The Permeability Characteristics of Silicone Rubber

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ABSTRACT

Silicone rubber is universally regarded as the best-in-class elastomer for extreme environments. In addition, silicone rubber is one of the most permeable elastomers. This property is a key advantage for silicone rubber in many design situations. However, some applications which require silicone performance in extreme environments also require low gas permeability. Applications that require such material characteristics cover a range of aerospace components such as inflatables, ducting, and diaphragms. This paper presents a technical review of the gas permeability characteristics of silicone rubber, including analysis of the gas penetration mechanism through the elastomer. The chemical structure of silicone rubber affects permeability, as do other governing factors such as temperature and gas type. In particular, phenyl vinyl methyl silicone (PVMQ) has the lowest glass transition temperature (-120°C) of all elastomers, but its gas permeability is very high. Arlon has developed a proprietary technology to reduce the gas permeability of PVMQ. Arlon's technological approach produces large gains in gas permeability reduction without sacrificing excellent low temperature elastomeric flexibility.

KEY WORDS: Silicone, Permeability, Low Temperature Flexibility

1. INTRODUCTION

The high flexibility of the silicon-oxygen chain in silicone provides "openings" which are free volume and permit gas diffusion. The typical silicones such as vinyl methyl siloxane, (VMQ) and PVMQ, are two of the most permeable elastomers [1]. High permeability of silicone can be applied in membranes for blood oxygenation, gas separation, drug delivery, and fundamental studies to gain insight of the molecular structure of silicone elastomer [1]. The penetration mechanism of gas in polymer can also be applied to silicone rubber to help understand gas permeability.

Free volume or "holes" exists in the rubber matrix. "Holes" thermally form and disappear with the movement of polymer chains. Gases are soluble in rubberlike substance. When rubber is exposed to a gas, solution occurs at the surface and the dissolved gas molecules diffuse into the interior. The diffusion of gas molecules in the rubber membrane is a process in which the gas molecules migrate from "holes" (free volume) to "holes" (free volume). The permeation of gas through a membrane involves in solution on one side, diffusion through the membrane to the other side, and finally evaporation out of membrane [2], as shown in **Figure 1.** The rate of permeation is a specific function of a given gas and rubber [3]. The rate of permeation depends on both solubility and the diffusion rate.

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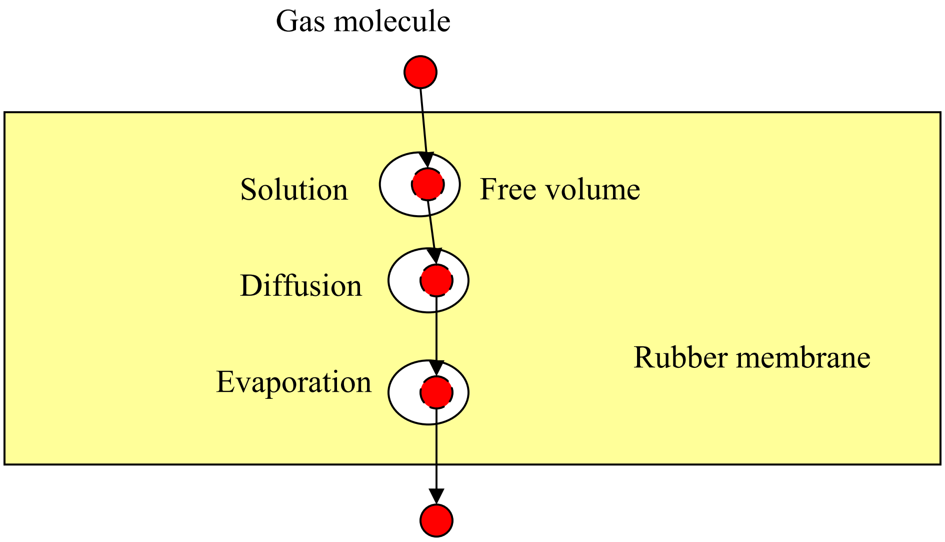

Figure 1 The schematic of gas permeation in a rubber membrane

The solution and evaporation phenomena conform to Henry's law [4]:

$$c=S*p \qquad \textbf{Equation (1)}$$

Where, c is the concentration of gas molecules in rubber, S is the solubility of gas in rubber, and p is the pressure of gas.

Diffusion theory is based on the hypothesis that the net rate of transfer of a diffusing substance through a unit sectional area of an isotropic material is proportional to the concentration gradient normal to the section. The diffusion conforms to Fick's first law (steady state) and Fick's second law (non steady state or time dependant). One dimension Fick's first law is described as:

$$F = -D\frac{dc}{dx} \qquad \textbf{Equation (2)}$$

Where, F (flux) is the rate of transfer per unit area, c is the concentration of gas molecules at position x in the rubber matrix, and D is the diffusion coefficient.

One dimensional Fick's second law (time-dependent diffusion equation) is described as:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad \textbf{Equation (3)}$$

Where, t is time

In most of applications, permeability of a membrane is used to characterize the rate of permeation. Permeability is usually calculated by the following equation [2, 3, 5, 6, 7, 8],

$$P = \frac{v \cdot \delta}{A \cdot t \cdot (p_1 - p_0)} \qquad \textbf{Equation (4)}$$

Where, P is the permeability for a given gas in a given membrane, v is the volume of gas which penetrates through the membrane, δ is the thickness of membrane, A is the area of membrane, t is time, p_1 is the partial pressure of the gas on the higher pressure side of the membrane, and p_0 is the partial pressure of the gas on the lower pressure side of the membrane.

In aerospace applications, where material weight is critical, δ is often replaced by the weight per unit area of membrane.

$$P = \frac{v \cdot w}{A \cdot t \cdot (p_1 - p_0)} \qquad \textbf{Equation (5)}$$

Where, w is the weight of membrane per unit area

2. EXPERIMENTAL

2.1 Materials

PVMQ (phenyl vinyl methyl siloxane) in this study is SILASTIC® LT-50 of Dow Corning. Loperm M-4342 is a type fluorosilicone rubber of Dow Corning. The formulations in this study are mixed on the two-roll mill. Some special components are added into formulation to obtain Arlon modified PVMQ. Then, the rubber compound is calendered and hot-air cured (150°C for 3 minutes) in oven to ~5 mils membrane for gas permeability test. ASTM slabs are prepared by pressing curing (121°C for 20minutes) for stress-strain test.

2.2 Gas permeability test

Gas permeability in this study is tested through ASTM D1434-82, procedure V-Volumetric. The instrument is CSI-135 Permeability Cell of Custom Scientific Instruments, Inc. Gas used in this study is helium. The test temperature is controlled by water bath.

2.3 Stress-strain test

Stress-strain test is performed on Instron 1130 of Instru-Met Corporation. An environment chamber with liquid nitrogen tank is used to control the temperature of samples to -100°C±5°C. ASTM slabs are cut to microtensile "Dog Bone" sample specified in ASTM D1708.

3. THE FACTORS WHICH AFFECT THE PERMEABILITY OF SILICONE RUBBER

3.1 Gas type

The types of gas affect both solubility and diffusivity of the gas. Diffusivity greatly depends on the size of the gas molecule. The smaller the size of the gas molecule, the faster the diffusivity

[1]. Solubility depends on the polarity of both the gas molecule and silicone rubber. If the gas molecule has a similar polarity to silicone, it has a higher solubility in silicone rubber. If it is gas mixture, different gases do not affect each other, and permeability is calculated by their partial pressures.

3.2 Silicone type and formulation

Silicone elastomers have low intermolecular forces and relatively unhindered single bonds that link the silicon and oxygen backbone chain atoms together. It results in a higher than normal amount of free volume and a high degree of chain mobility [14]. Consequently silicone rubber is most permeable elastomer, as shown in **Table 1**. Permeability of silicone rubber decreases significantly with an increase in the polarity of the pendent groups along the siloxane chains. Permeability of silicone rubber is controlled more by the solubility of a given gas than by its diffusivity [1]. As shown in **Table 2**, Permeability of methane, nitrogen, oxygen, and carbon dioxide differ significantly, while their diffusivity is essentially equal. On the other hand, helium, which has a very high diffusivity, shows comparable permeability versus nitrogen because of its low solubility in silicone rubber.

Crosslink density at the level required in silicone rubber showed little effect on permeability. Filler levels reduce permeability in proportion to volume fraction [9, 10]. However, fillers also increase the specific density. The fillers in silicone rubber increase the enthalpy of the solution of gas, which indicates that the fillers directly participate in dissolution or that the character of polymer matrix is changed. Gas diffusivity decreases with silica filler loading. Gas diffusivity changes in inverse proportion to diffusion path tortuosity and chain immobilization from filler attachment [10].

Nano-clay filled poly (dimethylsiloxane) (PDMS) was investigated [11-13]. It was found that nano-clay provides substantial polymer reinforcement, though the gas permeability of the nanocomposite remains high despite the large nanolayer aspect ratio. The random orientation of the clay nanolayers in the polymer matrix is responsible for the lack of an effective gas barrier property.

Table 1 Oxygen permeability of silicone rubber [9]

Polymer	Permeability*10^9, cm^3*cm/(s*cm^2*cmHg)
Dimethylsilicone rubber	60.0
Fluorosilicone	11.0
Nitrile rubber	8.5
Natural rubber	2.4
Polyethylene, low density	0.8
Butyl rubber	0.14
Polystyrene	0.12
Polyethylene, high density	0.10
Nylon 6	0.004
Poly(ethylene terephthalate)	0.0019
“Teflon”	0.0004

Table 2 Gaseous permeability of dimethylsilicone rubber [9]

Gas	Permeability*10^9, cm^3*cm/(s*cm^2*cmHg)	Diffusivity*10^6, cm^2/s	Solubility, cm^3(STP)/cm^3*atm)
H_2	65	43	0.12
He	35	60	0.045
CO_2	323	11	2.2
N_2	28	15	0.15
O_2	62	16	0.31
CH_4	95	13	0.57

3.3 Pressure

In the **Equation (4)**, the value of permeability does not depend on the pressure. Permeability is normalized by pressure. However, the amount of gas which diffuses through membrane does depend on the pressure. A lower pressure differential equates to less gas diffusing through the membrane. When gas is a mixture, the calculation of permeability in **Equation (4)** is based on the partial pressures of the individual gases in the mixture.

3.4 Temperature

The effect of temperature on permeability has two aspects.

1) Silicone rubber. The free volume of silicone rubber depends on temperature. Lower temperature results in less free volume and consequently lower permeability. Meanwhile, the mobility of polymer chain of silicone rubber is low at lower temperature. Low mobility of the polymer chains restricts the diffusion of gas molecules. If the ambient temperature is lower than the crystallization temperature or glass transition temperature of the polymer, permeability is significantly reduced and a transition occurs like its physical properties.

2) Gas molecules. The mobility of gas molecules significantly depends on temperature. Lower temperature means slower gas mobility which subsequently results in lower gas diffusivity and permeability. Temperature also affects the solubility of gas molecules in silicone rubber, as shown in **Equation (6)**.

$$S = S_0 e^{\frac{-\Delta H_s}{RT}}$$ **Equation (6)**

Where, S is solubility, ΔH_s is the enthalpy of solution, S_0 is pre-exponential factors, R is the gas constant, T is Kelvin temperature.

ΔH_s can be negative or positive. If solution enthalpy is negative or discharging heat, gas solubility increases with decreasing temperature. If solution enthalpy is positive or absorbing heat, gas solubility decreases with decreasing temperature. The gas solubility is proportional to polymer permeability.

Experiment results at Arlon show that temperature has a significant effect on the permeability of silicone rubber. The results validate that lower temperatures results in lower gas permeability, as shown in **Figure 2**.

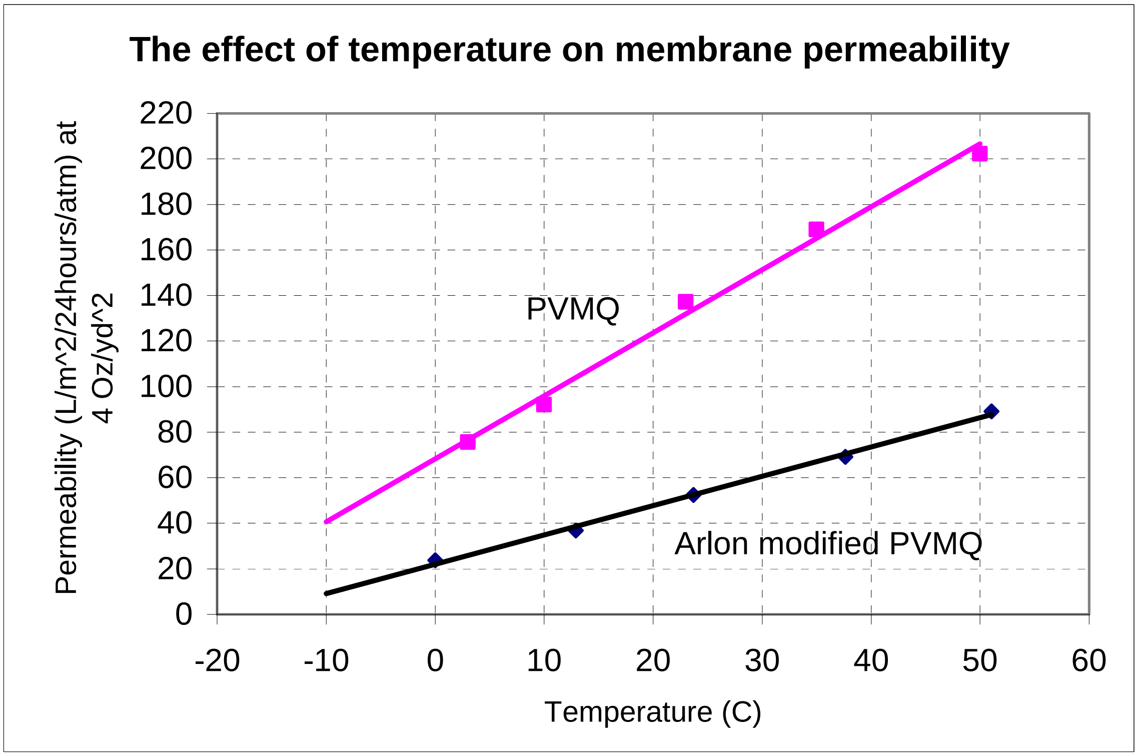

Figure 2 The effect of temperature on gas permeability (helium) of silicone rubber membrane

3.5 Thickness

In the **Equation (4)**, permeability is normalized by thickness. The value of permeability is independent of the thickness. However, the amount of gas that diffuses through the membrane does depend on the thickness, meaning that thicker membranes result in less total gas diffusion.

3.6 Area

In the **Equation (4)**, permeability is normalized by area. The value of permeability is independent of the membrane area. However, the amount of gas which diffuses through the membrane does depend on the area, meaning that smaller membrane areas result in the less total gas diffusion.

4. SILICONE RUBBER WITH LOW GAS PERMEABILITY

Since silicone rubber has a much higher gas permeability than most of other rubbers, silicone rubber is usually not considered in applications requiring low gas permeability. However, some special applications require both low gas permeability and high performance requirements, which only silicone rubber can achieve. One such example is low temperature flexibility of an elastomer to temperatures as low as -100°C. In these applications with extreme environmental demands, silicone rubber has to be used. Meanwhile, silicone rubber has to be modified to meet the requirement of low gas permeability.

Commercially standard silicone rubber like VMQ has a glass transition temperature of -120°C which is the lowest in all elastomers. All other elastomers have glass transition temperatures higher than -80°C. However, VMQ tends to crystallize at approximately -50°C. The addition of phenyl pendant groups on the polymer chain of silicone rubber makes PVMQ (phenyl vinyl methyl siloxane) not to crystallize. Consequently PVMQ is flexible down to -120°C [14]. To combining the demanding requirement of both low temperature flexibility and low permeability for PVMQ, Arlon has developed a proprietary technology to modify PVMQ. Arlon modified PVMQ has not only low temperature flexibility, but also lower permeability than PVMQ and other silicone elastomers (VMQ, fluorosilicone, etc.).

Gas permeability (helium) of PVMQ, Arlon modified PVMQ, and Dow Corning LoPerm M-4342 (fluorosilicone) are tested at Arlon and shown in **Figure 3**. Arlon modified PVMQ has a lower permeability than PVMQ and Loperm M-4342 (fluorosilicone) of Dow Corning.

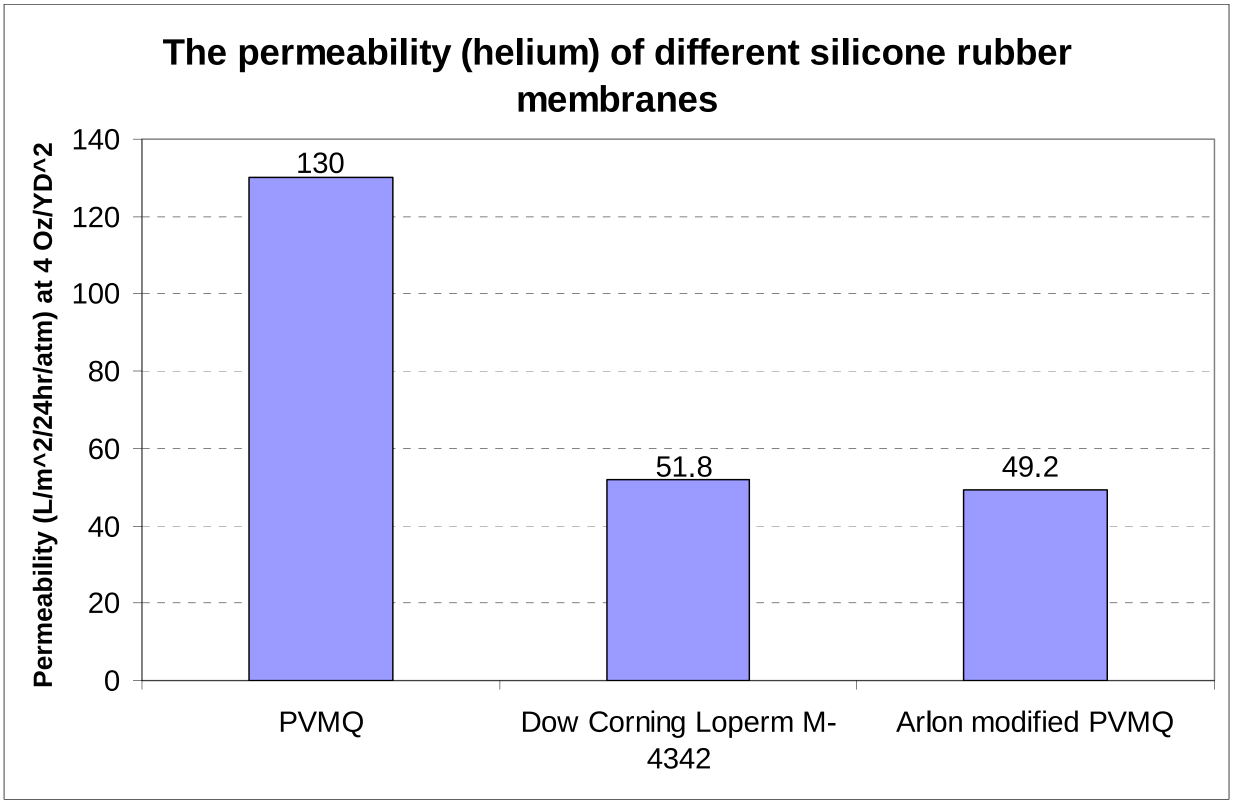

Figure 3 The helium permeability (23°C) of different silicone rubber membrane

There are some standard ASTM methods to test low temperature flexibility such as ASTM 6182. In this study, low temperature flexibility of silicone rubber membrane is characterized by

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elongation at -100°C. When a membrane with thickness of δ is put around a rod with radius of r, the outside the membrane is stretched, and inside is compressed, as shown in **Figure 4**. The center of membrane is not stretched or compressed. If the elongation of the membrane material is ε, it can be correlated to the radius of rod and the thickness of membrane as **Equation (7)**.

$$\varepsilon = \frac{2\pi(r+\delta) - 2\pi(r+\delta/2)}{2\pi(r+\delta/2)}$$

$$r = \frac{1-\varepsilon}{2\varepsilon}\delta$$ **Equation (7)**

In the **Equation (7)**, the value of r gives us a general idea about the flexibility of membrane. Smaller the value of r, better the flexibility. So, if the membrane is thinner, the value of r is smaller, consequently the flexibility is better. If the elongation of membrane material is bigger, the value of r is smaller, consequently the flexibility is better.

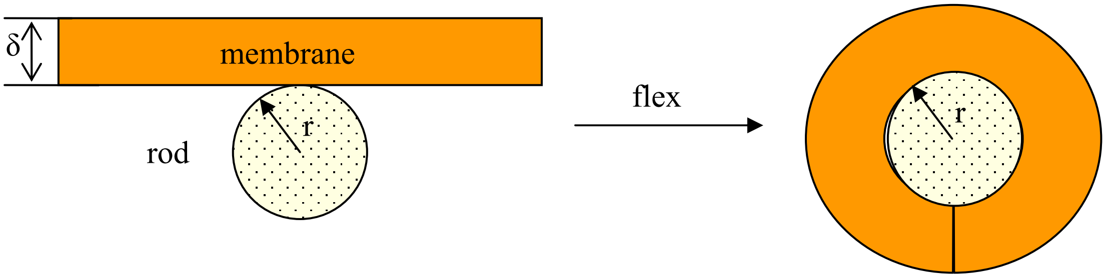

Figure 4 Schematic of material flexibility

The elongation of PVMQ, Arlon modified PVMQ, and LoPerm M-4342 of Dow Corning at -100°C are tested at Arlon and shown in **Figure 5**. Loperm M-4342 is a type of fluorosilicone developed by Dow Corning. Its glass transition temperature (T_g) is -71°C. It totally loses elasticity and cracks immediately at -100°C, so its elongation at -100°C is almost zero. Glass transition temperature of PVMQ is -120°C. It still keeps an excellent elongation of approximately 500% at -100°C. This indicates that it is still flexible. Arlon modified PVMQ is mainly based on PVMQ. Compared to pure PVMQ, its elongation is less and approximately 30% due to material modification. However, the material is still elastic due to extremely low T_g of PVMQ. It does not rip during stress-strain testing but Loperm M-4342 of Dow Corning does. Its elasticity is good enough for most of applications however low temperature flexibility needs to be tested according to the specific requirement such as ASTM 6182.

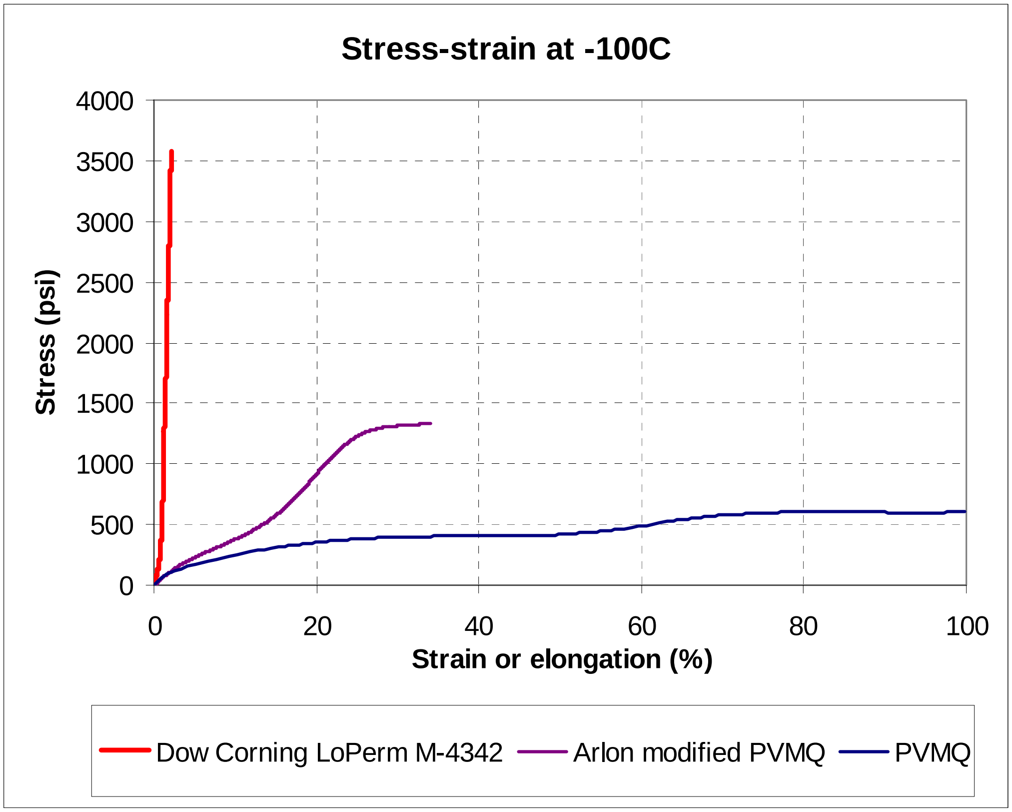

Figure 5 The stress-strain plot at -100C of different silicone rubbers

5. SUMMARY

Silicone rubber has one of the highest permeation rates among all types of rubber. The applications of silicone rubber related to permeability generally focus' on its high permeability. However, some special applications, require both low gas permeability and other extremely high performance in extreme environments, which only silicone rubber can provide. One particular case is low gas permeability coupled with low temperature flexibility down to -100°C. Silicone rubber has to be used in these applications. Arlon has developed a proprietary technology to reduce gas permeability of PVMQ. It results in an elastomer that optimizes the compromise between low permeability and good low temperature flexibility. Arlon modified PVMQ has both low gas permeability and low temperature flexibility.

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