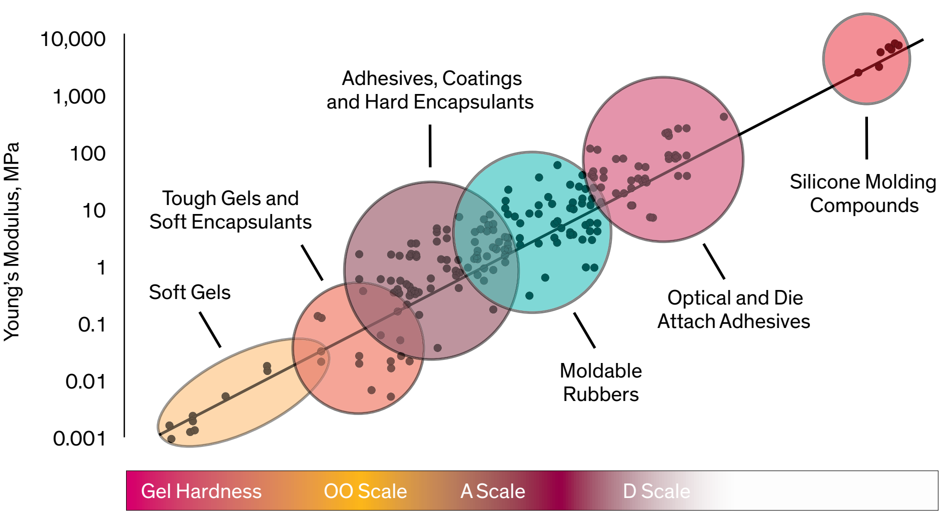
Dow White Paper

Can You Estimate Modulus From Durometer Hardness for Silicones?

Yes, but only roughly . . . and you must choose your modulus carefully!

By Kent Larson



Introduction

Durometer Testing

Durometer hardness testing is a very simple, inexpensive and fast way to characterize elastomers. When used within the boundaries of 10-90 points (or even 20-80) it is quite reproducible and is often used as roughly correlating to Young's modulus. Young's modulus, on the other hand, is not so simply measured, and what many tend to refer to as Young's modulus is in fact only an estimate – and sometimes a poor one at that. Data is also sometimes referred to as a "modulus" when instead it is a tensile strength at a given elongation.

Durometer hardness is measured with a spring loaded indenter. Readings can be impacted by:

- Non-planarity of the material's surface
- Surface defects
- Voids or other defects near the surface (may not be visible)
- Macro non-homogeneities near the surface, such as from poor mixing of two component formulations

The extent of cure/crosslinking of an elastomer has a large impact on the durometer hardness. Products cured at low temperatures can often see a 5A hardness increase when heat cured or after a hot post-cure. Less well known is that concentration gradients can begin to form in many products immediately upon dispensing as some mobile ingredients move toward the container or air interface. For room temperature condensation cure products, such crosslinker and adhesion promoter movement can create a 3-5A hardness difference between the bottom and the top of a sample cured in an open container.

Young's Modulus Testing

Testing of Young's modulus (= "Tensile" modulus = Modulus of Elasticity) is most commonly done by generating a stress/strain curve in tension. Young's modulus is defined as the initial slope of the stress/strain response. However, measuring slope is not as easy, while taking a tensile strength at a given elongation is. Tensile strength divided by elongation is a "Secant" modulus. Such a Secant modulus = Young's modulus only when the stress/strain response is linear. For products that have such a very linear response over a long range of strain, the simplest reasonable estimate of Young's modulus is the tensile strength at 100% elongation.

However, most products do not have such a linear stress/strain relationship. It is common to see an initial steeper slope, followed by a much lower slope that eventually steepens again as the material approaches failure/breakage.

For these products, a Secant modulus at 100% elongation (often referred to as a "100% modulus") may grossly underestimate Young's modulus. In an attempt to refine the estimate, sometimes values will be reported at some smaller strain, such as "10% Modulus" or "25% Modulus". In some cases this will be a Secant modulus, where, for instance, the tensile strength at 10% strain is divided by that strain (0.1). In other cases what is reported may just be the tensile strength at that strain. Generally, a Secant modulus can be a reasonably good estimate of Young's modulus at sufficiently low strains – for many products such as LSRs it seems 25% or less is reasonable, though for other products much lower strains of <5% may be required.

The common practice of reporting "modulus" as the 100% Secant modulus can be misinterpreted as being essentially the same as Young's modulus, but in some applications such a Secant modulus may better describe a material's properties in a given application where typical movement may fall within that range of strain. Likewise, for applications with considerable strain cycling and especially with products having a pronounced Mullins effect, a modulus taken at an application-dependent strain and after a prescribed movement history may be most appropriate to understand performance.

Two other means of estimating Young's modulus are commonly used:

- Dynamic Mechanical Analysis (DMA)
- Rheometric Dynamic Analysis (RDA) or Moving Die Rheometer (MDR)

Common data outputs from both are in the form of storage (G') and loss (G") moduli.

The complex storage modulus (G^*) is defined as: $G^{*2} = G'^2 + G''^2$.

For most curable silicones with a durometer hardness at least into the 00 scale, G' >> G", with G' often >10G". In this case G^* can be reasonably approximated by G'. Note that this may not be the case with very soft materials such as gels, or more "lossy" materials like psa's, hot melts and TPSiVs.

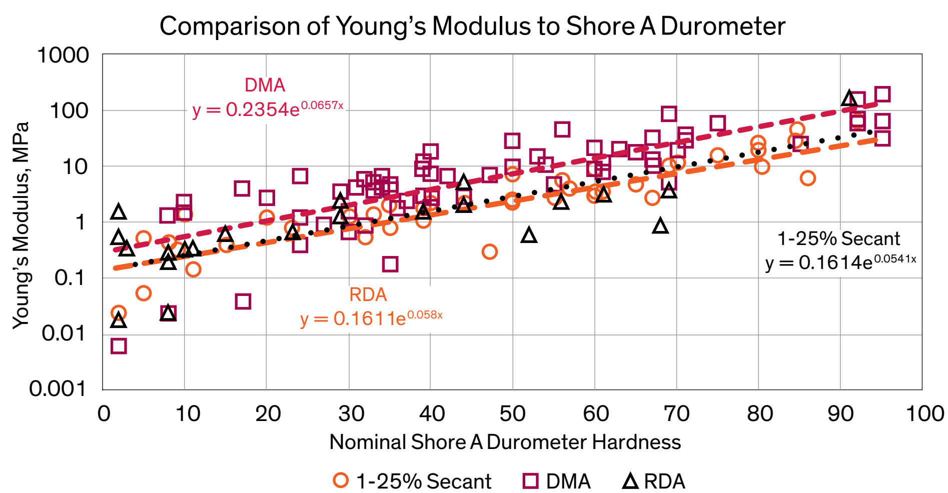
Young's modulus (E) is approximated as: $E = 2G^*(1+ v)$, where v = Poisson's Ratio. For silicones, Poisson's ratio is commonly taken as 0.48-0.495. With 1 + v therefore essentially = 1.5, the equation can be simplified to: E = 3G'.

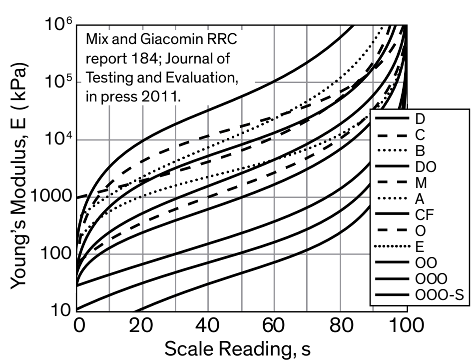
Correlations Between Durometer and Young's Modulus

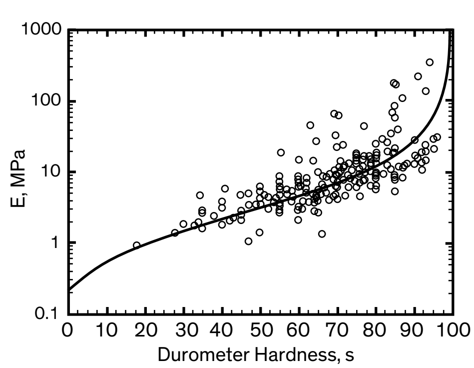
Perhaps the most widely known correlation of durometer values to Young's modulus was put forth in 1958 by A. N. Gent[1]:

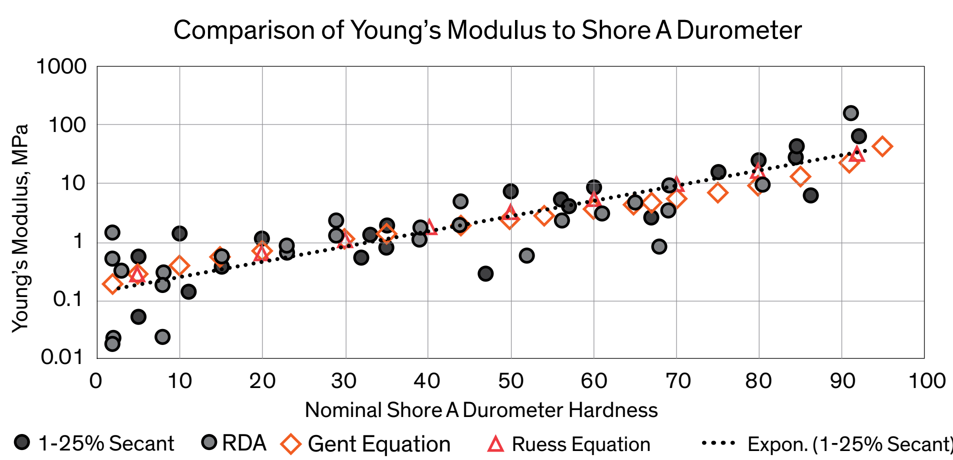
$$E = \frac{0.0981(56 + 7.62336S)}{0.137505(254 - 2.54S)}$$

Where E = Young's modulus in MPa and *S* = ASTM D2240 Type A durometer hardness. This equation is considered a









good first-order approximation of Young's modulus from A hardness of 80 down to 20, though some have considered it of less value below a hardness of 40A. Other equations have also been postulated by Ruess such as[2]:

Shore-A to Young's Modulus (in MPa):
$$\log_{10} E = 0.0235S - 0.6403$$

Shore-D to Young's Modulus (in MPa):
$$\log_{10} E = 0.0235(S + 50) - 0.6403$$

An estimate of the relation between ASTM D2240 type D hardness and the elastic modulus for a conical indenter with a 15° cone is given by Qi[3]:

$$S_D = 100 - \frac{20(-78.188 + \sqrt{6113.36 + 781.88E})}{E}$$

where S_D is the ASTM D2240 type D hardness, and E is in MPa.

Mix and Giacomin[4] derive comparable equations for all 12 scales that are standardized by ASTM D2240.

All of these proposed correlations have been created empirically and suffer from a common issue – significant scatter in whatever data sets they have worked with.

Results

Durometer Scale A – All Products

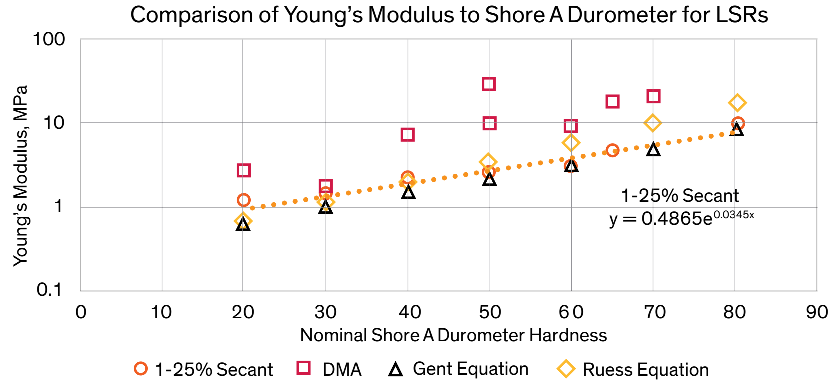
Even with the scatter, there are clear trends. The RDA and Secant derived data have exceptionally similar curve fits, while that of the DMA data is shifted to higher modulus in comparison.

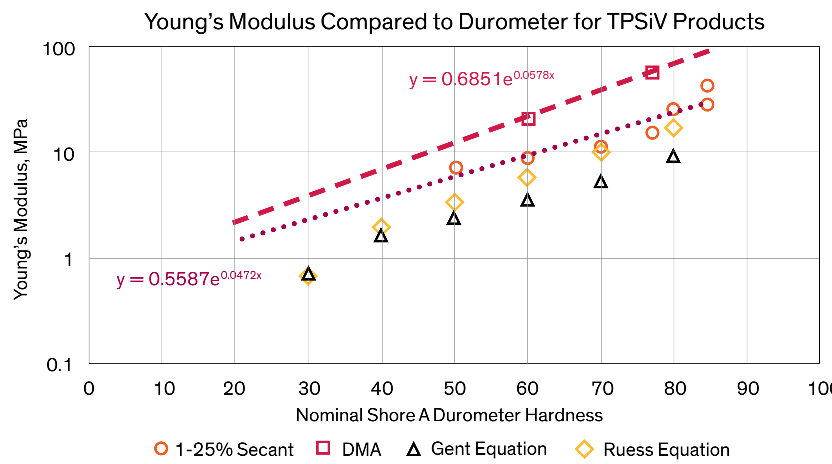
Comparing the Secant and RDA data to the Gent and Ruess equations shows reasonably good correlation, with the Ruess equation perhaps fitting somewhat better.

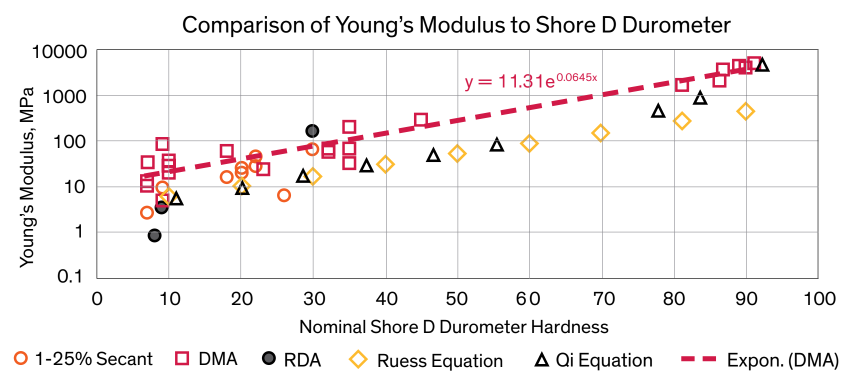
Durometer Scale A – LSRs

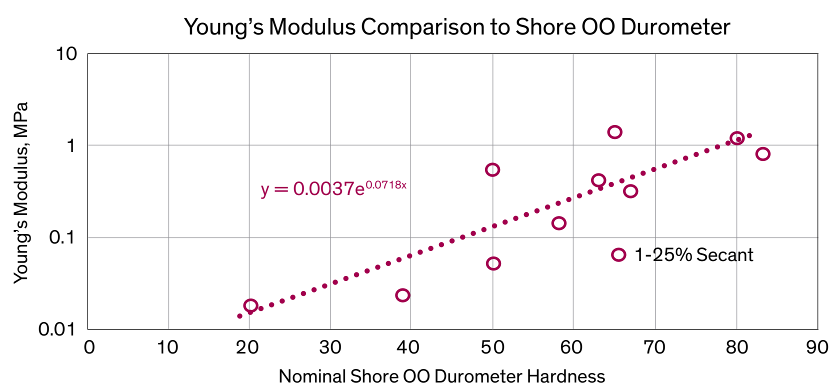
While a great deal of scatter was found within the data when looking across all products within the A hardness scale, much less so was found when narrowing the focus to a given family of products, such as to LSRs.

Here Gent's equation appears to model the data quite well, at least down to 30-40A durometer. The Excel derived









exponential curve fit also appears to fit very well to the data. Again, the DMA derived modulus is significantly higher than that from stress/strain curves (there was not enough RDA data available to plot).

Durometer Scale D

The D durometer hardness scale typically aligns with silicone products with 80A = 20D. This data also had a lot of scatter, and far fewer products that used this hardness scale. The data points above 80D are from Silicone Molding Compounds, assuming their measured Flexural modulus should be a good estimate for Young's modulus[5].

The Ruess and Qi equations do not seem to fit the data very well above 20-30D, although the Qi equation does again fit at about 90D. However, this does follow relatively closely with a comparison of Young's modulus and Shore D durometer found by Pampush[6].

Durometer Scale 00

There was considerable scatter in the data when the durometer values moved into the 00 scale, where a 65 00 usually = about 8A. Looking at just the stress/ strain data, a reasonable fit can be made with an exponential curve.

Limitations When Converting Durometer to Modulus

Besides the obviously large scatter in the data, especially at low hardness values, other factors also influence how a material performs in application induced extensions (and compressions).

- Cyclic stress give way to the Mullins effect, where stress/strain responses are impacted by prior maximum loading stress. Such changes are often recoverable at low strains, but can become permanent at higher strains.
- Material fatigue over time and/or cycling count can induce defects such as tears or cracks that dramatically reduce the stress required to cause failure.
- Exposures to high temperatures, and especially when coupled with compressive pressure can often lead to further crosslinking which can increase modulus and hardness values. This is commonly observed in compression set testing. Such changes can be thought of as further curing at milder temperatures, or they can be a result of oxidative or other degradation mechanisms at higher temperatures.
- Exposure to soluble liquids and oils can cause plasticization, which lowers modulus and hardness. Such changes can be temporary or permanent, depending on the volatility of the contaminant.
- Stress/strain characteristics can be profoundly affected by temperature. Most silicones undergo a slight crystallization around -48°C. Below that transition temperature, these elastomers will be significantly harder and higher modulus. Some silicones contain semi-crystalline silicone resins which can exhibit a melting or softening point. Durometer and modulus characteristics can significantly change when the temperature crosses such transitions.
- Modulus can be impacted by cyclic strain frequency. DMA and RDA are commonly used to characterize property responses over temperature and frequency ranges.

Modifying Modulus

Properties of commercial products are designed to meet standards usually called out in technical data sheets and sales specifications. Modulus and hardness can be unwittingly or purposely modified in several ways.

For two-part products, the specified mix ratio will create a mixture that meets the intended property profile. Products are formulated to allow for expected mix tolerances from dispense equipment, which typically should be ± 3% from reputable vendors. Many products can tolerate ± 5% in the mix ratio without significant impact on cured properties. Going beyond that tolerance can shift modulus, durometer and other properties outside of the product specifications and warranties. In general, using less crosslinker will make cured products softer and lower modulus, while adding more has minimal impact (note, for the extremely soft gels, adding more crosslinker can significantly increase hardness and modulus).

As mentioned in the Limitations, exposure to soluble liquids and oils will essentially plasticize silicones, lowering hardness and modulus. Some formulators will purposely add silicone or organic oils to achieve the same purpose. However, such practices can lead to unintentional consequences, such as oil migration out of the cured silicone (called bleed) which can cause visual blemishes and negatively impact adhesion of adhesives, sealants, paints and inks on nearby surfaces. Over time, such modified silicones may appear to harden and stiffen as the plasticizing oil migrates away. It is generally not recommended to use this approach to modify properties unless there is a very clear understanding of the long term durability effects on the silicone itself and on surrounding surfaces. Note that some silicones are originally formulated with small amounts of such oils – these are commonly called out as "self-lubricating" or other terminology to indicate their presence. Two-part room temperature curing condensation cure silicones also commonly include a small amount of non-curing silicone polymer used as a diluent for the cure catalyst.

Modulus and hardness modifications can be achieved as above, but these can be prone to poor durability of the desired properties as well as other unintended consequences. Other methods to reduce crosslink density in a more stable manner or change reinforcing filler levels can create products with desired hardness and modulus characteristics.

Conclusions

Durometer hardness and Young's modulus should be related since one relates applied stress to extension and the other to an indenter compression. From data collected over a wide range of silicone products the following conclusions could be drawn:

- Curve fits for RDA and stress/strain data matched closely for hardness scales of A and 00.
- DMA showed a higher Young's modulus estimate vs RDA and stress/strain data.
- There was far less scatter in the data when comparing products within at least some formulation series or type, such as for LSRs.
- The RDA and stress/strain data fit reasonable well to equations by Gent and Ruess within the Shore A scale.
- The data also fit reasonably well to a simple exponential curve fit.
- Fitting gel hardness and 00, A and D hardness scales to overlay on known crossover points from the data, Young's modulus could be tracked over seven orders of magnitude within silicone formulations.

The curve fits should allow for calculations of an estimated Young's modulus from durometer readings to a "first order" accuracy that is likely sufficient for many uses.

References

1. A. N. Gent (1958), On the relation between indentation hardness and Young's modulus, Institution of Rubber Industry – Transactions, 34, pp. 46–57.
2. Https://www.3dvision.com/blog/entry/2011/07/14/convert-durometer-to-youngs-modulus.html
3. Qi, H. J., Joyce, K., Boyce, M. C. (2003), Durometer hardness and the stress-strain behavior of elastomeric materials, Rubber Chemistry and Technology, 76(2), pp. 419–435.
4. A. W. Mix and A. J. Giacomin (2011), Standardized Polymer Durometry, Journal of Testing and Evaluation, 39(4), pp. 1–10.
5. Keith Pedersen, CAPinc CAPUniversity, Frequently Asked Questions on Material Properties for Simulation Answered on September 25, 2013.
6. J. D. Pampush, et. al., Technical Note: Converting Durometer Data into Elastic Modulus in Biological Materials, Am. J. OF Physical Anthropology 146:650–653 (2011).

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