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Explaining the spread in measurement of PDMS elastic properties: influence of test method and curing protocol†

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Accuracy in the measurement of mechanical properties is essential for precision engineering and for the interrogation of composition–property relationships. Conventional methods of mechanical testing, such as uniaxial tension, compression, and nanoindentation, provide highly repeatable and reliable results for stiff materials, for which they were originally developed. However, when applied to the characterization of soft and biological materials, the same cannot be said, and the spread of reported properties of similar materials is vast. Polydimethylsiloxane (PDMS), commonly obtained from Dow as SYLGARD 184, is a ubiquitous such material, which has been integral to the rapid development of biocompatible microfluidic devices and flexible electronics in recent decades. However, reported shear moduli of this material range over 2 orders of magnitude for similar chemical compositions. Taking advantage of the increased mechanical scrutiny afforded to SYLGARD 184 in recent years, we combine both published and new experimental data obtained using 9 mechanical test methods. A statistical analysis then elucidates the significant bias induced by the test method itself, and distinguishes this bias from the influence of curing protocols on the mechanical properties. The goal of this work is thus two-fold: (i) it provides a quantitative understanding of the different factors that influence reported properties of this particular material, and (ii) it serves as a cautionary tale. As researchers in the field of mechanics strive to quantify the properties of increasingly complex soft and biological materials, converging on a standardized measurement of PDMS is a necessary first step.

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1 Introduction

Modern engineering of material systems relies on the testing and quantification of a material's mechanical response. The tension, compression, indentation and impact testing methods that most engineers first encounter are all standard for metal samples but may not be appropriate for soft materials, which are significantly more challenging to test. Nonetheless, the use of soft materials is becoming increasingly prevalent in engineering, as researchers try to better understand and interface with the human body, and develop smaller and more compliant material structures and devices. Comparing measurements from a range of techniques, several studies^{1–3} report wide discrepancies in measured stiffness of soft biological materials.

It is notable that despite well documented variations in biological tissue, these discrepancies are often attributed primarily to the testing method and not to material variations.

Even commercially available synthetic materials are hard to test. One example is polydimethylsiloxane (PDMS) where reported elastic moduli range by 2 orders of magnitude for similar compositions, as shown herein. PDMS is a two-part material system and the stiffness of the resulting silicone polymer can be easily tuned to suit the needs of an application. PDMS will cure at room temperature, or can have the curing accelerated with an oven cure. It is widely used in microfluidics,^{4–6} medical devices, and electronics.^{7–9} In engineering mechanics, it is a common surrogate material for method development in the measurement of elastic, adhesion, and fracture response,^{10–14} and as a component in the development of tough materials that can undergo large deformations before failure.^{15–21} The flexibility of composition and cure is particularly useful in the context of biological research where PDMS has been proposed as a scaffold for cell growth,^{22–25} as a biological membrane mimic in microfluidics,²⁶ and in biohybrid devices.^{27–29} Given its widespread use in biology, numerous authors have worked to modify the adhesion, wettability,

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absorptivity, dielectric properties, and mechanical characteristics of PDMS, with comprehensive reviews provided by Wolf *et al.*,³⁰ Zhou *et al.*,³¹ Abbasi *et al.*,³² Teixeira *et al.*³³ and Murphy *et al.*³⁴ However, far less attention has been paid to systematically understanding and measuring the bulk properties of PDMS (or, often, the commercially branded product Dow SYLGARD 184³⁵). The same fabrication flexibility and wide availability that makes commercial SYLGARD 184 applicable across a range of fields also highlights a critical problem of mechanical reproducibility.

The primary goal of this work is to elucidate the bias induced by the testing method in determining the elastic response of soft materials. To this end, we choose SYLGARD 184 as a test case, taking advantage of the breadth of available data in the literature spanning a range of test methods, and combined with new volume controlled cavity expansion (VCCE) data, reported here. The secondary goal of this work is, thus, the interrogation of SYLGARD 184 mechanical properties. While frequent users of SYLGARD 184 often expect minor inconsistencies in the mechanical properties due to changes from the manufacturer[‡], we hypothesize instate that measurement discrepancies can be mainly attributed to bias imparted by: (1) different mechanical testing methods, and (2) wide variation in the cure conditions used for similar mixing ratios.

“Round Robin” studies have been used to compare test methodologies and increase the “reliability and repeatability” of measurements in ceramics,^{39,40} composites,⁴¹ adhesives,⁴² concrete,⁴³ steel,⁴⁴ and many other materials and industries. In their versailles advanced materials and standards report, Kubler *et al.*³⁹ articulate their motivation for conducting the study to determine if the Single-edge-V-Notched beam method for measuring fracture toughness is “user-friendly, reliable and... comparable to other recognised methods.” A similar effort in the context of PDMS elasticity characterization is, in the view of the authors, overdue. To this end, we embark on this study in an effort to understand the magnitude of the problem at hand. We present the scale of variability observed across literature and in our own data, and hope to motivate the community to converge on more consistent preparation, and testing methodologies to improve repeatability for PDMS and across the field of soft material mechanics.

This paper is organized as follows: we begin by describing how studies were chosen for inclusion in this *meta*-analysis (Section 2.1) and provide a brief description of the mechanical testing methods used across the included studies (Section 2.2). We then present the results of our analysis (Section 3) and include new data for moduli obtained *via* VCCE (detailed in

Section 2 of the ESI,[†] Table T1). Finally, we conclude with remarks and cautions on stiffnesses reported in literature for PDMS (Section 4).

2 Methods

2.1 Data gathering

Articles surveyed for this review were found through key word searches and references lists of included articles. Keywords included “elasticity” or “modulus” or “stiffness” and “PDMS” or “polydimethylsiloxane” or “SYLGARD 184”, as well as related derivatives and searches were performed across Google Scholar and Web of Science from January–August 2023. Studies included in the results presented here were those with defined (a) mix ratios for curing agent and base, (b) cure time, and (c) cure temperature. We restrict this study to Dow’s SYLGARD 184. Hence, studies that used other commercial formulations such as GE RTV PDMS silicones were excluded (such as by Liu *et al.*⁴⁵ and some results reported by Schneider *et al.*⁴⁶). Note that one of the most commonly cited studies on PDMS moduli (see Fig. F1 in ESI[†]), Lötters⁷ has not been included as the authors used ABCR PS851 PDMS.

All included studies are summarized in Table T2 of Section S3 (ESI[†]). Studies with parameters listed as “variable” intentionally survey a large range of values and are therefore not listed in the table (though included where appropriate in corresponding figures). New data collected by the authors and included in Table T2 (ESI[†]), is described in Section S2 (ESI[†]) with fabrication and measurement detailed in T1 (ESI[†]).

Dow recommends a mixing ratio of 10 parts base to 1 part curing agent (crosslinker) on a weight to weight basis; we will abbreviate this as 10:1 or more generally $w_B:w_C$. Where the mix ratio was instead reported as a percent, we have converted to the X parts base:1 part curing agent format. All stiffnesses are reported here as shear modulus, μ . Where authors initially reported the stiffness as an elastic or Young’s modulus, E , incompressibility is assumed with a Poisson’s ratio $\nu = 0.5$ ⁴⁷ and $\mu = E/(2(1 + \nu)) = 3E$. For studies investigating viscoelastic material parameters or high strain rate responses, the quasi-static modulus is reported in the summary charts and where only an instantaneous modulus is reported, we denote it as μ_0 . For studies reporting a cure at room temperature, 25 °C was used in plotting and comparison tables.

2.2. Test methodologies

Authors have used a diverse range of test methods to establish the stiffness of PDMS depending on the curing agent ratio in question and goal of the study. The fundamental assumptions and geometries of the different methods are discussed below and depicted in Fig. 1.

2.2.1. Tension. Tension testing was undertaken using a commercial tension test machine in all cases except Brown *et al.*²² who use a fixed applied weight, Upadhyay *et al.*⁴⁸ who perform dynamic testing with a modified split Hopkinson bar, and Fuard *et al.*²⁵ who use a custom stretching tool and load

[‡] The exact composition of SYLGARD 184 is proprietary. Reading the product literature and safety data sheets provides the following insights.^{30,36–38} The base contains a majority dimethylvinyl-terminated dimethyl siloxane (>60%), with a significant portion of silica fillers (30–60% dimethylvinylated and trimethylated silica), as well as 1–5% tetra(trimethylsiloxy) silane and small amounts of ethylbenzene, xylene and a platinum catalyst (<1% each). The curing agent is a majority the cross linking agent dimethyl methylhydrogen siloxane (40–70%), additional methylated silica and siloxanes, and 1–5% the inhibitor tetramethyl tetra vinyl cyclotetrasiloxane.



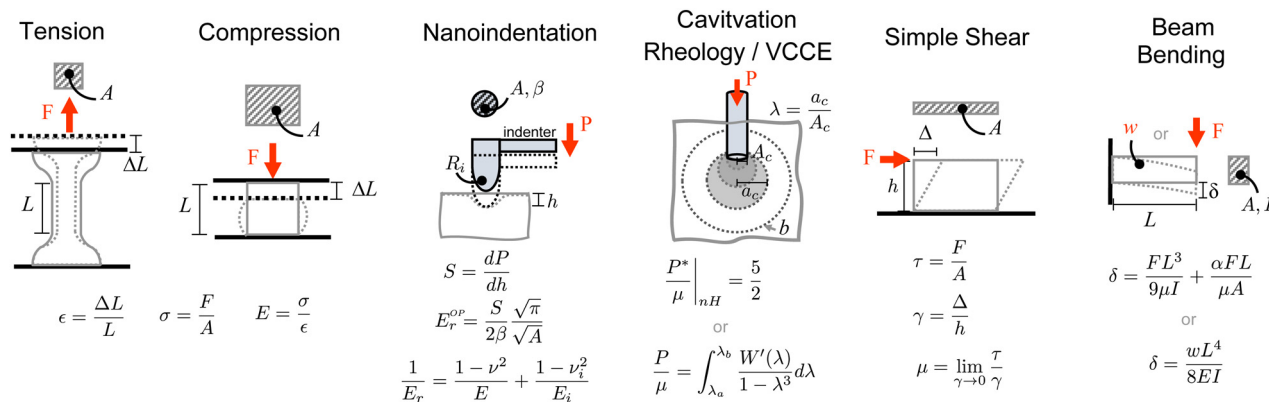


Fig. 1 Common types of testing used to determine shear or elastic modulus, μ and E for PDMS. Variable definitions are included in the text.

cell. Tracking the force F , and sample extension ΔL , from initial length L , the material stiffness is calculated as $\sigma = E\epsilon$ in the linear regime where $\sigma = F/A$ and $\epsilon = \Delta L/L$ are the stress and strain, respectively, for a sample cross sectional area, A . Clamp displacement is used for tracking average sample extension. In ref. 15, 46 and 49–52, while Upadhyay *et al.*⁴⁸ use particle tracking and digital image correlation, Mills *et al.*,⁵³ Seghir and Arscott⁵⁴ and Fuard *et al.*²⁵ use optical image capture and post process with a known calibration, and Brown *et al.*²² use direct measurement. The ASTM Standard D412 for a “Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension”⁵⁵ includes a set of defined sample geometries, ramp rates, and test conditions and was used by^{49,51,52,56,57} who all focus on only a 10:1 base to curing agent ratio.

2.2.2. Compression. Unconfined compression (using $\sigma = E\epsilon$ to determine the elastic stiffness in the linear regime as with tension testing) was employed by Carrillo *et al.*⁵⁸ to compare against nanoindentation, as well as by Wang *et al.*⁵⁹ in their comparison of moduli across curing agent ratios.

2.2.3. Nanoindentation. With an indenter tip possessing a projected contact area A , and geometry described by β , the modulus of a material near a free surface can be determined from the slope of the pressure–displacement curve $S = dP/dh$ of an indentation. Calculating the reduced modulus E_r based on the indenter geometry, then combining with the indenter modulus E_i and Poisson’s ratio ν_i returns the sample modulus, E . Commercially available hardware was used by most authors, however, Mata *et al.*⁵⁷ were the only authors to use the standard analysis method included with their tool, while all other authors reported specifics of their analysis: Patel *et al.*¹³ used the Oliver Pharr method (not accounting for adhesion) to determine E_r^{op} . To avoid the overestimate of modulus that is typical in polymers when using Oliver Pharr, Cheng *et al.*⁶⁰ instead used a Hertzian contact model, whereby

$$E_H = \sqrt{\frac{S^3(1 - \nu^2)^2}{6R_i P_{\max}}}$$

for a spherical indenter with radius of curvature R_i and ν is assumed to be 0.5 for PDMS. Multiple authors acknowledge the significance of adhesion in nanoindentation measurements

and employ the Johnson, Kendall, Roberts (JKR) model instead of Hertzian contact,^{14,58,61} or in addition to it.^{62,63} However, authors disagreed whether the Hertzian contact model returned a higher moduli than the JKR model⁵⁸ or a lower moduli.¹⁴

2.2.4. Volume controlled cavity expansion (VCCE). Controlled injection of an incompressible working fluid at the tip of an injection needle is used to expand a spherical cavity in a sample.^{11,64} The resisting pressure in the cavity P is simultaneously measured to obtain a nonlinear pressure–volume relationship, or equivalently $P = P(a_c)$, where a_c is the effective cavity radius. Comparison with theoretical prediction of elastic, spherically symmetric, cavity expansion in incompressible hyperelastic materials, namely

$$P(a_c) = \int_{a_c/A_c}^1 \frac{W'(\lambda)}{1 - \lambda^3} d\lambda, \quad (1)$$

then allows the determination of material parameters. Here, λ is the circumferential stretch, which varies from a_c/A_c at the cavity wall to 1 in the remote field, $W(\lambda)$ is the corresponding elastic potential energy, and A_c is the initial defect size, which needs to be determined. This method can also be applied to probe viscoelastic properties.⁶⁵

Li *et al.*⁶⁶ use similar assumptions in a cylindrical geometry, finding a very good match between analytical and experimental results.

2.2.5. Cavitation rheology (CR). Alternately, a second type of cavity expansion, cavitation rheology, aims to identify the peak value of the resisting pressure, P^* , and assumes that it is well represented by the theoretical cavitation limit which is then used to determine the material parameters. In contrast to VCCE, this approach does not require control of the injected volume (it typically uses gas as an injection medium). Milner^{67,68} and Yang *et al.*⁶⁹ assume a neo-Hookean material model, which implies $P^* = \frac{5}{2}\mu_{nH}$.

2.2.6. Simple shear. Both Upadhyay *et al.*⁷⁰ and Nunes⁷¹ assume linear (small strain) deformations in simple shear. An

§ This result can be obtained directly from eqn (1) at the limit $\lambda \rightarrow \infty$, with a neo-Hookean form of $W(\lambda)$, as shown in ref. 64.



applied shear force, F , induces a displacement, Δ , and corresponding shear strain $\gamma = \Delta/h$. The shear modulus is then estimated as $\mu = \tau/\gamma$, where the shear stress is $\tau = F/A$ and h and A are sample height and area shown in Fig. 1.

2.2.7. Beam bending. This method relies on connecting the displacement of a beam with known geometry to an applied load. Armani *et al.*⁴⁷ measured tip deflection, δ , of a length L cantilever beam that was displaced under its own weight (w per unit length) and calculated modulus using $\delta = \frac{wL^4}{8EI}$ with I describing the second moment of area. By contrast, Du *et al.*⁷² considered a point load at the tip of a low aspect ratio beam and added a Timoshenko term $\frac{\alpha FL}{EA}$ with the shear coefficient α .

2.2.8. Membrane deflection. A unique measurement method by Thangawng *et al.*,⁷³ uses optical profilometry to measure the membrane deflection of a nanometer thickness layer of spin coated PDMS on a silicone wafer. By pressurizing a circular portion of the membrane with radius r and thickness t , the authors were able to connect deflection, δ , and material modulus as

$$\frac{P}{\delta} = \frac{C_1 t}{r^2} \sigma_0 + \frac{C_2 f(\nu) t}{r^4} \frac{E}{1 - \nu} \delta^2$$

using geometric coefficients C_1, C_2 and $f(\nu)$ and residual stress σ_0 , and again assuming $\nu = 0.5$.

2.3. Correlation analysis

Compiled data is visualized to observe trends and the monotonicity of relationships is quantified using Spearman rank⁷⁴ correlation coefficient, ρ . The Spearman correlation presents the null hypothesis that there is no correlation between an input (predictor) variable and the output, and returns $-1 \leq \rho \leq 1$ indicating whether a monotonic correlation exists, and whether it is negative or positive, respectively. A significance $p < 0.05$ indicates confidence in rejecting the null hypothesis of the data originating from an uncorrelated dataset (more precisely, from a dataset that is less well correlated than indicated by the magnitude of ρ). Spearman correlation is used given the non-normal distribution of all predictor variables, and the desire to not impose a linear relationship between the inputs and stiffness.⁷⁵ Further discussion of the statistical distribution of the predictor variables is given in Section 4 of the ESI.†

The correlation is executed *via* MATLAB 2023 and is applied between preparation conditions (cure temperature, time) and within subgroups of individual test methods in order to isolate where monotonicity might hold internal to a test method, but not within the entire population. While ρ provides indication of how monotonic the relation between two inputs is ($0.3 \leq |\rho| < 0.6$: fair, $0.6 \leq |\rho| < 0.8$: moderate, $0.8 \leq |\rho| < 1$: very strong, $|\rho| = 1$: perfect⁷⁶), it does not indicate the magnitude or linearity of an effect.

3 Results & discussion

3.1 Wide modulus variability and dominance of 10:1 ratio

Despite reportedly identical mix ratios, the measured shear moduli vary by two orders of magnitude between different studies as shown in Fig. 2. We observe that this is due to three main factors: (1) different test methods producing ranging results, (2) variation in specified cure schedule, and (3) the inclusion of non-reactive oils in the base mixture that are sometimes added to manipulate the viscoelasticity of the cured silicone. The histogram in Fig. 2 shows a count of how many experimental results exist by test method across a range of curing agent ratios and highlights how different test methods tend to be used for different stiffness of materials. While combining all the data is useful to inspire caution when using literature reported “stiffness” for SYLGARD 184, diving further into the data is necessary to try and identify the sources of the variability and the key parameters driving the reported ranges.

Table 1 presents the Spearman correlation between shear modulus and key process parameters: curing agent ratio, cure temperature, and cure time. Correlations are calculated for all tests and cure ratios combined using the number of data points N_{tests} listed in Table 1, then separately for select testing methods with data from multiple authors (and conditions) for $N_{\text{tests}} > 10$. The second section of the table presents only tests performed at the 10:1 ratio (that recommended on the product technical data sheet (TDS)³⁵), followed by those excluding this ratio.

Tension testing results tend to be less correlated than other test methods. All comparisons between stiffness and curing agent ratio indicate very strong correlations with an exceptionally low p -value, as expected from the reaction chemistry described in ESI.5.† However, for those tests performed using tension testing, the correlation is only fair to moderate. Examining cure temperature, when all curing agent ratios are considered, the correlation with cure temperature is higher within tension testing than across other methods. However, at the 10:1 ratio where one would expect the dependency to be most cleanly expressed given the elimination of one variable entirely, this trend does not hold and the data fail the correlation with $p = 0.12$. Cure time is weakly correlated when examining all tests combined. However, within individual test methods correlation routinely fails the null hypothesis and predicts a weaker or inverted correlation when evaluated with tension testing. Across all test methods and within tension testing, additional data are required to conclude that there is monotonic correlation.

Note that in the TDS, Dow reports a tensile modulus of 6.7 MPa for a 10:1 mix ratio.³⁵ Though not included in Fig. 2 or Table 1 given incomplete information on test method and cure conditions, this is significantly above all results compiled here.

3.2 False equivalencies arise due to test method

Mix ratio and cure temperature are expected to consistently effect stiffness regardless of the test method. Indeed,



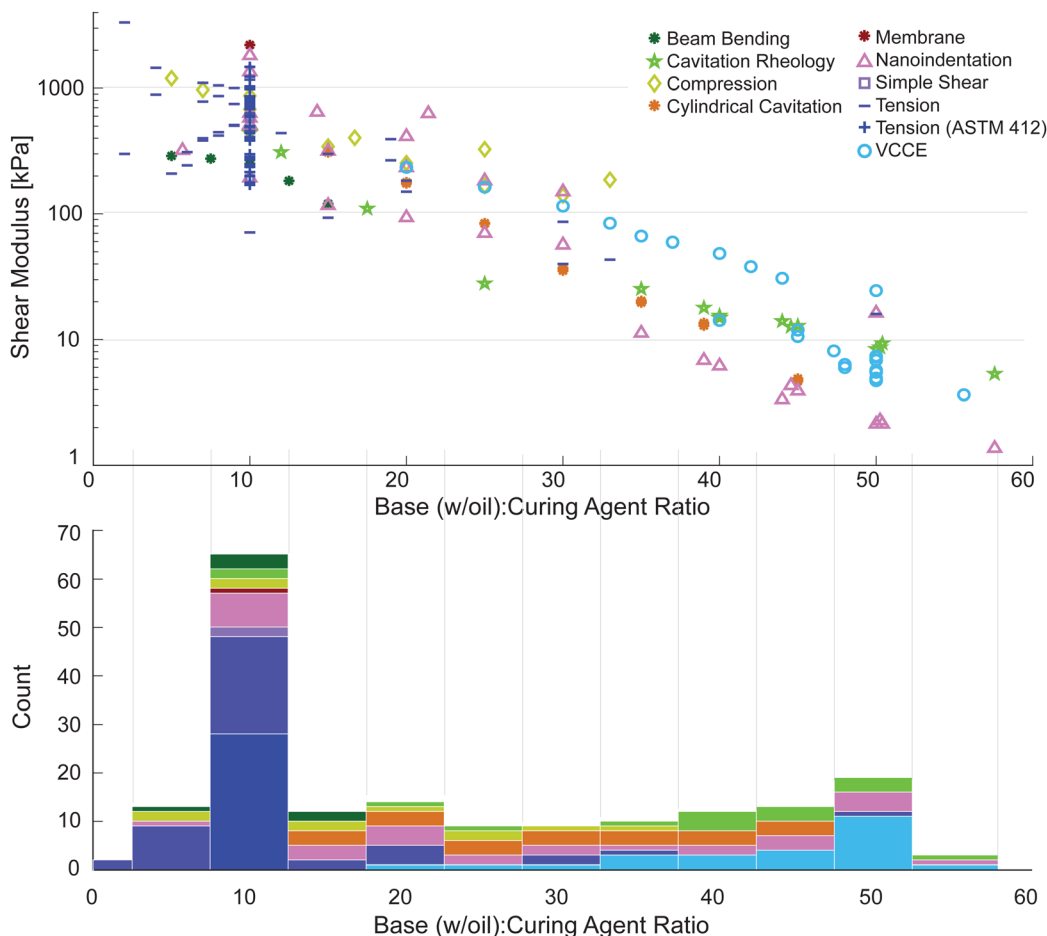


Fig. 2 Stiffness data from all included studies relative to material composition show wide variability in reported moduli. Sorting by test methodology reveals trends in how test methods correspond to mix ratios. The stacked histogram shows that the TDS recommended mix ratio of 10 : 1 $w_B : w_C$ has the most reported data for moduli in literature. The abundance of data at 10 : 1 makes trend interpretation for combined data challenging when studies reporting only a value are averaged in with studies exploring stiffness by mix ratio. Tension testing is common for stiffer samples, however cavity expansion dominates in softer mix ratios while nanoindentation and compression have been used across a range of compositions.

Table 1 Correlations of stiffness with preparation conditions (ρ) and p -value of each. Very strong negative correlations between curing agent ratio and modulus across all test methods and groups of samples appears as expected. The later two sections of the table isolate samples prepared at the 10 : 1 $w_B : w_C$ in order to remove the disproportionate number of tests recorded at this ratio from biasing the results. Blanks in the table indicate cases where conditions are the same for all trials within the row

Test type	N_{datasets}	N_{tests}	Curing agent ratio		Cure temperature		Cure time	
			ρ	p	ρ	p	ρ	p
All tests	36	178	-0.88	0.00	0.32	0.00	-0.29	0.00
Cavitation rheology	3	16	-0.98	0.00				
Compression	2	11	-0.94	0.00	0.52	0.10	-0.52	0.10
Nanoindentation	9	30	-0.90	0.00	0.72	0.00	-0.37	0.05
Tension	12	66	-0.44	0.00	0.43	0.00	-0.16	0.20
VCCE	4	25	-0.92	0.00	-0.85	0.00	0.85	0.00
All tests 10 : 1	27	53			0.30	0.03	-0.37	0.01
Tension	12	38			0.26	0.12	-0.46	0.00
All tests excluding 10 : 1	24	122	-0.92	0.00	0.24	0.01	-0.13	0.14
Nanoindentation	6	23	-0.91	0.00	0.61	0.00	-0.05	0.82
Tension	6	28	-0.63	0.00	0.62	0.00	0.33	0.09

examining Table 1, correlations of stiffness with curing agent ratio and temperature are observed within a given test method.

However, when all methods are combined this correlation is weaker. This provides evidence of test method bias.



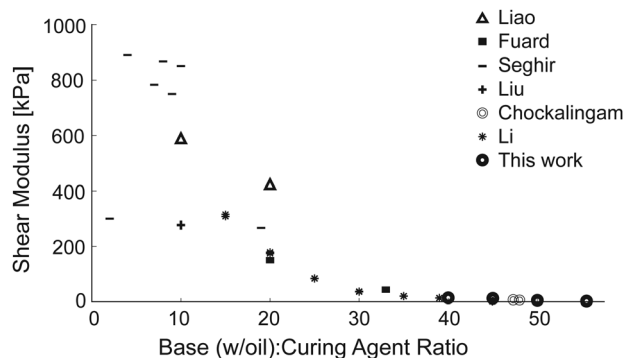


Fig. 3 Test method imparts variability even when a similar cure schedule is used: 120 minutes at between 85 and 100 °C. Test type indicated by marker shape matching those used in Fig. 2.

We hypothesize that the variation imparted by test method is driven by a number of factors including, but not limited to: material rate dependence, such that different methods measure the instantaneous *vs.* relaxed modulus, the additional models required to separate stiffness from adhesion effects in contact measurements, and sample preparation and fixturing imparting imperfections in boundary conditions and defect nucleation.

In an effort to isolate the influence of cure schedule from that of the test method, Fig. 3 compares stiffness for samples cured 120 minutes at 85–100 °C across multiple authors. Particularly for the lower $w_B:w_C$ ratio samples, the measured stiffness varies by hundreds of kilopascals between testing methods. Tension testing inconsistently reports moduli both higher and lower than nanoindentation, and is not used for softer samples. While the general softening trend with higher base ratios can provide a rough qualitative understanding of polymer composition's influence on stiffness, there is minimal overlap in test methods that are used between soft samples and stiff samples, leaving open the question that the trends are due to the test methodology.

Restricting the $w_B:w_C$ ratio to a more narrow range and examining three cavity-expansion based methods, encourages caution about biases that may be more pervasive in the dataset. Fig. 4 compares the μ_0 of Yang *et al.*⁶⁹ measured through CR and assuming a neo-Hookean material model, to results obtained *via* VCCE for comparable mix ratios (oil containing samples are excluded). The VCCE results from Raayai-Ardakani *et al.*^{11,64} are also μ_0 , while those of Chockalingam *et al.*⁶⁵ and this work are μ .

As expected from a solid mechanics perspective, $\mu < \mu_0$ when measured with VCCE with instantaneous moduli more than double the quasistatic moduli for comparable $w_B:w_C$ ratio. However, in these datasets, all samples used to measure μ were cured hotter and for less time than all samples to measure μ_0 . This results in the inversion of ρ in Table 1 for both cure temperature and time when considering VCCE independently. This inversion is another indication that the comparison of measured stiffness between different test methods and/or cure protocols can be misleading.

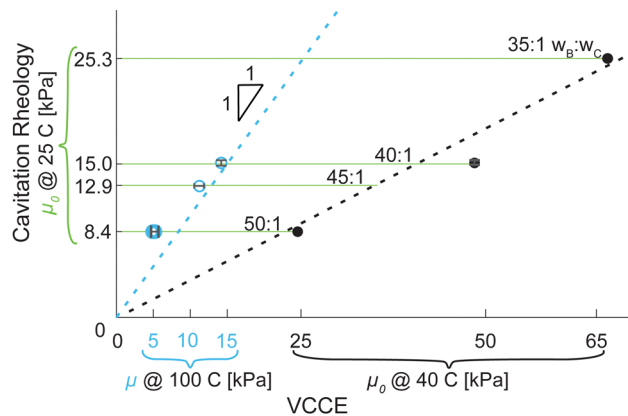


Fig. 4 VCCE results of^{11,64} for μ_0 (filled marker), as well as μ from Chockalingam⁶⁵ and this work (unfilled cyan circle, cyan axis labels) compared to CR results for μ_0 by Yang *et al.*⁶⁹ Horizontal green lines specify the measured μ_0 from cavitation rheology for comparable mix ratios ($w_B:w_C$ as noted on plot) measured with VCCE. Dashed lines are visual aids depicting both a 1:1 correlation for $\mu:\mu_0$ and lack of correlation for $\mu_0:\mu_0$.

Furthermore, it can be seen on Fig. 4 that μ_0 does not correlate 1:1 between CR and VCCE. The observed deviation between Raayai-Ardakani and Yang *et al.* can therefore be attributed to the 6 day room temperature cure of Yang *et al.* producing softer samples than the 3 days at 40 °C cure schedule used by Raayai-Ardakani. By contrast, the unexpected 1:1 correlation between μ_0 by CR and μ by VCCE (blue line on Fig. 4) is likely attributed to the discrepancy between the room temperature cure schedule used by Yang *et al.*⁶⁹ and the 100 °C 2 h schedule used by Chockalingam *et al.*⁶⁵ and this work.

3.3. Hotter cures result in stiffer material

An increase in cure temperature is more directly correlated to a monotonic increase measured stiffness (fair correlations considering the full data set) than is an increase cure time (weak – fair correlations). Fig. 5 shows that cure temperatures evaluated

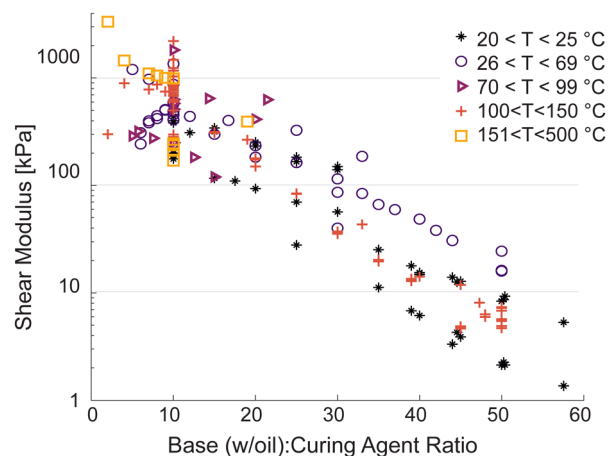


Fig. 5 Cure temperatures are not equally likely across all $w_{B+oil}:w_C$ ratios. Room temperature cures are more common for larger ratio samples and cure temperatures over 150 °C are rarely seen for mix ratios over 10:1.



are not uniformly distributed amongst the base:curing agent ratios, with larger ratios being more often cured at room temperature and never over 150 °C compared to the stiffer, low ratio, samples. This likely compounds the effect of higher mix ratio samples appearing softer due to both lower temperature and less curing agent.

Table 1 also shows the counterintuitive result that longer cure times correlate with softer samples, however this is likely due to the significantly longer times used with room temperature curing. While stiffness does not follow a linear trend with all predictor variables (as is clear from Fig. 3) a basic regression performed on the complete data set provides insights into the relative importance of temperature, time, and curing agent ratio. Utilizing MATLAB 2023b to fit a linear regression model, cure temperature is connected to stiffness as 2.71 kPa °C⁻¹ (standard error SE of 0.74 kPa °C⁻¹) while cure time is effected as 0.004 kPa min⁻¹ cure (SE 0.006 kPa min⁻¹ and a $p > 0.05$, thus failing the assumption of a linear correlation). Curing agent ratio is most strongly linked to stiffness as -15.5 kPa/1 w_{B+oil} (SE 1.7 kPa/1 w_{B+oil}). Contour plots depicting the interplay between all three predictors can be seen in Section S6 of the ESI.† With the strength of the correlation between temperature and stiffness, the tendency of lower temperature curing to produce softer samples overshadows the effect of longer cure times producing stiffer samples.

In an effort to reduce the variability imparted by different test methods, Table 1 is subdivided by test types and further to isolate 10:1 ratio samples. Across nanoindentation and tension testing, the correlation between cure temperature and stiffness increases to moderate – strong when test methods are considered independently, and is even stronger when 10:1 ratio samples are excluded (confirming that the number of tests performed only at this ratio may be biasing the overall trends in results).

There is, however, a limit at which higher temperatures will no longer produce stiffer samples and instead will degrade the polymer. Liu *et al.*⁵¹ set out to study the effect of heating on PDMS mechanical properties and also observe that stiffness increase between 100 and 150 °C, but decreases for 200 °C and 300 °C samples.¶

3.4. Nonreactive oils act as part of the w_B in stiffness trends

Oil-based thinners have been proposed as a method to decouple the viscoelastic and elastic responses of PDMS without effecting the stiffness.^{56,69} An unspecified “thinner” was used by Schneider *et al.*⁴⁶ while Moučka *et al.*⁵⁶ use 194 cSt silicone oil and Chockalingam *et al.*,⁶⁵ Yang *et al.*⁶⁹ and the new results presented in this work use 350 cSt silicone oil added to the base.

Fig. 6 shows that the correlation of shear modulus to mix compositions is stronger when the added oil is included in the w_B than when it is not. The correlation for Yang *et al.* increased

¶ The data displayed here from Liu *et al.*⁵¹ have been down selected to only the 100 °C and 200 °C data, though 150 °C and 300 °C cure temperatures were also evaluated in the original work.

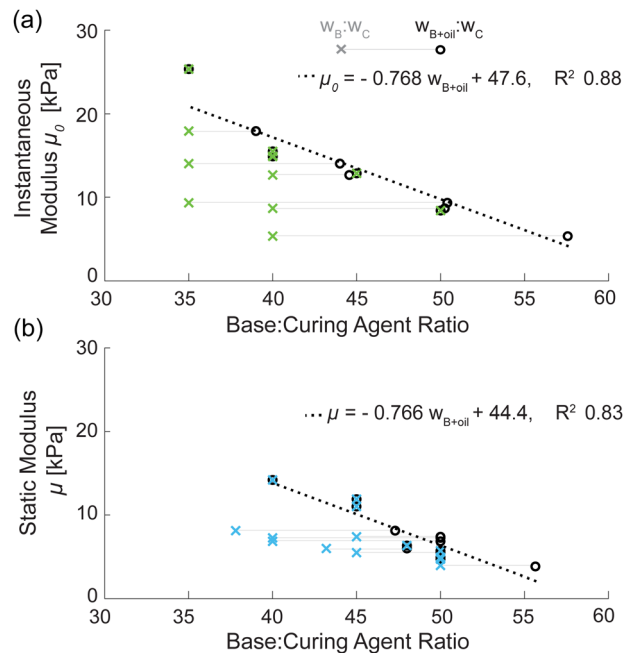


Fig. 6 If $w_B:w_C$ is considered without taking oil into account (crosses), the correlation of ratio with stiffness is not as strong as when $w_{B+oil}:w_C$ is considered (circles) and the R^2 of a linear fit drops from 0.88 to 0.21 for CR and 0.83 to 0.31 for VCCE. (a) shows μ_0 from Yang *et al.*⁶⁹ against an abscissa calculated both with and without oil included in w_B ; (b) depicts μ from Chockalingam *et al.*⁶⁵ and this work.

to $|\rho| = 0.96$ from $|\rho| = 0.47$ and $|\rho| = 0.85$ from $|\rho| = 0.74$ combining Chockalingam *et al.* and this work. Across both sets of data, increasing $w_{B+oil}:w_C$ reduces the observed shear modulus (μ or μ_0) by a similar amount (0.768 vs. 0.766 kPa per added w_{B+oil} with a linear fit to the data in this region). While all authors report changes to the viscoelastic time constants when including nonreactive oils, the trend in softening with increasing w_{B+oil} for soft PDMS is shown to be consistent (a) regardless as to whether the ratio is altered with base or oil, and (b) in both instantaneous and quasistatic modulus.

3.5. Reaction chemistry offers hypotheses for variation

A number of the studies point out changes in mechanical properties of SYLGARD 184 within days to weeks after completing cure.^{60,65} Cheng *et al.* showed nearly a doubling in stiffness with 18 vs. 3 days of storage at room temperature after an initial cure. In their work with pure PDMS, Esteves *et al.* propose that secondary reactions occur as PDMS polymerizes.⁷⁷ They observed that consumption of Si-H groups in the cross linker cannot be fully explained by hydrosylation (the conventionally understood pathway of PDMS cross linking) thus requiring that additional pathways are present. These additional pathways would be effected by ambient oxygen and moisture, pointing to relative humidity during fabrication as an additional parameter to consider in fabrication and storage of PDMS.

Recent work by Bardelli *et al.*⁷⁸ points to cure temperature as a factor in changing the molecular weight between crosslinks M_c in PDMS. As described in ESI.5,† M_c is directly connected to



the stiffness of a polymer. Bardelli *et al.* observe nearly a doubling of μ between a 4 hour cure at 65 °C compared to 150 °C (with M_c decreasing from 2050 to 1050 g mol⁻¹). Additionally, if lower temperature cures allow for more secondary reactions to take place, this could explain the resulting solid being softer.

4. Conclusions

The choice of mechanical testing method can have a significant influence of the measured stiffness of soft materials. Using commercially available PDMS (SYLGARD 184) as a test case, we examine this bias by combining new experimental data and that surveyed from 33 published papers, spanning 9 different testing methods. Statistical analysis reveals that bias imparted by test method is compounded by inconsistent curing approaches. The current methods of both testing and reporting are thus far from providing reproducible results for the mechanical properties of SYLGARD 184 and, by extension, for other soft and biological materials. A number of steps must be taken to better observe the properties that so many authors to date have claimed to measure.

Test method has been implicated previously as returning variable measurements within identical soft material samples, and PDMS is no exception. Tension tests on PDMS reported the widest variation of stiffness, with nanoindentation also providing widely variable results. Though these are both common testing techniques, we recommend caution in the use of both methods. At low mixing ratios PDMS is brittle⁵⁴ and tension testing is highly sensitive to surface imperfections on the sample, while at higher $w_B : w_C$ ratios, the soft modulus means that results are influenced by the clamping conditions, without a guarantee that it is possible to set up a successful test at all. The variability of nanoindentation is likely due to the uncertain nature of the adhesion between the sample and indenter tip, which was the focus of many of the authors referenced here. Using such a method that relies on consistent surface adhesion, in a material where surface treatments are applied to widely varying degrees, will continue to produce imprecise results.

The limitations of testing make it challenging to characterize the composition–property relationship of SYLGARD 184. This difficulty is further accentuated by the inconsistency of fabrication conditions and reporting of curing protocols. At present, cure schedules ranged widely between researchers with very little overlap if the authors were not currently or historically from the same research group. Of utmost importance is fully reporting the cure schedule and preparation method, as well as timing between cure and test. Unifying how PDMS is cured to obtain well characterized responses could help to enhance data comparisons and reliability. Hence, we would propose three temperatures for PDMS where control of mechanical properties is desired: a 25 °C room temperature, a “moderate” 60 °C at or below the glass transition temperature of plastics commonly used in additive manufacturing, and a

“hot” 100 °C for rapid curing. Curing times may vary depending on sample geometry.

Each researcher has unique needs and capabilities for their research, and not each mechanical testing method is possible for a given sample. As soft materials research continues to expand into more complex and biological systems that present additional challenges for reproducible measurements, building agreement around common synthetic soft materials is worthwhile for the community. By noting the current discrepancies in literature on PDMS and by advocating that work going forward place a greater emphasis on consistency and comparison to the full body of literature (not selected works that happen to align with ones results), we anticipate better agreement in measured mechanical properties is easily attainable and hope that this manuscript motivates this as a community goal.

Author contributions

Hannah Varner: writing – original draft, writing – review & editing, conceptualization, investigation, data curation, methodology, formal analysis, visualization. Tal Cohen: conceptualization, writing – review & editing, resources, supervision.

Data availability

All of the data for this paper is provided in the main text and the ESI.†

Conflicts of interest

There are no conflicts to declare.

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