fluoro functional groups to change properties such as refractive index, thermal stability and chemical resistance as needed (See examples of R groups in Table 2). These factors affect the rate at which water vapor (or other gases) can be transported as well as the chemical solubility of water through the system.

TABLE 2. Chemical composition and properties of R groups

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 Fluorosilicones 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 higher the % phenyl the RI > 1.41

Calculating the theoretical rate of moisture permeability

Clearly, there is a complex relationship between diffusion and solubility of moisture through a silicone material. Not only do permeability rates depend on the chemical composition, but also on material thickness, environmental factors such as temperature, % Relative Humidity (RH), and pressure. As earlier discussed, 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

Permeability rates also depend on material thickness where:

$P = KD/\Delta x$

where K is the partition coefficient which can be calculated to define S
D is Diffusion Coefficient
X is film thickness

TEST METHODS

All materials were tested by Mocon Testing Service using the Mocon Permatran-W 3/33 Water Vapor Permeability Instrument (See Figure 3). Standards that apply to this instrument are ASTM F-1249, TAPPI T557 and JIS K-7129. This test uses the silicone sample as a barrier film between the water containing top side and the nitrogen gas sweep on the bottom side of the film that sweeps the water vapor to the detector. Once the rate of water vapor detected remains constant the test is considered complete. All samples were run in duplicate and the average is reported. All samples were nominal 0.075 in (1.9 mm) thick and rates measured at 40.0°C, 90 % RH and 760 mmHg barometric pressure.

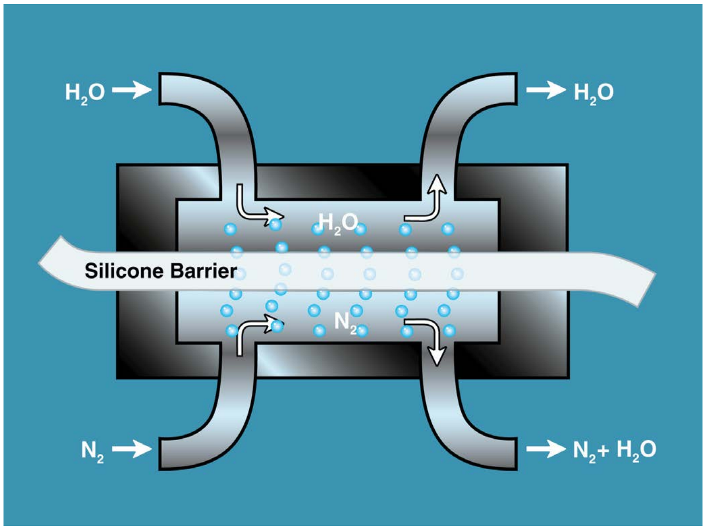

FIGURE 3. NuSil Interpretation of Mocon Isostatic Permeation Cell

TABLE 3. Materials Tested and Results

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

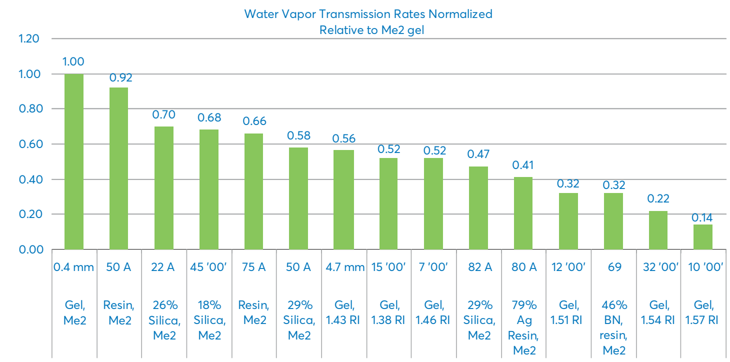

FIGURE 4. Analysis of Durometer, Silica and Chemical Composition

MATERIALS AND RESULTS

There are many variables within each formulation, thus they will not be incorporated into the data analysis, as it is beyond the scope of this study. The samples chosen where based on their bulk physical and chemical properties. Table 3 lists the materials, their corresponding durometers as well as a brief chemical description of each. Figure 4 graphically displays the WVTR relative to the most permeable silicone tested, the dimethyl silicone gel with no fillers and low crosslink density.

General Description	Overall ~ % Filler (W/W)	Durometer	Average WVTR (gm/m2-day)"	Relative to Me² gel
Gel, Me²	0	0.4 mm	67.54	1
Resin, Me²	0	50 A	62.22	0.92
Silica, Me²	26	22 A	47.2	0.7
Silica, Me²	18	45 '00'	45.85	0.68
Resin, Me²	0	75 A	44.5	0.66
Silica, Me²	29	50 A	39	0.58
Gel, 1.43 RI	0	4.7 mm	38.11	0.56
Gel, 1.38 RI	0	15 '00'	34.93	0.52
Gel, 1.46 RI	0	7 '00'	35.4	0.52
Silica, Me2	29	82 A	31.53	0.47
Ag filled Resin, Me²	79	80 A	27.76	0.41
Gel, 1.51 RI	0	12 '00'	21.61	0.32
BN filled, resin, Me²	46	69	21.82	0.32
Gel, 1.54 RI	0	32 '00'	14.66	0.22
Gel, 1.57 RI	0	10 '00'	9.46	0.14

RESULTS & ANALYSIS:

R Group

The first observation made after testing a wide variety of the materials in Case Study 1 & 2 is that the R groups have the largest impact on the WVTR of the silicone. For example, a dimethyl gel had the highest WVTR, while diphenyl gel had the lowest WVTR as depicted in Figures 4 and 5. The data suggests that R groups have an impact on the free volume and solubility of the formulation at a molecular level that can significantly increase or decrease permeability. In Figure 5, there are multiple gels similar in durometer – gels that do not contain fillers. They do have varying WVTR, suggesting that the corresponding backbone chemistries are one of the main influences on the permeability of silicones. Seemingly, the more phenyl content there is in a system, the more it will inversely affects WVTR. Note that silicones are named in reference to the Refractive Index at 589 nm. Also note, that phenyl content increases with increasing RI, were 1.57 > 1.54 1.51 > 1.46 > 1.43>. The gel with the 1.38 R.I. represents a 100% Mol fluorosilicone gel.

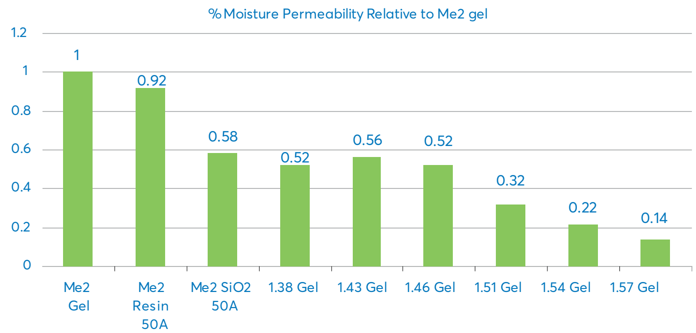

FIGURE 5: Phase 1 and 2 Analysis: Filler and chemical composition relative to Me2 gel

Filler type and loading

After analyzing the data, the results suggest that fillers decrease WVTR. A silica reinforced silicone had lower WVTR than an unfilled silicone at the same durometer. The very highly filled silicones (>50% w/w) had lower WVTR than silica filled (~ 25% w/w). The type of filler used influences the WVTR – more than the filler loading level. For example, the silver sphere filled product has almost two times the amount of filler than the Boron Nitride (BN) filler, yet it has a WVTR almost 10% higher than the BN filler. Researchers hypothesize that this difference is a result of the shape of the filler. The BN filler particles are usually shaped like platelets, which have a higher aspect ratio (length versus height) than spheres. The platelet structures can align in one axis (Z axis) that forms a non permeable barrier, thereby decreasing WVTR. Figure 6 depicts different types of fillers, their loading levels, and tested WVTR.

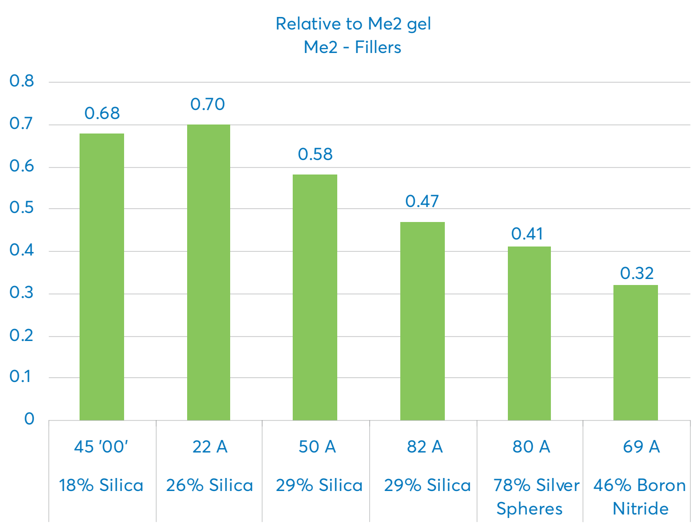

FIGURE 6: Relative Permeability Rates of filled systems Silica, Silver, Boron Nitride

Filler vs. Durometer

The third aspect of focus is the filler loading level and type of filler used versus durometer. After comparing two PDMS (Me2) based silicone elastomers with similar durometer it was determined that the "Me2 with Silica 50A" polymer had a lower WVTR by 34% than the "Me2 Resin 50A" polymer. This comparison was made in an effort to show that the filler has a larger impact than the durometer of the material on WVTR. When comparing products with no filler and different durometers, the data shows that the harder a silicone is the less permeable it is (See figure 4). However, when testing 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 durometer does not significantly reduce the WVTR of PDMS systems.

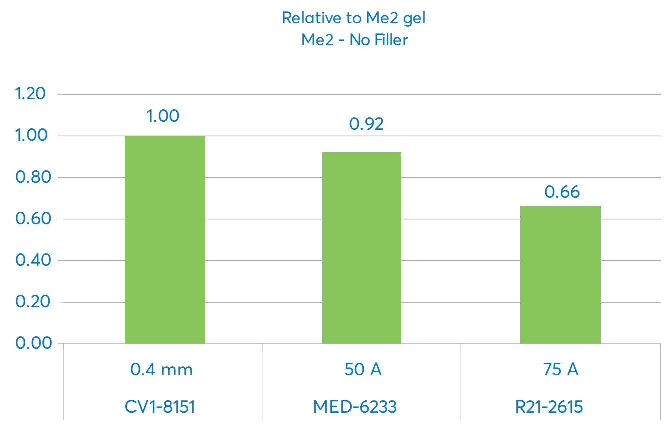

FIGURE 7: Relative Permeability Rates of PDMS to Me2 Gel: No Filler, Different Hardness

CONCLUSION

WVTR are significantly impacted by multiple variables which are not all covered under the testing of Case Study 2.
In Case Study 1, researchers conducted preliminary tests to assess the influence of R Groups on moisture permeability. Subsequently, case study 2 was completed with further testing on a broader range of products. Researchers discovered that there is useful data when looking at trends within specific group of products:

- The radical substituents on the polymer chain are the largest factor in determining WVTR. Researchers discovered that a soft diphenyl gel was the least permeable of all the samples tested. An increase in the amount of phenyl in a system decreases permeability.
- Fillers compounded into formulations decrease WVTR. Most times, the type of filler is a more influential factor on permeability in silicones than the filler loading level.
- In a Polydimethylsiloxane (PDMS) system durometer and crosslink density decrease the WVTR where as a softer material is usually more permeable.

Choosing the right silicone with the desired WVTR involves evaluating R groups, filler type, filler loading levels, durometer and assessing what combination would work best. The information herein should be used solely as guidelines and not for specifications. NuSil may apply what was learned to make recommendations for all its product lines from the formulations based on applications where water vapor is of interest. Contact NuSil Technology, LLC for further references and information.

References:

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