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Crosslinking Effect on Polydimethylsiloxane Elastic Modulus Measured by Custom-Built Compression Instrument

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ABSTRACT: A macroscopic compression test utilizing a simple custom-built instrument was employed to measure polydimethylsiloxane (PDMS) elastic modulus. PDMS samples with varying crosslinking density were prepared with the elastomer base to the curing agent ratio ranging from 5 : 1 to 33 : 1. The PDMS network elastic modulus varied linearly with the amount of crosslinker, ranging from 0.57 MPa to 3.7 MPa for the samples tested. PDMS elastic modulus in MPa can be expressed as 20 MPa/PDMS base to curing agent ratio. This article describes a simple method for measuring elastic properties of soft polymeric materials. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41050.

KEYWORDS: crosslinking; mechanical properties; properties and characterization

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INTRODUCTION

Polydimethylsiloxane (PDMS) is one of the most widely used silicone-based organic polymers.[1] PDMS can be used as the substrate to grow mammalian cells, including stem cells, because of its controllable range of elastic properties.[2–4] Varying the degree of crosslinking in the polymer network allows tuning its mechanical properties in a range similar to the living tissues. The lower the degree of PDMS network's crosslinking, the lower its stiffness.[5] Conversely, the higher the degree of crosslinking, the stiffer the sample will be. To study the PDMS network stiffness effect on the growth and behavior of cells, one would need to characterize the mechanical properties of a series of PDMS network samples cured to different crosslink densities.

There are several studies focusing on measuring PDMS mechanical properties. Some researchers resorted to tensile testing using standard testing equipment.[4,6] However, challenges may arise when testing soft polymers, as they exhibit a significant toe region in the stress–strain curves.[7] This toe region is often observed at the beginning of the stress–strain curve, which is an artifact caused by the slack and specimen misalignment, and must be compensated for. This region can be quite large in terms of the strain range. Ideally, the sample elongation should be measured directly on the sample, and not between the tensile machine grips, which may be challenging for the softer PDMS samples. The elastic modulus of the stiffer PDMS samples is below 5 MPa, and the softer ones are well below 1 MPa, measured using the tensile test.[4] It is clear that the calculated engineering stress–strain curves are not linear, especially at the higher strain levels.[5,6] Other challenges may arise trying to manufacture the standard specimens per ASTM geometry, which may be not feasible for several reasons, including the lack of material. Additionally, there are also challenges associated with fixing the sample in the grips without local damage and slippage. For example, it is clearly seen that the slope of the stress–strain curves in Figure 1 of Ref. 4 is higher at the lower strain levels, compared with the larger strain.

Nanoindentation can also be used to measure PDMS local mechanical properties. However, there are issues associated with determining the initial point of contact of the indenter tip, and advanced *in situ* tests inside the scanning electron microscope may be required to accurately determine the contact area.[8] There are other high resolution approaches. For example, Levental et al. used a 40 nm resolution hydraulic micromanipulator and a 1 μN resolution tensiometric force probe adapted from the surface tension measurement apparatus of a Langmuir monolayer trough to set up an indentation device for measuring micrometer-scale tissue stiffness, which potentially could also be used for PDMS.[9] Verifying the validity of the mechanical properties values obtained by nanoindentation using both static and dynamic techniques with the indenter tips of different geometry will be the subject of another paper. Another advanced approach utilizes the buckling of a polystyrene thin film sensor, which is attached to a polymer surface with an elastic modulus below 10 MPa.[10] Dynamic mechanical analysis (DMA) is also a viable alternative to test the complex modulus of the PDMS network,[11] however it was not utilized in this study, which

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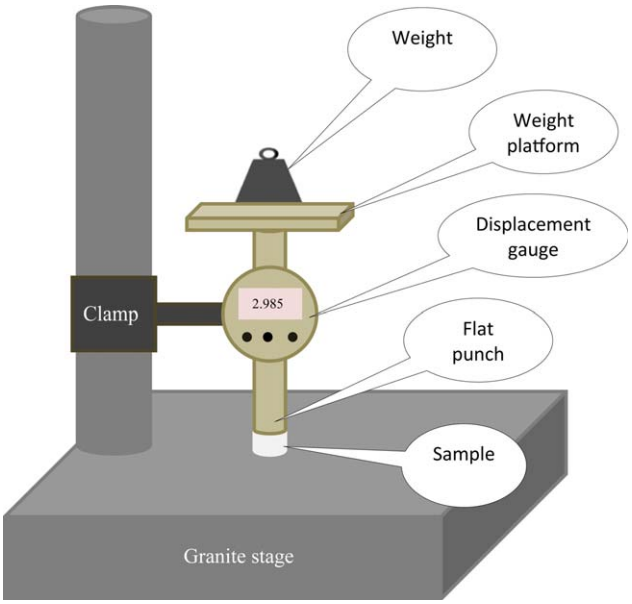

Figure 1. Schematic illustration of the macroscopic compression instrument setup. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

introduces a simpler method based on the unconfined macroscopic compression test. Here, a custom-built macroscopic compression instrument was used for reliable and repeatable measurements of the PDMS network stiffness with varied degrees of crosslinking. The reason a custom-built instrument was needed is because some of the softer PDMS samples could not be tested in compliance with the ASTM standard requirements.[12]

MATERIALS AND METHODS

Sample Preparation

Sylgard 184 silicone elastomer base and Sylgard 184 silicone elastomer curing agent manufactured by Dow Corning (Midland, MI) were used to make the PDMS network.[13] For this study, a series of PDMS network samples with different base/curing agent mass ratios were used to explore the relationship between the elastic modulus and different amount of PDMS network's crosslinking, whose base/agent mass ratios were 5 : 1, 7 : 1, 10 : 1, 16.7 : 1, 25 : 1, and 33 : 1, respectively.[13,14]

Sheets of PDMS (2.5–3 mm thick) were made by thoroughly mixing the corresponding elastomer base and the curing agent mixtures, pouring the mixture into a flat bottom polystyrene dish and degassing the PDMS under vacuum to remove air bubbles. The PDMS was cured in an oven at 65°C for 1 h. After curing, the PDMS network samples were cut out into 3 mm and 4 mm nominal diameter cylinders with the stainless steel cylindrical biopsy punches. The actual diameter of each cut out sample was measured using electronic calipers prior to compression testing.

Compression Instrument

A custom-built compression test apparatus is shown schematically in Figure 1. The stage is made from a thick polished granite slab to provide a stable working platform and minimize vibration. The vertical post and the clamp are made from stainless steel. The Mitutoyo digital depth gauge (Model 547-258, made in the USA) is attached to the stage by the horizontal clamp. The spring inside the Mitutoyo depth gauge was removed to minimize the additional force exerted on the sample by the gauge. A weight supporting platform was added on top of the vertical displacement pin passing through the gauge, and a flat cylindrical punch, 5 mm in diameter, was screwed into the bottom of the gauge. The displacement resolution of the gauge is 1 μm. The displacement gauge calibration was checked using thickness standards and digital calipers.

Figure 1 illustrates how the macroscopic compression test is conducted. The weight placed on the platform attached to the top of the gauge applied a force to the sample, compressing it. Initially, the sample was pre-loaded to make sure that the cylindrical flat punch and the sample are in full contact. Otherwise, the toe-like effects were observed on some samples, similar to the tensile testing case.[7] In this study, the preload of 50 g was used. The additional weight of the flat punch with the gauge center rod assembly was offset by the small friction in the gauge, as the unsupported unloaded rod would not move at any position because the spring was intentionally removed from the displacement gauge. The gauge measured the displacement as more weights were added to the platform, up to the total of 250 g, corresponding to about 10–25% maximum strain, depending on the sample. Four samples were tested for each type of the PDMS network, two 3 mm diameter samples and two 4 mm diameter samples, except for the softer 25 : 1 and 33 : 1 samples, for which only two samples were tested. The softer 25 : 1 and 33 : 1 samples are quite tacky, making it challenging

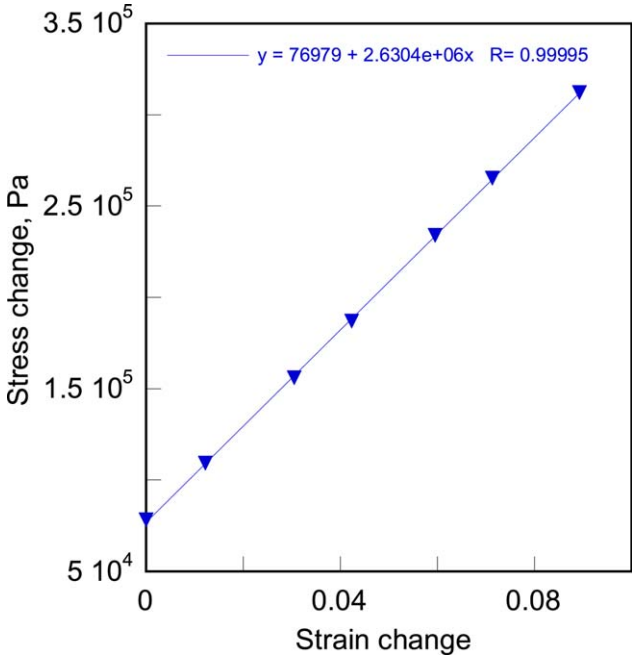

Figure 2. 10 : 1 PDMS network compression test results. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Elastic Modulus of PDMS Network Samples with Different Amount of Crosslinking

	4 mm diameter		3 mm diameter		
Sample	E_1 (MPa)	E_2 (MPa)	E_3 (MPa)	E_4 (MPa)	E_{ave} (MPa)
PDMS 5 : 1	3.584	3.728	3.458	3.582	3.59 ± 0.11
PDMS 7 : 1	2.950	2.924	2.867	2.894	2.91 ± 0.036
PDMS 10 : 1	2.605	2.633	2.587	2.630	2.61 ± 0.021
PDMS 16.7 : 1	1.109	1.234	1.265	1.227	1.21 ± 0.069
PDMS 25 : 1	0.954	-	1.006	-	0.98 ± 0.037
PDMS 33 : 1	0.548	0.577	-	-	0.56 ± 0.021

to cut a cylinder with a smaller 3 mm diameter. Each sample was tested only once to avoid the Mullins effect.[15,16]

Compression Data Analysis

The change in the compressive stress can be calculated as:

$$\Delta\sigma = \frac{\Delta m \cdot 9.8 \times 4}{\pi D^2} = \frac{12.477 \cdot \Delta m}{D^2}, \quad (1)$$

where Δm is the additional mass placed on the platform above the gauge and D is the sample diameter (3 mm or 4 mm). The corresponding change of the sample strain is:

$$\Delta\varepsilon = \frac{\Delta L}{L_0}, \quad (2)$$

where ΔL is the change in the sample height under compressive force measured by the displacement gauge, and L_0 is the original sample height. The original sample height was measured by using both the displacement gauge and the digital calipers.

According to Hooke's law, the Young's modulus, E, is expressed as:

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} \quad (3)$$

for an ideal elastic solid, where $\Delta\sigma$ is the change of the stress and $\Delta\varepsilon$ is the corresponding change of the strain. The strain range in this study was 1–25%, accounting for the pre-load weight. The advantage of this approach is that the change of the strain is calculated as a function of the change of the applied stress, minimizing initial contact ambiguities.

Figure 2 shows the results of the 10 : 1 PDMS network compression test. A linear fit of the data gives the slope of 2.63 E+06 Pa, meaning that the elastic modulus of the 10 : 1 PDMS network sample is 2.63 MPa. It is important to properly determine the necessary pre-loading weight to develop full contact between the flat punch and the sample, which depends on the sample geometry and the elastic modulus. The approach is to gradually increase the pre-loading weight, until the linearity of the applied load with the sample deformation is reached. At the same time, the pre-loading should not generate strain that exceeds a couple of percent. In this case, 50 g pre-load was the optimal for all tested samples.

RESULTS AND DISCUSSION

The elastic modulus results of the tested PDMS samples are listed in Table I. It is clear that the PDMS elastic modulus is related to the elastomer base/curing agent ratio, i.e. the degrees of crosslinking.[17,18] The measured PDMS network elastic modulus varies linearly with the amount of crosslinker for the tested

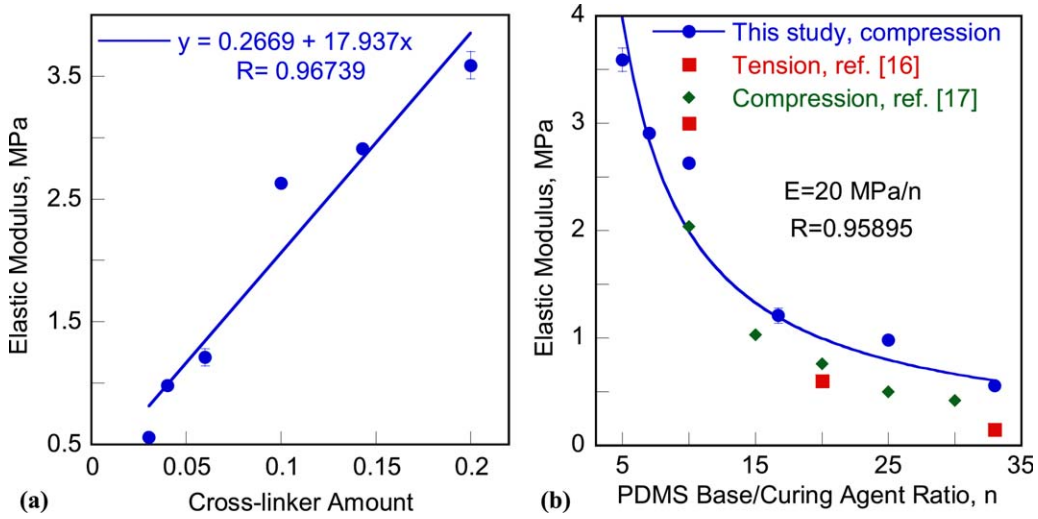

Figure 3. (a) PDMS elastic modulus as a function of the curing agent/base weight ratio; (b) PDMS network elastic modulus comparison with other studies. The error bars represent one standard deviation of the data, assumed to be the experimental uncertainty of the measurements. Some error bars are smaller than the symbols. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

range, as seen in Figure 3(a). Thus, the elastic modulus, E, in MPa can be expressed as a function of the PDMS base/curing agent weight ratio, n, as:

$$E = \frac{20\,\text{MPa}}{n}, \quad (4)$$

shown in Figure 3(b). Increasing the amount of the crosslinker up to 20% stiffens the PDMS network. However, other reports show that for the higher concentrations of the curing agent the modulus is reduced, since the crosslink sites are saturated and the excess curing agent leads to voids or a dilution of the network, thus reducing the stiffness, especially when measured in tension.[10,19]

Based on the Fuard et al. study, which utilized the true tensile stress–strain curves, the Young's modulus of the PDMS network with the base/agent weight ratio of 10 : 1, 20 : 1, and 33 : 1 is 3 MPa, 0.6 MPa, and 0.15 MPa, respectively, as seen in Figure 3(b) (100°C cure temperature and 12 h curing time).[20] Carrillo et al. measured PDMS network elastic modulus with nanoindentation and unconfined compression testing, similar to this study.[21] Both sets of data are in the same ballpark as the current results, shown in Figure 3(b). The differences between these studies may arise from the different PDMS network curing conditions and the testing methods. The cure temperature in this study was 65°C, compared with 100°C for the Fuard's study, while Carrillo's samples were cured at room temperature. Notice that the Carrillo's compression test results are closer to the ones in this study, compared with the Fuard's tensile test results.

CONCLUSIONS

In conclusion, this article presents a simple method to test soft materials' elastic modulus. It also compares and summarizes the elastic modulus of PDMS network with various amount of crosslinker. A custom-built compression test apparatus was utilized to measure elastic modulus of PDMS samples with the base/curing agent ratio ranging from 5 : 1 to 33 : 1. PDMS elastic modulus range is between 0.57 MPa and 3.7 MPa, and varies linearly with the amount of crosslinker in the tested range. It is important that full contact is developed between the sample and the flat punch by pre-loading, and the use of the flat punch ensures constant contact area throughout the test. This method of testing is simple and reproducible, without the need of complex sample preparation or data interpretation.

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