Proceedings of the ASME 2011 International Mechanical Engineering Congress & Exposition
IMECE2011
November 11-17, 2011, Denver, Colorado, USA

IMECE2011-64335

INDENTATION DEPTH DEPENDENT HARDNESS IN POLYDIMETHYLSILOXANE

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ABSTRACT

Size dependent deformation in polymers has been observed in various experiments including microbeam bending, foams, composites and indentation. For indentation depths from 100 microns down to hundreds of nanometers strong increases in the hardness has been observed where the hardness has been determined with a Berkovich indenter tip on polydimethylsiloxane. These observations are related to other existing experimental data of the literature and possible rationales for these indentation size effects are discussed.

INTRODUCTION

Indentation size effects are quite well known in metals where the hardness increases with decreasing indentation depths. The mechanisms and rationale of these size effects in metals have been extensively studied in the literature. Size effect have however also been found in polymers [Chong/Lam 1999, Han 2010, Han/Nikolov 2007].

Among polymers silicone exhibits very strong indentation size effects which will be studied here. Astonishing indentation size effects in a silicone elastomer have been reported in [Zhang/Xu 2002] where the hardness increased by a factor of about 6 between indentation depths of about 200 and 1000 nm. The silicone elastomer turned out to be a much harder material at the nanoscale than many polymers while it is known to be a quite soft material at the macroscale. Unfortunately the details of the experiments setting or the material where not provided in [Zhang/Xu 2002]. In [Tatiraju/Han 2010] the indentation size effects of filled silicone were studied where also strong size effects have been found at indentation depths between 25 to 500 microns.

Polydimethylsiloxane (PDMS) is an easily fabricated, low cost elastomer used extensively in biomedical applications, coatings, micro-channel fluid delivery, and cell framework applications [Ye et al. 2010, Vestad et al. 2004]. In this paper the indentation depth dependent hardness of PDMS is studied over a very broad range with 200 nm at the low end and 100 microns at the high end. The results are analyzed with a hardness model for polymers suggested in [Han/Nikolov 2007] and discussed.

EXPERIMENTAL SETTING

Polymer samples. The PDMS material was fabricated from materials provided from Gelest (Morrisville, PA). The chemical components to fabricate the PDMS consists of a base of divinyl-terminated-polydimethylsiloxane (molecular weight (MW) = 17,200 g/mol) and a curing/crosslinking agent, tetrakis(dimethylsiloxy)silane (MW = 328.73 g/mol).

The vinyl base and Karstedt's catalyst solution are combined in a 60 mL cup and mixed for 2 min at 1300 RPM with a Speed Mixer DAC 150FVE-K. This solution is then placed in vacuum oven for fifteen minutes to remove air bubbles present within the mix. The curing/crosslinking agent is then added and the entire mix is placed in the mixer for an additional 30 seconds. The entire solution is then deposited into polystyrene Petri-dishes (47 mm or 35 mm diameter, Fisher Scientific, Waltham, MA) ground down to a 2.5mm depth to avoid deformation and damage to the material during handling. Finally, the PDMS solution is then cured at room temperature for 24 hours, and then additionally cured for 4 weeks at room temperature before testing. The samples are prepared with a crosslinker agent mass ratio ($M_{crosslinker}/M_{total}$) of 0.6 g/40.0 g, where $M_{crosslinker}$ is the mass of the crosslinker and M_{total} is the total mass of the mixture. The prepared samples were transparent with smooth surfaces and no visible defects.

Indentation testing. Both nano- and microindentation tests have been conducted on the PDMS samples. The nanoindentation was performed on a MTS NanoXP (MTS Systems, Eden Prairie, MN), while all microindentation was performed using a Fischerscope HM2000s indenter (Fischer Technologies, Windsor, CT). Experiments were conducted using a linear loading and unloading at ambient room temperature of approximately 20° C. Force controlled

techniques were used for the tests and displacement was recorded digitally by the machines with the hardness evaluated in accordance with [ISO 14557-1 2002] with the max indentation force record. A Berkovich indenter tip was used for all tests. Indentation depth range in the performed tests is from 100 nm to about 120 µm (the maximum depth of the micro-indenter system) across both indentation systems. During the indentation tests, the indentation systems recorded both applied force F and indentation depth h where h is defined as the displacement of the indenter tip after first contact as illustrated in Figure 1. More details on the experimental setting can be found in [Wrucke 2011].

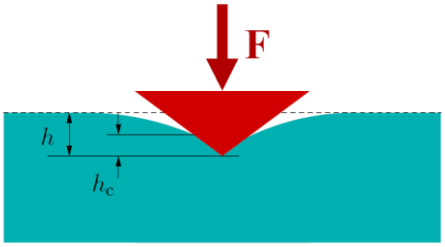

Figure 1: Indentation depth h.

EXPERIMENTAL RESULTS

The PDMS samples exhibited almost purely elastic deformation across the whole testing range. The loading was applied linearly in time with the total loading time being 5 and 80 sec. In Figure 2 is typical loading and unloading curve of the indentation tests on PDMS is shown, where the loading and unloading sequences are almost identical so that the determined elastic part of total indentation work was more than 98% in all indentation tests.

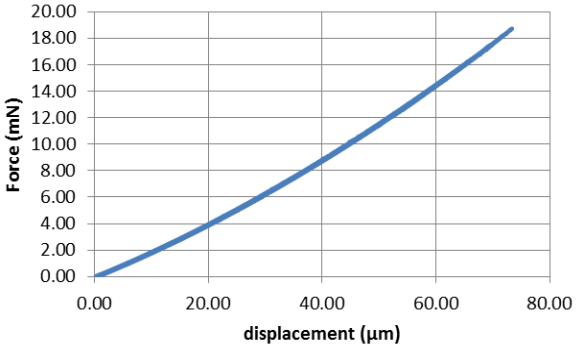

Figure 2: Typical loading and unloading curve of an indentation test.

For such highly elastic materials the indentation hardness as defined in [ISO 14557-1 2002] does not result to reasonable results [Lim/Chaudhri 2006] whereas the Universal Hardness – also known as Martens Hardness – H_U can be applied for all materials is given as

$$H_U = \frac{F}{26.43h^2} \qquad (1)$$

for a Berkovich indenter tip. To study the indentation size effect of the PDMS samples the Universal Hardness H_U is evaluated at different indentation depths. The experimental results with respect to hardness and indentation depth are shown in Figure 3 where both the x- and y-axis are plotted in logarithmic scale. As can be seen therein the indentation tests were not significantly dependent on the loading time. With decreasing indentation depth h however amazing increases in the Universal Hardness have been determined increasing from about 0.1 MPa up to 100 MPa. Consequently an increase in the Universal Hardness by a factor of 1000 has been observed between indentation depths ranging from 100 to 100,000 nm.

It should also be noted that the experimental results of the two different indentation systems overlapped at about 15,000 nm and both types of systems yielded experimental data with reasonable agreement. The indentation experiments have been performed on different samples over a period of several weeks which resulted in some scatter in the experimental data which may be related to aging or curing of the samples at room temperature which resulted in slight increases in the hardness.

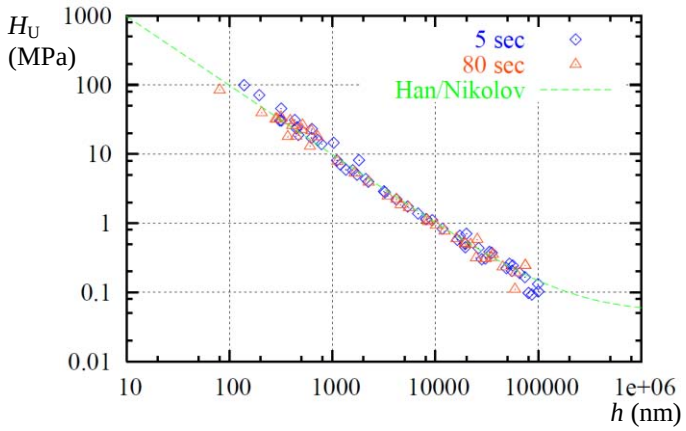

Figure 3: Typical loading and unloading curve of an indentation test.

ANALYSIS

A depth dependent hardness model has been suggested in [Han/Nikolov 2007] as

$$H = H_0\left(1-\frac{c_\ell}{h}\right) \qquad (2)$$

with the length scale parameter c_ℓ and the macroscopic hardness H_0. This model is based on the strain gradient elasticity model of [Nikolov/Han/Raabe 2007] which links the strain gradients to the molecular interactions during deformation. The parameters c_ℓ and H_0 have been fitted to the experimental data and the resulting curve has been plotted in Figure 3 with the experimental data. As can be seen therein the hardness model (2) agrees well with the experimental data over the whole range of h.

DISCUSSION

It should be noted that in [Zhang/Xu 2002] a maximal Indentation Hardness – determined with the contact depth h_c of Figure 1 – of about 700 MPa were reported at an indentation depth of about 200 nm. At a similar indentation depth the hardness values determined here in this paper are therefore significantly lower which may be due to the differences between the Indentation Hardness and the here applied Universal Hardness.

Depth dependent hardness was also observed in [Lim/Chaudhri 2006] at indentation depths between about 50 to 500 microns for polydimethylsiloxane samples with higher cross link densities. For these samples – not considering strain gradients – higher elasticity moduli were determined (following the approach of [Oliver/Pharr 1992] and analytical solutions such as [Sneddon 1965]) at smaller indentation depths. While not investigating indentation size effects, polydimethylsiloxane has also been examined in [Charitidis 2011] at indentation depth between 200 and 4000 nm. Therein the elasticity modulus determined according to [Oliver/Pharr 1992] was found to increase from about 4 to 53 MPa. An explanation why such an increase in the elasticity modulus should be present in the material was however not provided. Other rationale for the indentation size effects are discussed in [Han 2010].

With the hardness model (2) the indentation size effects in silicone are viewed as a result of strain gradient effects within the polydimethylsiloxane samples which can also be micromechanically motivated [Nikolov/Han/Raabe 2007]. Compared to the indentation size effects observed in other polymers (see [Han 2011] for a review) the indentation size effect in polydimethylsiloxane are however quite enormous. Still similar to epoxy [Lam/Chong 2000] increases of the size effect are also found with increasing cross link density in polydimethylsiloxane [Wrucke 2011].

ACKNOWLEDGMENTS

The support of this work through the National Science Foundation's CAREER award, Grant CMMI 1102764, is highly appreciated.

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