

Silicone Pressure Testing: Thermal Expansion and Solvent Swelling



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Silicones are well known for having a large expansion when they are heated (CTE) and also for their tendency to swell considerably when exposed to soluble liquids. Both volumetric expansions create pressure. Measurements show that heated silicone gels and soft elastomers (low to mid-00 scale hardness) create very liquid-like pressures while A scale silicones create pressures that more closely follow elastomer predictions. Solvent swelling produced very similar results, though the measured data for the harder elastomers fell between the liquid and elastomer predictions. Within the limited data, it appears that the crossover between liquid and elastomer pressure generation behavior lies somewhere in the upper 00 / 1-10A hardness scales, or 0.1 – 0.2 MPa Young’s modulus range. Details are provided to allow for pressure generation estimates for both thermal expansion and liquid swell.

Introduction

Silicones are known for having some of the highest coefficients of Thermal Expansion (CTE) of all elastomers. It is common for users to factor in an air headspace when filling modules to account for this expansion and the pressure it will generate. Usually the need for this is observed after filling just a few enclosures completely full and then heating – housings crack, lids warp, screws are stripped and more sensitive internal components can be broken.

The pressure generated by thermal expansion is generally accepted as being defined by the following three equations:

- Liquids: pressure = CTE x Bulk modulus
- Solids: pressure = CTE x Young’s modulus
- Elastomers: pressure = CTE x Young’s modulus x (1-p)
Where p = Poisson’s Ratio
- Bulk modulus = Young’s modulus/[3 x (1-2p)]

The Bulk modulus is therefore much larger than the Young’s modulus, and very sensitive to an exact value for Poisson’s ratio when this value is close to 0.5. Generally, we do not have precise measurements for this value, and it is commonly accepted to assume that an unfilled and low crosslink density silicone may have a

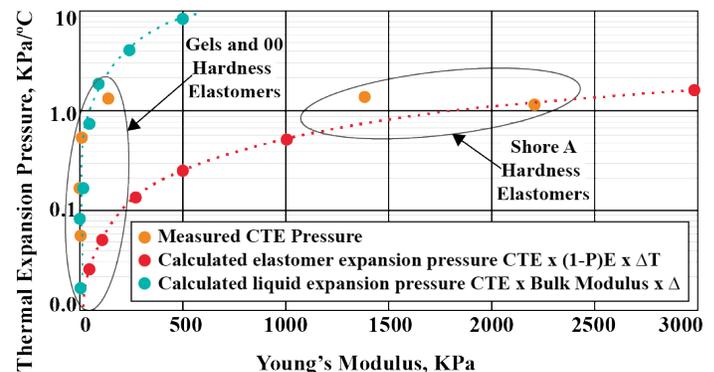
Poisson’s ratio of approximately 0.495 while a moderately filled and crosslink density elastomer may be about 0.48. Very highly filled and/or crosslink density silicones may be lower, but they were outside of the scope of the data available.

Determining the pressure generated by the swelling of solids with liquids is a much more complicated process, and one that has been lately finding considerable commercial interest with elastomers used for the oil and gas wells¹⁴ and in O-ring gasket simulations⁵. The scope of this report was to gather existing swelling data and associated durometer changes, convert the durometers to estimated Young’s modulus values, and compare the swelling pressures to those from thermal expansion.

Data was generated by curing the silicone materials in a metal cylinder and positioning a Texture Analyzer probe to just contact the upper surface. Materials were then heated and the resulting pressure measured.

Young’s modulus data was taken from both stress/strain measurements at <10% strain or derived from storage and loss modulus data from RDA studies.

Thermal Expansion Pressure in Silicone Elastomers

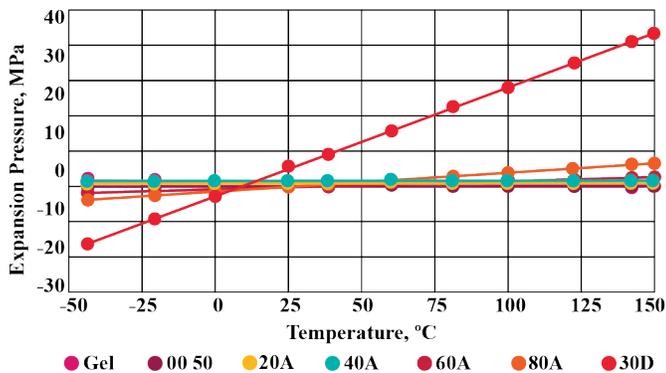


CTE values were obtained via TMA. Poisson's ratio was estimated based on the filler content and rough level of crosslink density based on the product's formulation. Bulk modulus was calculated from Young's modulus and the estimated Poisson's ratio. Theoretical curves were generated for pressures based on the liquid and the elastomer equations above assuming a Poisson's Ratio of 0.49 and a volumetric CTE of 0.001 and shown with the measured data.

It can be seen that the measured thermal pressure for the three softest silicone products fit extremely well to what would be expected from liquids with the same bulk modulus. The product with the mid-high OO hardness is shown to start to deviate from the liquid theory line. The two harder elastomers fit much better to the predicted elastomer trend line.

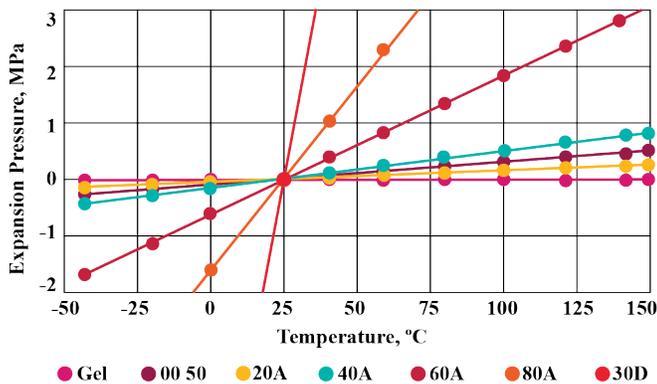
With the above split between liquid-like gels plus extremely soft elastomers versus harder elastomers, estimates could be made for a range of durometer hardness/modulus materials. The charts below assume the stress at 25°C = zero and that there is no appreciable compression set occurring. The calculated pressure values shown are for a given hardness/modulus silicone heated or cooled to the shown temperature.

Thermal Expansion Pressure over Silicone Durometer Ranges



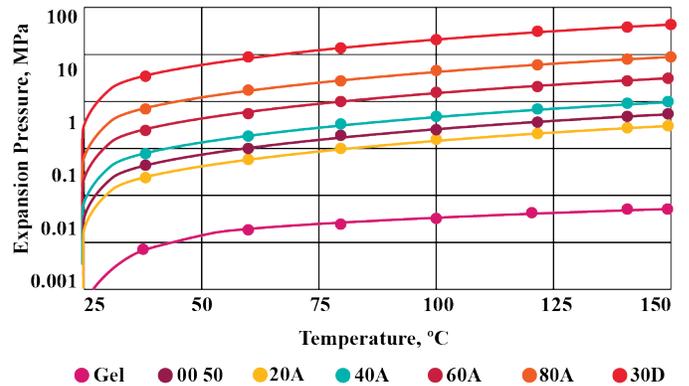
An interesting feature of the above is that the 00 50 hardness material shows a higher thermal expansion pressure than the 20A hardness material. This is of course due to using the liquid pressure equation vs. the elastomer equation.

Thermal Expansion Pressure Over Silicone Durometer Ranges



The most detail and perhaps utility comes from a log plot of the expansion pressure. This chart shows the predicted pressure generated by a given hardness silicone elastomer when heated from 25°C.

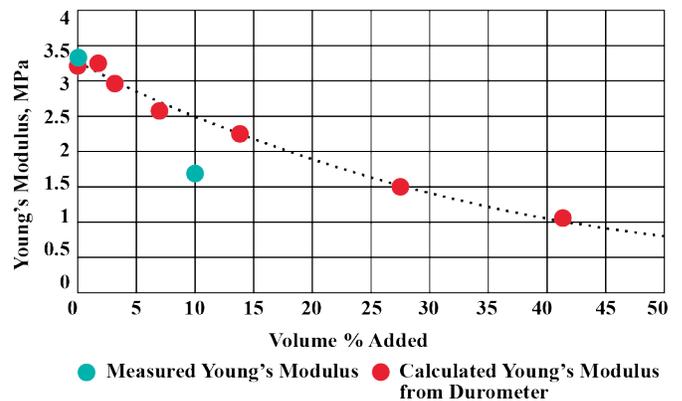
Thermal Expansion Pressure Over Silicone Durometer Ranges



Solvent Swelling Pressure

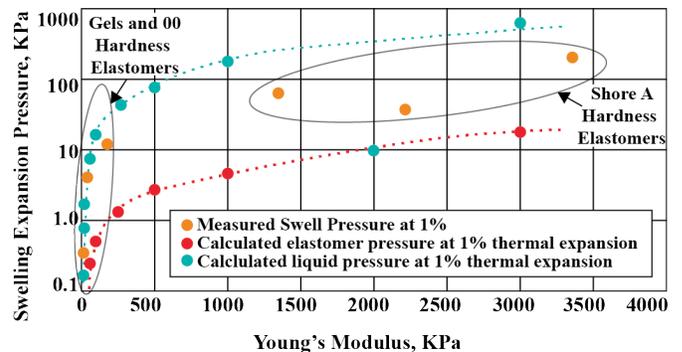
Durometer data was obtained from additions of non-functional polydimethyl siloxane (pdms) fluid to a silicone elastomer. The durometer was converted to Young's modulus and plotted. It should be noted that considerable scatter is typically associated with such conversion plots, but that the calculated modulus has been shown to give a reasonable estimate of the expected modulus at low strains.

Change in Modulus with Volume Swell for a Silicone Adhesive



Pressures were measured for 1% pdms swelling in silicone materials over a wide hardness range. The data has a remarkable resemblance to the pressure graph for thermal expansion, with the main difference being that the harder elastomers were in-between the theoretical lines for liquid-like and elastomer-like expected behavior.

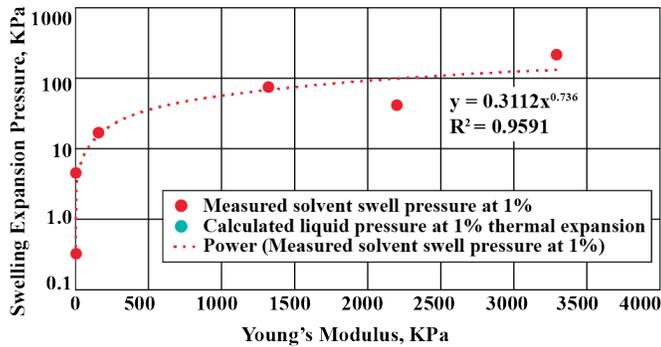
Swelling Expansion Pressure in Silicone Elastomers



The very low modulus, low crosslink density silicone products displayed nearly identical expansion pressures, whether from thermal or solvent swell conditions. Some differences appear to be present above a Young's modulus of about 1 MPa, though with the limited data points it is not known if this difference is truly significant.

Looking at only the measured swelling pressures, the data fits remarkably well to a power equation.

Swelling Expansion Pressure in Silicone Elastomers



Conclusion

Mid-00 hardness and softer silicones were shown to generate expansion pressures that fit well with liquid-like theoretical predictions under both thermal and solvent exposures. Harder silicone elastomers fit well with elastomer-like predictions for thermal expansion, but were in-between liquid and elastomer predictions with solvent swell.

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