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Comparison of the macroscale and microscale tests for measuring elastic properties of polydimethylsiloxane

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ABSTRACT: Polydimethylsiloxane (PDMS) has many biomedical applications, since it is biocompatible, easy to fabricate and inexpensive. The response of biological cells and tissues is affected by the mechanical properties of the PDMS surface, which can be controlled by varying the crosslinking percentage. It is essential to find reliable ways to measure elastic properties of PDMS prepared with different surface conditions or stiffness gradients. In this paper, the elastic modulus of PDMS was measured at different scales as a function of the crosslinking percentage varied from 2% to 9%. Macroscopic compression and tension tests were used and compared with the nano-JKR (Johnson-Kendall-Roberts) method applied to a microindentation test. Depending on the test, the PDMS elastic modulus increased from 10 to 85 fold with the crosslinking percentage change from 2% to 9%. The PDMS elastic modulus varied as a sigmoid function with the crosslinking percentage for each type of test. The compression macroscale test is the easiest way to estimate the elastic modulus of stiffer PDMS with higher crosslinking percentage. For the more compliant and tacky PDMS samples with lower crosslinking percentage the nano-JKR test is more suitable, as it is sensitive and accounts for the surface adhesion forces. The samples with the lower crosslinking percentage are much less stiff in tension than in compression, resembling liquid-like behavior. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42680.

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INTRODUCTION

Polydimethylsiloxane (PDMS) is a synthetic silicone polymer, which is widely used in biomaterials research for several reasons, including biocompatibility and lack of toxicity. PDMS also has adequate mechanical stiffness for biological applications. PDMS mechanical properties can be controlled by changing the weight percentage of the crosslinker, curing time or temperature.[1–3] PDMS is inexpensive and can be easily fabricated into different shapes and sizes, which makes it attractive for many biomedical applications.[4,5]

Characterizing mechanical properties of cured PDMS is an essential step for using it in medical applications, since biomaterials mechanical properties have a notable effect on cells and tissues response.[6,7] However, measuring the elastic modulus of PDMS is challenging for several reasons. First, many experimental factors can affect the measured data, such as the loading rate and the sample geometry. Second, during the tensile test PDMS undergoes large deformation under quite low load before its measured stiffness increases. Third, PDMS can be formed with stiffness gradients,[8] or have its surface spatially modified,[9] rendering it non-uniform and unsuitable for tensile testing. Furthermore, PDMS is a high surface energy material, thus the adhesion force between the PDMS surface and the tip during a compression test can affect the measurement.

This study focuses on measuring the elastic modulus of PDMS over a wide range of physiologically relevant stiffness, using compression testing at the macroscopic and microscopic length scales. All the samples were prepared using the same procedure, and two different methods at different scales were used to confirm the change of PDMS elastic modulus as a function of the crosslinking percentage. The results were compared with the tensile tests, and the sigmoid stiffness dependence on crosslinking was obtained, providing a simple way to predict elastic modulus over a wide range of crosslinking percentage.

THEORETICAL BACKGROUND

The Macroscale Compression Model

There are multiple chemical and physical factors, which can affect the mechanical properties of PDMS, or limit the ability to measure these properties.[10–12] Chemically all the samples should

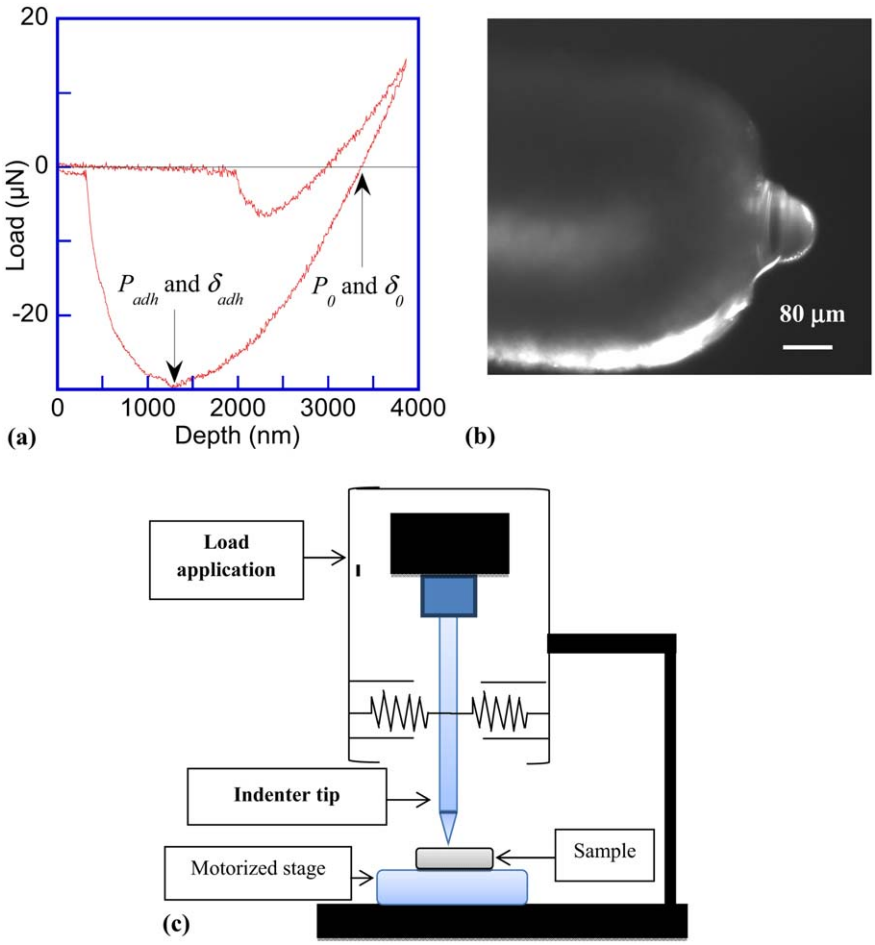

Figure 1. (a) Load-displacement indentation and pull-off curves for the 20 : 1 PDMS obtained with the spherical 80 μm diameter tip; (b) Optical image of the custom-made 80 μm diameter spherical tip. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be prepared in the same way. The strain rate and the sample dimensions have an obvious effect on the measured elastic modulus with the macroscale test, which has been detected in previous work using the same compression device as in this study.[10] In order to avoid the influence of the sample shape and the loading rate on the resulting data, an elastic half-space model has been used in this paper. This model was first offered by Lambe and Whitman in 1969, and consists of applying a constant compression load on top of a planar sample.[13] In this model, a uniform load is applied over a small area of the soft sample. Sample thickness and the diameter of the loaded area should not be higher than the 1/4 of the diameter of the total tested surface.[14] Normal force and displacement were recorded and used to solve the following equation for the elastic modulus:[15]

$$E=\frac{2(1-v^2)qa}{w} \quad (1)$$

Here, E is the elastic modulus in MPa, v is the Poisson's ratio (0.49 for PDMS),[14] w is the recorded displacement, q is the applied load density, i.e., stress, and a is the radius of the circular contact area under load.

For comparison, PDMS strips were subjected to a macroscopic tensile test. Hooke's law was used to calculate the elastic modulus:

$$E=\frac{qL}{\Delta L} \quad (2)$$

Here, L is the initial sample length and ΔL is the change of the sample length as a result of the applied stress, q.

The Nano-JKR Model

For the microscale compression testing using an indenter, the measured stiffness is highly sensitive to the contact area between the probe and the sample. The surface energy of this soft material results in the adhesion force, which causes pull-in and pull-off events, obscuring the point of initial contact and thus affecting the contact area estimation. These factors present major challenges for the microscale characterization of soft materials, including PDMS.[16,17]

Ebenstein described a Johnson-Kendall-Roberts (nano-JKR) method using the spherical tip to overcome these limitations.[18] This model requires collecting the full loading and unloading force-displacement curve [Figure 1(a)]. The spherical tip should be placed well above the sample surface, so that the full tip-surface interaction during the initial approach and loading is captured. The data collection should continue during the unloading to capture the tip pull-off event, until no force is sensed by the indenter. This model is known as the nano-JKR force curve and only requires two data points from the unloading

portion of the curve to calculate the reduced modulus, P_0 at δ_0 and P_{adh} at δ_{adh} [Figure 1(a)]. The first point is when the unloading force equals zero (P_0 and δ_0), whereas P is the applied force and δ is the displacement. The second point is recorded when the unloading curve reaches the minimum force, which represents the adhesion force (P_{adh} and δ_{adh}).[19,20] By knowing these two points, the following equation allows to calculate the reduced modulus, E_r:[18]

$$E_r = \frac{-0.95P_{adh}}{\sqrt{R}}(\delta_0 - \delta_{adh})^{-3/2} \quad (3)$$

Here, R is the spherical tip radius, and the minus sign accounts for the measured negative pull-off force. Using the reduced modulus, E_r, and the Poisson's ratio, v, the elastic modulus, E, can be calculated as:

$$E = (1 - v^2)E_r \quad (4)$$

The nano-JKR force curve model is applicable only for materials with low elastic modulus and high surface energy, and a large diameter spherical probe tip is required ($R \geq 30$ μm).[21] The special spherical tip with the 80 μm diameter was made for these measurements, shown in Figure 1(b).

MATERIALS AND METHODS

Sample Preparation

PDMS was purchased from Dow Corning Corporation as a kit of two components (Sylgard 184, Dow Corning Corporation, Midland, MI), prepolymer base and crosslinker. The components were mixed and cured to form the elastomer network. Seven different PDMS base to elastomer weight ratios were tested in this experiment, 10 : 1, 11.5 : 1, 16.5 : 1, 20 : 1, 30 : 1, 40 : 1, and 50 : 1. These PDMS samples were prepared by well mixing of the polymer base with the crosslinker, and using different weight ratios of the curing agent to get different polymer stiffness. It was manually mixed for 15 minutes for the higher crosslinker amounts and 30 minutes for the lower crosslinker amounts. All PDMS mixtures were degassed using a vacuum pump, and then poured over clean polystyrene Petri dishes. All the samples were about 1–2 mm thick. They were cured at 65°C for 20–24 hours. Parallel samples from the same three preparations were used for all three methods. In some, but not all, cases identical samples were tested with both compression methods.

Macroscale Compression Test

In this study, a custom-built load-displacement measuring device was used to run a compression test and measure the elastic modulus.[21] PDMS samples were peeled from the Petri dishes and then subjected to a constant load of 20 g, and after 15 sec from loading the maximum displacements were recorded. By knowing the Poisson's ratio of the PDMS samples (0.49), eq. (1) was used to calculate the elastic modulus for each sample. Three different samples were tested for each stiffness and five different positions of each sample were loaded, then the average resulting value was calculated as the elastic modulus.

Macroscale Tensile Test

Pelham and Wang's procedure was followed for tensile testing.[22] The thickness of PDMS samples that were subjected to tensile load was about 2 mm, while the cross section area of these samples ranged from 6.8×10^{-6} m^2 to 1.6×10^{-5} m^2. During tensile testing the force between 1 N and 9 N for the stiffer strips and between 0.5 N and 4 N for the softest samples was used with the maximum strain of 1.3. About 30 seconds after loading, a minimum of 5 displacements were recorded for PDMS samples stretched by the applied force, and the elastic modulus was estimated from the linear slope of the stress versus strain plot. Figure 2 represents schematic diagrams of macrosacle compression and tensile test setups.

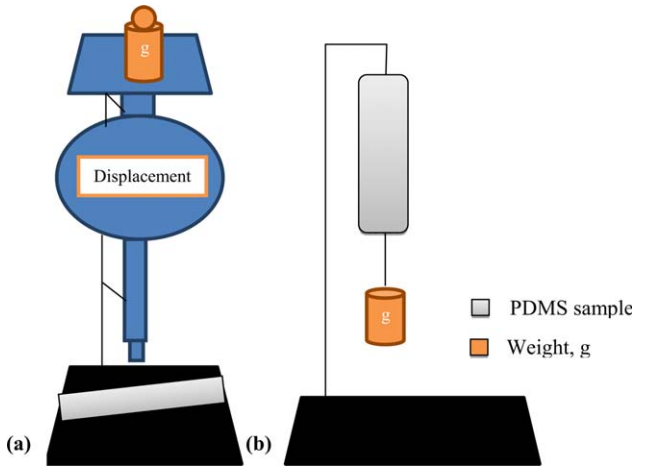

Figure 2. Schematic diagrams of the macroscale (a) compression and (b) tensile test setups. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Microscale Nano-JKR Force Curve Test

Cured PDMS polymer was peeled and cut into 1 × 1 cm^2 square sample with a knife, and then placed on the nanoindenter stage. Hysitron Triboindenter (Hysitron, USA) was used for the nano-JKR experiments equipped with the custom-built spherical tip. To make the spherical tip, 80±2 μm borosilicate glass microsphere (Corpuscular, Cold Spring, NY) was glued onto the end of 1 cm long tungsten wire with 550 μm radius. The radii of the glass microsphere and the tungsten wire were measured using the Nikon Eclipse Ti-U microscope. The optical image of the tip is shown in Figure 1(b). The setup of this test is shown in Figure 1(c).

According to the previous study, slow loading rate (≤100 nm/s) is preferred to provide accurate adhesion force measurements.[16] In this study, all samples were loaded under constant rate of 60 nm/s, and the loading started from about 2 μm above the sample surface. Force-displacement curves were recorded for seven different stiffness PDMS samples, and three samples were tested for each stiffness (crosslinking percentage).

RESULTS

Measuring the elastic modulus of the PDMS samples of different stiffness is challenging because of its tendency for large deformation. The PDMS samples with the crosslinking ratio of 30 : 1 or higher were increasingly tacky. Thus, the maximum ratio tested was 50 : 1 base to crosslinker weight ratio. The minimum base to crosslinking ratio tested was 10 : 1. In general, most PDMS for biological applications is made with the weight

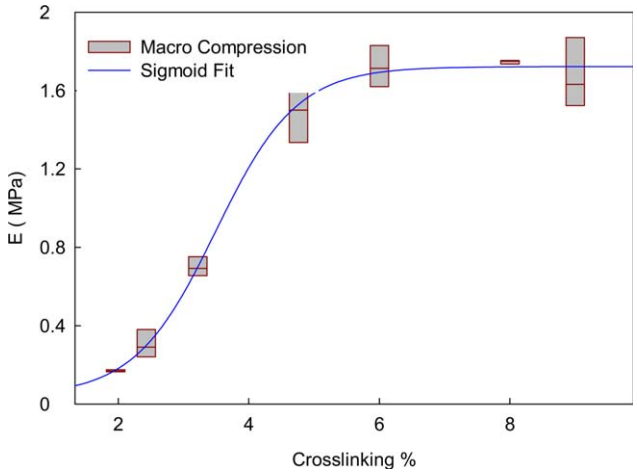

Figure 3. The macroscale PDMS compression test elastic modulus results and the corresponding sigmoid cure fit. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

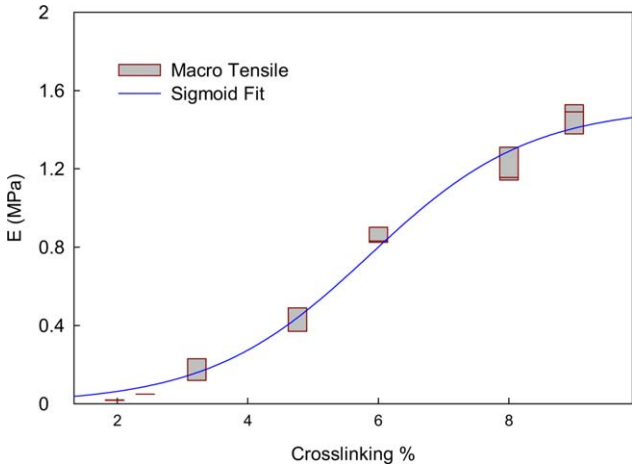

Figure 4. The macroscale PDMS tensile test elastic modulus results and the corresponding sigmoid cure fit. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ratios no higher than 10 : 1.[1] When the 5 : 1 and 2.5 : 1 ratios were tested at the macroscale, there were no noticeable differences between those samples and the 10 : 1 PDMS (data not shown). In fact, the elastic modulus of the higher base to crosslinking weight ratio was slightly less than the elastic modulus of the 10 : 1 PDMS, and close to the elastic modulus of 20 : 1 PDMS. This behavior has been reported previously, presumably due to voids or inhomogeneities caused by the excess crosslinker.[23] All measured elastic moduli were plotted as a function of the crosslinking percentage, which is the inverse of the base to the crosslinker weight ratio.

Macroscale Testing Results

Consistent with the PDMS material stiffness increase by adding more crosslinker, there was a 10 to 85 fold increase in the elastic modulus when the crosslinking ratio increased from 1.96% (50 : 1 PDMS) to 9% (10 : 1 PDMS). Figures 3 and 4 present the data range of the compression test and tensile test results, respectively. The corresponding average values are listed in Tables I and II for compression and tensile tests, respectively. 1.75 ± 0.08 MPa was the maximum elastic modulus measured for the 10 : 1 PDMS, while the lower 0.17 ± 0.009 MPa value of the elastic modulus was measured for the highest tested crosslinking ratio of 50 : 1. Tensile testing showed a similar trend, however, the elastic modulus increased over 85 fold from 0.018 ± 0.0011 MPa to 1.545 ± 0.122 MPa with the higher crosslinker percentage. This difference between the measured elastic properties in tension vs. compression can be attributed to the less compliant samples behaving more like a liquid rather than a solid in tension. While it is possible to measure water stiffness in hydrostatic compression, a tensile test on water would be challenging, with larger contribution of the surface tension forces. Ashby argued that a true solid would have an elastic modulus above 1 GPa, thus the samples tested here do not qualify as the "true" solids, according to this approach.[24]

Microscale Testing Results

As expected, changing the testing scale and procedure changed the resulting elastic modulus values. However, the change of PDMS stiffness still has a similar trend with the increasing crosslinking percentage (Figure 5 and Table III). In general, the measured elastic modulus values using the nano-JKR force curve method are less than those measured with the macroscale tests, in which the elastic modulus of the 10 : 1 PDMS samples is 1.24 ± 0.08 MPa and for the 50 : 1 PDMS it is 0.1 ± 0.02 MPa.

Table I. PDMS Macroscale Compression Test Elastic Modulus Results

Base to crosslinker ratio	10 : 1	11.5 : 1	16.5 : 1	20 : 1	30 : 1	40 : 1	50 : 1
Crosslinking (wt %)	9	8	6	4.76	3.22	2.43	1.96
E (MPa)	1.75	1.74	1.72	1.7	0.83	0.33	0.17
Standard deviation	0.08	.009	.0104	0.05	0.039	0.005	0.009

Table II. PDMS Macroscale Tensile Test Elastic Modulus Results

Base to crosslinker ratio	10 : 1	11.5 : 1	16.5 : 1	20 : 1	30 : 1	40 : 1	50 : 1
Crosslinking (wt %)	9	8	6	4.76	3.22	2.43	1.96
E (MPa)	1.545	1.2	0.0852	0.445	0.17	0.05	0.018
Standard deviation	0.122	0.09	0.042	0.09	0.07	0.0035	0.0011

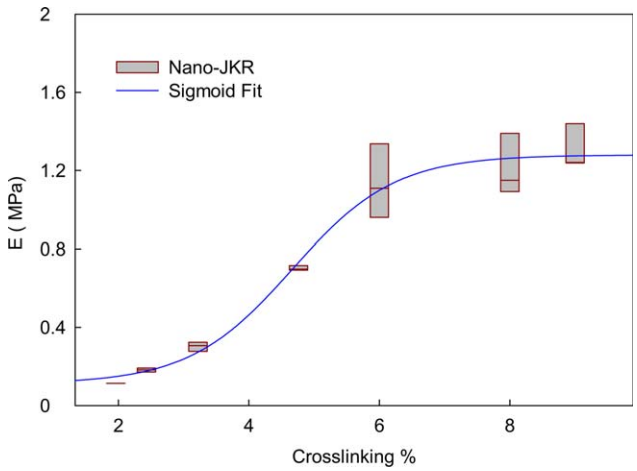

Figure 5. The microscale PDMS nano-JKR test elastic modulus results and the corresponding sigmoid cure fit. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Modulus Dependence on the Crosslinker Percentage

Wang *et al.* stated that the PDMS elastic modulus, E, in MPa can be estimated from the base to crosslinker weight ratio, n, as:[21]

$$E = \frac{20}{n} \tag{5}$$

However, this approach can be used for PDMS with the narrow base to crosslinker weight ratio range, not higher than 10 : 1. The 10 : 1 is the optimal base to crosslinker weight ratio, and adding more crosslinker does not necessarily make the PDMS network stiffer, as would be predicted by eq. (5).

In the macroscale test, it was obvious that the PDMS elastic modulus only slightly changed by increasing the crosslinking percentage more that 5%, which can be counted as the plateau region. In addition, below 2% crosslinking, the elastic modulus seems to be slightly affected by decreasing the crosslinking percentage. On the other hand, reducing the crosslinking percentage from 5% to 2.5% resulted in the elastic modulus decrease of about 9 fold. It can be inferred that the elastic modulus changed as a sigmoid function with respect to the crosslinking percentage. This non-linear behavior is explained by polymer gelation and network formation theory; specifically the distance between crosslinks and the extent of network formation.[25] As crosslinks are introduced the polymer solution transitions from a liquid to a gel. Further increases lead to an interconnected network that behaves as an elastic solid with high failure strain (e.g., elastomers or rubbers). This increasing elastic behavior plateaus as the available crosslinking sites on the base polymer are saturated. For this reason, the Boltzmann equation was used to fit the sigmoid curve to the data in Figure 3:

$$E = E_0 + \frac{E_1}{1+\exp\left(\frac{X-X_0}{b}\right)} \tag{6}$$

Here, E is the PDMS elastic modulus in MPa at the crosslinking percentage X; E_0 is the minimum value of the elastic modulus, E_1 is the maximum minus the minimum value of the elastic modulus (total elastic modulus range); X_0 is the crosslinking percentage halfway between the highest and lowest value of the elastic modulus, and b is a constant related to the slope of the center portion of the curve.

For the macroscopic compression test data: $E_1 = 1.68$ MPa, $E_0 = 0.042$ MPa, $X_0 = 3.49$, and $b = 0.62$. The R^2 value for the eq. (6) fit equals 0.97. For the macroscopic tensile test data: $E_1 = 1.51$ MPa, $E_0 = 9.8 \times 10^{-10}$ MPa, $X_0 = 5.8$, and $b = 1.23$. The R^2 value for the eq. (6) fit equals 0.98.

The same sigmoid trend of the PDMS stiffness was observed with the microscale nano-JKR testing. However, slightly lower values of the elastic modulus were measured. Equation (6) can be also used for the microscale test to calculate the elastic modulus of PDMS samples at any stiffness, but with different values of the fitting parameter of eq. (6). The Sigma Plot software version 11.2 was used to fit the data and calculate the corresponding parameters: $E_1 = 1.16$ MPa, $E_0 = 0.11$ MPa, $X_0 = 4.66$, and $b = 0.788$. The R^2 value for the eq. (6) fit is 0.96 (Figure 5).

DISCUSSION

It is very important to identify the changes that would happen in the elastic modulus because of changing the base to crosslinker weight ratio, and measure it at different stiffness, taking into account all the parameters that could affect the results. Generally, tensile testing is the gold standard to measure the elastic modulus, but it is not applicable for all materials, especially for characterization of biomaterials with gradient properties and/or materials with surface modification. For this reason, it was essential to find another testing method that can measure the elastic modulus of soft and tacky materials with high spatial resolution, and provide reliable data.

Using the Lambe and Whitman's model and the nano-JKR force curve method is useful to avoid the effects of material shape and thickness. The distance between the tested surface and the probe has a great effect on the measured values, and this effect was totally avoided by applying the Lambe and Whitman's model and the nano-JKR force curve method. The adhesion force between the PDMS samples and the indenter tip was considered only in the nano-JKR testing, while in the macroscale compression testing it was not, which resulted in higher elastic modulus values when using macroscale compression testing.

Even though the mechanical properties of PDMS polymer have been previously investigated, none of these studies focused on

Table III. PDMS Microscale Nano-JKR Test Elastic Modulus Results

Base to crosslinker ratio	10 : 1	11.5 : 1	16.5 : 1	20 : 1	30 : 1	40 : 1	50 : 1
Crosslinking (wt %)	9	8	6	4.76	3.22	2.43	1.96
E (MPa)	1.75	1.21	1.135	0.83	0.28	0.17	0.1
Standard deviation	0.08	0.15	0.19	0.1	0.05	0.03	0.02

the change of the elastic modulus over a wider range of the crosslinking weight ratios.[26–28] Most of the studies tested 2 or maximum 3 different stiffnesses, which is not enough to fully understand the effect of the crosslinking percentage on the elastic modulus of PDMS. In this study, working with a wider range of crosslinking ratios was beneficial to reveal the sigmoid trend of the PDMS elastic properties, and predict the elastic modulus over a larger range of the crosslinking percentage using different test methods.

CONCLUSIONS

Two important points can be concluded from this study. First, PDMS material is stiffer under the macroscale compression test than the tensile and microscle tests. This may be a result of the adhesion force between the PDMS sample and the compressing tip, which was not taken into account during the compression test. Thus, the macroscale compression test can be considered a good method to estimate the elastic modulus, but it is not sensitive enough to be used for the softer materials with the elastic modulus of less than 1 MPa. Second, these data show that the microscale nanoindentation results are close in magnitude and trend to the tensile test results for the stiffer samples, meaning that the nanoindentation nano-JKR test can be applied to measure the elastic modulus of PDMS material instead of the tensile test to avoid its difficulties. Nanoindentation also provides an easy way to measure the elastic modulus of PDMS samples with mechanical gradients, which cannot be achieved with regular tensile testing.

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