Modified-creep experiment of an elastomer film on a rigid substrate using nanoindentation with a flat-ended cylindrical tip

Seung Tae Choi,[a †] **Su Jeong Jeong,**[b ‡] **and Youn Young Earmme**[b]

[a] *Micro Systems Lab, SAIT, P.O. Box 111, Suwon 440-600, Republic of Korea.*
[b] *Department of Mechanical Engineering, KAIST, Science Town, Daejeon 305-701, Republic of Korea*

We developed a modified creep experiment with nanoindenter to measure the viscoelastic properties of elastomer films. By using the Nano Indenter® XP with a flat-ended tip, load-controlled experiments on PDMS (polydimethylsiloxane) films were performed. By adapting the force-depth relation solved by Choi et al. [1], the indentation results were analyzed to obtain the relaxation modulus of the PDMS film as a function of time. Residual deformation on the indented PDMS film after unloading was measured with an atomic force microscope.

Keywords: Nanoindentation; Elastomer; Thin films; Creep.

Elastomer membranes and films such as PDMS (polydimethylsiloxane) are widely used in soft lithography, biomedical applications, micro fluidic and optical systems, etc. as can be seen from several limited references [2-7]. The mechanical response of elastomers under applied loading is one of major issues in some applications such as tunable microdoublet lenses [6] and dielectric elastomer actuators [7]. The mechanical behavior of polymers is usually described by viscoelastic and/or viscoplastic characteristics, depending on time (or frequency) as well as temperature, which make the mechanical response of the polymer systems complicated. A uniaxial tension test, a dynamic mechanical analyzer, and a dynamic mechanical thermal analyzer are commonly used to measure the thermomechanical properties of bulk polymers. Also, in accordance with the extensive applications of thin polymer films, experimental measurements using a nanoindenter and a scanning probe microscope have been widely performed. The indentation method is preferred to the conventional methods, due to its easy specimen preparation and experimental procedure, and it makes possible the study of the size effect on the mechanical properties in the micro- and nano-scales. However, indentation experiments can require complicated analysis, depending on the shape of the indenter tips, to extract the viscoelastic and/or viscoplastic properties of polymers from the experimental data.

The force-depth relation for the indentation on bulk polymers using flat tips was obtained by Oliver and Pharr [8]. In contrast, Lebedev and Ufliand [9] solved the problem of pressing a rigid stamp of a circular cross-section into an

---

[†] Corresponding author. Tel: +82-31-280-8418; fax: +82-31-280-8432; e-mail: stchoi@kaist.ac.kr

[‡] Current address: Vehicle CAE team, Advanced Technology Center, Hyundai & Kia Corporate Research & Development Division, Hwaseong-si, Gyeonggi-do, Republic of Korea

elastic layer supported (i.e., not bonded) on a rigid substrate without friction; their method was recently revisited by Yang [10] and applied to an incompressible elastic film bonded on a rigid substrate [11]. Recently, Choi et al. [1] extend the well-established method [9-11] to an elastic film of arbitrary Poisson's ratio bonded on a rigid substrate. By using the elastic-viscoelastic correspondence principle [12], the force-depth relation for elastic films can be converted to that for viscoelastic films, which enables to obtain the relaxation modulus of viscoelastic films from indentation experiments. In this study, by using the Nano Indenter® XP with a flat-ended cylindrical tip, the modified creep experiments on PDMS films were performed. The measured data were analyzed to obtain the relaxation modulus of the PDMS film with the aid of the force-depth relation obtained by Choi et al. [1].

PDMS (Sylgard 184 Silicone Elastomer from Dow Corning Co.) was used in this indentation experiment. A Sylgard 184 Silicone Elastomer is supplied as two-part liquid component kits comprising Base/Curing Agent to be mixed in a 10:1 ratio by weight or volume. After the liquid components were thoroughly mixed, they were spin-coated on a 4-inch (100) silicon wafer of thickness 500 μm. Spin coating at 5000 rpm for 60 seconds was performed to make PDMS film of thickness 14.7 μm on the silicon wafer. Then, the spin-coated PDMS film was cured for 60 minutes at 85 °C. Finally, the PDMS/silicon wafer was cut into chips of approximately 20 mm × 20 mm.

The experiments were performed with a Nano Indenter® XP (MTS Nano Instruments Innovation Center, Oak Ridge, TN) at room temperature (18 °C). A flat-ended cylindrical tip made of diamond was used for the tests. The bottom surface of the tip used is not perfectly circular; therefore, the deformation field of the specimen may not be axisymmetric. Choi et al. [1] analyzed the effect of a non-circular tip on the force-depth relation, showing that the non-circular tip can be treated as a circular tip with the area-equivalent radius as its radius with less than 1.5 % errors. The cross-sectional area of the tip used was 499.07 μm^2 so that the effective radius of the tip was assumed to be 12.7 μm. With the force-depth relation obtained by Choi et al. [1], the relaxation modulus and Poisson's ratio can be obtained from the experimental data. However, the Nano Indenter® XP provides basically load-controlled experiments. Therefore, we will describe the method to extract the viscoelastic properties from the experimental data obtained with the Nano Indenter® XP, together with an illustration of the indenter head dynamics.

Figure 1 shows the schematic illustration of the Nano Indenter® XP head (a) and its one-dimensional dynamic model, including a viscoelastic sample (b), in which the 'raw load' F_{Raw} is controlled by appropriately modulating the current in the coil that is surrounded by a magnet [13]. Using the Nano Indenter® XP 'basic creep method', load-controlled experiments were performed, in which F_{Raw} was raised by the amount of 0.2 mN in 4 seconds, and then F_{Raw} was held constant for 3,000 seconds, followed by unloading in 15 seconds. The 'raw displacement' $U_{Raw}(t)$ is measured by the capacitive displacement gauge, of which the damping effect represented by D_i is significant only in dynamic experiments and is ignored here for the creep experiments. When F_{Raw} is sufficiently small so that it is comparable to the force exerted by the support springs that support the indenter shaft, which is the case of PDMS, the measured F_{Raw} must be compensated to give the actual force acting on the specimen. The spring constant of the support springs is represented by K_s, and then the actual force $F(t)$ on the specimen is calculated by

$$F(t) = F_{Raw} - K_s U_{Raw}(t) . \tag{1}$$

Most of the raw displacement $U_{Raw}(t)$ measured by the capacitive displacement gauge is that of the specimen, but the load frame (test fixtures, sample stage, gantry, etc.) is inevitably deformed by some small amount. Once the stiffness of the load frame K_f is known, the 'displacement-into-surface' $\delta(t)$, which is the actual deformation of the specimen, is calculated by

$$\delta(t) = U_{Raw}(t) - F(t)/K_f \ . \tag{2}$$

It is worth noting that, in the indentation experiments on viscoelastic specimens, even though F_{Raw} is held constant during the hold, F can gradually change due to the support springs of the indenter head when the compliant specimen shows creep behavior, which we call the modified creep experiment. For terminological convenience, the 'load-on-sample', $F(t)$ is referred to as the applied force (or the force), and the 'displacement-into-surface' $\delta(t)$, as the penetration depth (or the depth).

Choi et al. [1] obtained the force-depth relation of the indentation with a flat-ended cylindrical tip on a viscoelastic film on a rigid substrate. They showed that the difference between the indentation of an elastic film on a rigid substrate and that of an elastic half-space is only the non-dimensional parameter $\alpha(\nu, h/a)$ defined in Eq. (10) of Choi et al. [1] and plotted in Fig. 2 of Choi et al. [1]. Poisson's ratio is assumed to be independent of time, and so is the parameter $\alpha(\nu, h/a)$. Therefore, the force-depth relation for a viscoelastic film on a rigid substrate will not be different from that for a viscoelastic half-space, except for the multiplying parameter $\alpha(\nu, h/a)$. Since, in the indentation using a flat-ended cylindrical tip, the types and regions of prescribed boundary conditions do not change with time, the elastic-viscoelastic correspondence principle [12] can be applied to Eq. (9) of Choi et al. [1], resulting in

$$F(t) = \frac{4a}{1-\nu}\alpha\left(\nu, \frac{h}{a}\right)\int_0^t \mu(t-\tau)\frac{d\delta(\tau)}{d\tau}d\tau \ , \tag{3}$$

or equivalently

$$\delta(t) = \frac{1-\nu}{4a\alpha\left(\nu, h/a\right)}\int_0^t J(t-\tau)\frac{dF(\tau)}{d\tau}d\tau \ , \tag{4}$$

in which $\mu(t)$ and $J(t)$ are, respectively, the relaxation modulus and creep compliance of a viscoelastic film appropriate to states of shear. The two functions are not independent but connected by the relation $\overline{J}(s) = [s^2\overline{\mu}(s)]^{-1}$, where the overbar represents the Laplace transformed function and s is the transform variable. The above equations (3) and (4) are the applied force-penetration depth relation for the indentation with a flat-ended cylindrical tip of a viscoelastic film on a rigid substrate.

With the force-depth relation (4), the relaxation modulus and Poisson's ratio can be obtained from the experimental data. Figure 2 shows the depth-time, force-time, and force-depth curves of the indentation experiments with the flat-ended diamond tip of radius a = 12.7 μm on the PDMS film of thickness h = 14.7 μm. When the unit-step force F_0 is applied at time t_0, the viscoelastic film spontaneously responds, as if it were an elastic film, causing the indenter to move into the film by an amount of the depth δ_0. Then, Eq. (4) provides us with

$$\mu(0) = \frac{(1-\nu)F_0}{4a\delta_0\alpha(\nu, h/a)}. \tag{5}$$

While F_{Raw} is held constant from $t = t_0$ to $t = t_f$, the penetration depth, as well as the applied force, gradually changes due to the creep behavior of the polymer film. Provided that the penetration depth is measured in the interval $[t_0, t_f]$, it can be curve-fitted into a Prony series as

$$\delta(t) = \delta_0 + \sum_{n=1}^{N} \delta_n \left[1 - \exp(-t/\tau_n)\right]. \tag{6}$$

From Eqs. (1) and (2), the relation between the force $F(t)$ and depth $\delta(t)$ turns out to be linear in the interval $[t_0, t_f]$, and the force as a function of time can be written as

$$F(t) = \frac{F_f - F_0}{\delta_f - \delta_0}\delta(t) + \frac{F_0\delta_f - F_f\delta_0}{\delta_f - \delta_0}, \tag{7}$$

where F_f and δ_f are the final force and the final depth, respectively, at $t = t_f$. Laplace-transforming Eq. (3) with Eq. (7), followed by inverting the transform, yields

$$\mu(t) = \frac{\mu(0)}{\delta_f/\delta_0 - 1}\left\{F_f/F_0 - 1 + \left(\delta_f/\delta_0 - F_f/F_0\right)\mathcal{L}^{-1}\left[\frac{\delta_0}{s^2\bar{\delta}(s)}\right]\right\}, \tag{8}$$

where the symbol $\mathcal{L}^{-1}$ represents the inverse Laplace transform. Eq. (8) can be used to obtain the relaxation modulus $\mu(t)$ of the viscoelastic film.

From the force-time, depth-time, and force-depth curves (Fig. 2) measured at 8 different positions in a specimen, the average initial force F_0 and penetration depth δ_0 are found to be 0.12692 mN (standard deviation: 0.001581) and 1195.1 nm (standard deviation: 20.13), respectively. After holding for 3,000 seconds, the final force F_f and penetration depth δ_f are determined to be 0.10201 mN (standard deviation: 0.001697) and 1482.8 nm (standard deviation: 8.765), respectively. When we use ν = 0.475 as the Poisson's ratio of the PDMS films, as measured by

Jeong [14], the non-dimensional parameter $\alpha(\nu = 0.475, h/a = 1.1557)$ equals 2.9029. From Eq. (5), the initial relaxation modulus becomes $\mu(0)$ = 377.51 kPa. Using the measured depth curves (Fig. 2(a)) and Eq. (6) with N = 4, the penetration depth can be curve-fitted to be

$$\delta(t) = 1652.9 - 34.9e^{-0.27105t} - 71.4e^{-0.021203t} - 70.4e^{-0.0030479t} - 278.4e^{-0.00016949t} \text{ (nm)}, \tag{9}$$

where the unit of time t is second. Performing the Laplace transform of Eq. (9), substituting it into Eq. (8), and doing the inverse Laplace transform in Eq. (8), we obtain the relaxation modulus of the PDMS film, as

$$\mu(t) = 188.59 + 19.78e^{-0.27901t} + 37.10e^{-0.022445t} + 32.47e^{-0.0032131t} + 99.97e^{-0.00020374t} \text{ (kPa)}, \tag{10}$$

which is also plotted in Fig. 3. The shortest time constant of the relaxation modulus in Eq. (10) is 1/0.2790 = 3.584 seconds, which turns out to be shorter than the rising time (4 seconds) of the raw load. (It is remarked that the curve-fitted $\delta(t)$ with N = 5 yields almost identical $\mu(t)$ within 0.07 % with the shortest time constant changed from 3.584 seconds to 3.396 seconds, and the other values slightly changed, accordingly.) Hence, at the beginning of the holding, the behavior of the PDMS film would be similar to a deformation due to a ramp force, rather than a step force. Therefore, we may infer that the initial relaxation modulus $\mu(0)$ should be larger than 377.51 kPa. This undesirable effect can be reduced if the raw load rate is increased. In addition, from Eq. (10), the equilibrium or relaxed modulus of the PDMS film is estimated to be $\mu(\infty)$ = 188.59 kPa. However, it should be noted that the relaxation modulus curve beyond 3,000 seconds is considered to be extrapolated from the data within 3,000 seconds.

The indentation experiments inherently involve permanent deformation underneath the indenter tip. To estimate the viscoplastic or permanent deformation after the indentation experiment, the indented PDMS surface is scanned with an atomic force microscope (AFM). Even after unloading, the film gradually deforms, due to the viscoelastic effect of the PDMS film; however, the magnitude of the deformation will decrease exponentially. Using the contact mode of AFM, the scan for a 30 μm × 30 μm region was performed in about 15 hours after unloading, of which the result is shown in Fig. 4. The shape of the indenter tip is distinctly marked on the PDMS surface, since the permanent deformation may occur predominantly near the sharp edge of the tip. The maximum residual deformation is measured to be roughly 150 nm, approximately 10 % of the final penetration depth, δ_f = 1482.8 nm, which may be a measure of the deviation from the linear theory of viscoelasticity. No significant plastic pile-up nor groove formation was observed. The factors that affect the residual deformation are presumed to be F, a/h, δ/h, and the hold time together with the material properties, which requires further study.

In conclusion, a modified-creep experiment was developed for the nano indentation of using a flat-ended tip on a polymer film on a rigid substrate. A PDMS film spin-coated on a Si substrate was indented with Nano Indenter XP® and a flat tip made of diamond. The force-depth relation obtained by the experiment was analyzed to give the relaxation modulus of the PDMS film as a function of time, of which the initial modulus and the equilibrium (or relaxed) modulus were estimated to be 377.51 kPa and 188.59 kPa, respectively. By scanning the indented PDMS surface with an atomic force microscope, residual deformation in the PDMS films in about 15 hours after unloading was also measured to be approximately 10 % of the final penetration depth.

This research has been supported by a grant (02-K14-01-012-1-0) from the Center for Nanoscale Mechatronics & Manufacturing of the 21st Century Frontier Research Program of Korea. The authors are thankful to Mr. J. N. An (Department of Electrical Engineering at KAIST) for his help in preparing the specimens.

[1] S. T. Choi, S. R. Lee, and Y. Y. Earmme, to be submitted in Acta Mat. (2007).

[2] M. Brehmer, L. Conrad, and L. Funk , J. Disper. Sci. Technol. 24 (2003) 291.

[3] T. Fujii, Microelectronic Engineering 61–62 (2002) 907.

[4] N. L. Jeon, D. T. Chiu, C. J. Wargo, H. Wu, I. S. Choi, J. R. Anderson, and G. M. Whitesides, Biomedical Microdevices 4 (2002) 117.

[5] M. Fleger and A. Neyer, Microelectronic Engineering 83 (2006) 1291.

[6] K.-H. Jeong, G. L. Liu, N. Chronis, and L. P. Lee, Optics Express 12 (2004) 2494.

[7] R. Pelrine, R. Kornbluh, Q. Pei, and J. Joseph, Science 287 (2000) 836.

[8] W. C. Oliver and G. M. Pharr, J. Mater. Res. 7 (1992) 1564.

[9] N. N. Lebedev and Ia. S. Ufliand, J. Appl. Math. Mech. 22 (1958) 320.

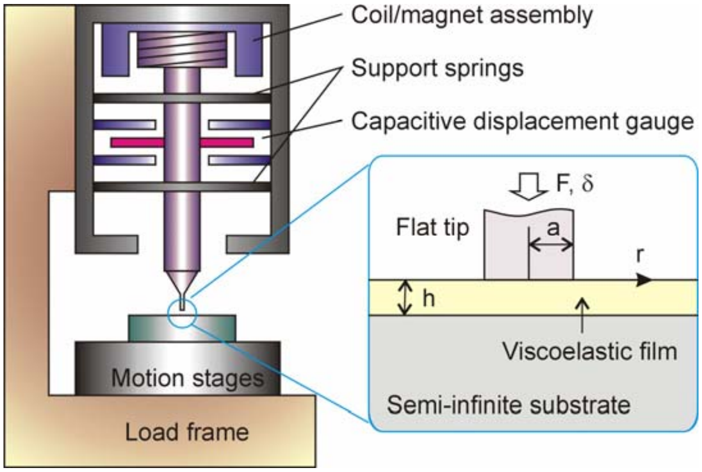
[10] F. Yang, Mat. Sci. Eng. A 358 (2003) 226.

[11] F. Yang, Mech. Mater. 30 (1998) 275.

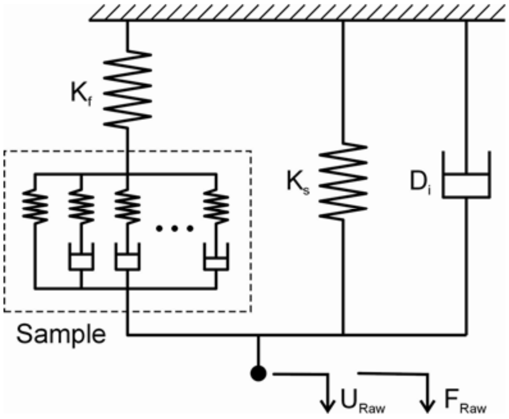
[12] R. M. Christensen, Theory of Viscoelasticity, Academic Press, New York, 1982.

[13] The Nano Indenter XP® User's Manual, Ver. 16, MTS Systems Corporation, 2002.

[14] S. J. Jeong, MS thesis, Department of Mechanical Engineering, KAIST, Republic of Korea, 2005.

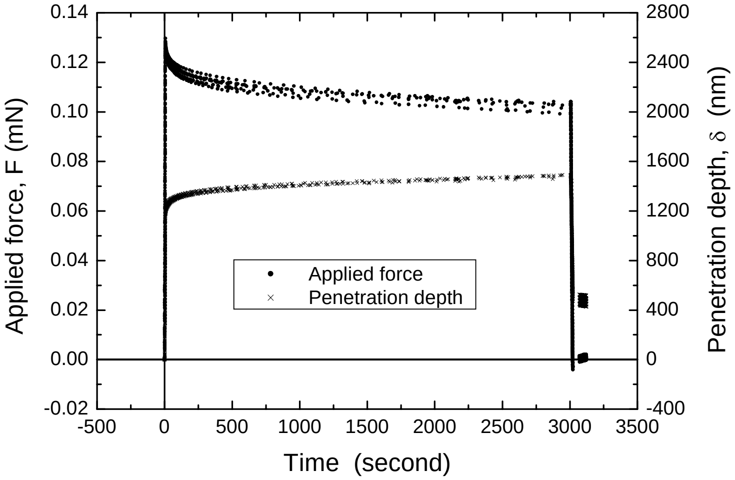


(a)

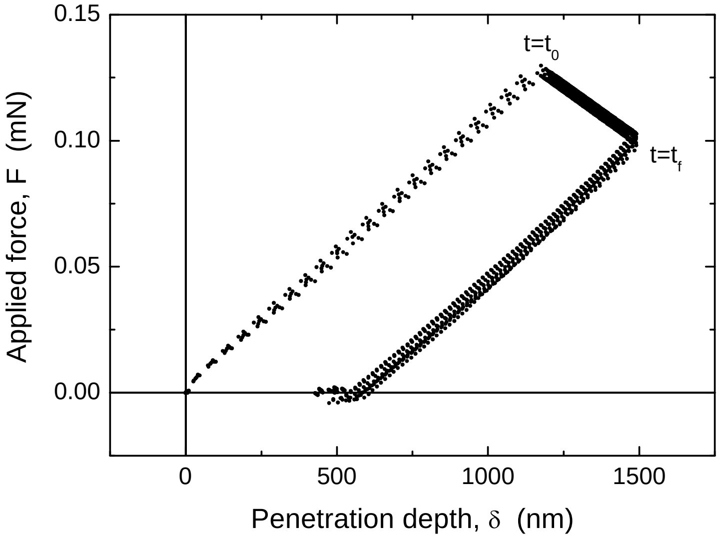


(b)

Figure 1. Schematic illustration of (a) a Nano Indenter® XP head and the indentation of a viscoelastic film using a flat-ended tip, and (b) the dynamic model of the indenter head in contact with a viscoelastic sample.



(a)



(b)

Figure 2. Results of the modified-creep indentation experiments using a flat-ended cylindrical tip measured at 8 different positions in a specimen of PDMS film of thickness h = 14.7 μm. (a) The applied force-time and penetration depth-time curves, (b) the force-depth curves.

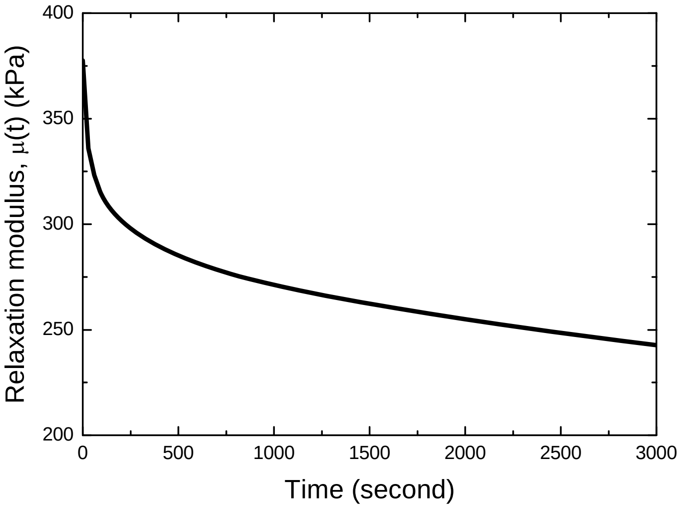
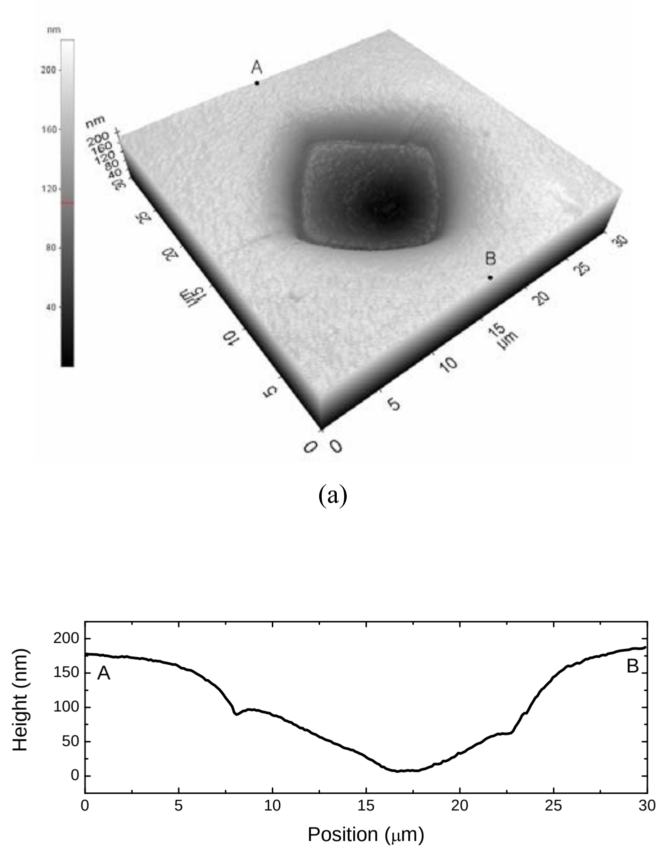


Figure 3. Measured relaxation modulus of the PDMS film.



(a)

(b)

Figure 4. Atomic force microscope image of the residual deformation in the indented PDMS film about 15 hours after unloading. (a) Three-dimensional view and (b) the depth profile along the line connecting the points A and B.