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

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We have developed a modified-creep experiment with nanoindenter to measure the viscoelastic properties of elastomer films. Load-controlled experiments on PDMS (polydimethylsiloxane) films were performed using the Nano Indenter® XP with a flat-ended tip. By adapting the force–depth relation obtained by Choi et al. [S.T. Choi, S.R. Lee, Y.Y. Earmme, Acta Mater. (submitted for publication)], 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 the literature [2–7]. The mechanical response of elastomers under applied loading is one of the 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 makes 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 other methods because both specimen preparation and experimental procedure are straightforward and it makes possible the study of size effects on mechanical properties at micro- and nano-scales. However, indentation experiments can require complicated analysis, depending on the shape of the indenter tip, to extract the viscoelastic and/or viscoplastic properties of polymers from experimental data.

The force–depth relation for indentation of 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 circular cross-section into an elastic layer supported on (i.e. not bonded to) a rigid substrate without friction; their method was recently revisited by Yang [10] and applied to an incompressible elastic film bonded onto a rigid substrate [11]. Recently, Choi et al. [1] extended the well-established method [9–11] to an elastic film of arbitrary Poisson's ratio bonded onto 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 makes it possible to obtain the relaxation modulus of viscoelastic films from indentation experiments. In this study, modified-creep experiments on PDMS films were performed using the Nano Indenter® XP with a flat-ended cylindrical tip. 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 experiment. A Sylgard 184 Silicone Elastomer is supplied as two-part liquid

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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 ont a 4 in. (1 0 0) silicon wafer of thickness 500 μm. Spin coating at 5000 rpm for 60 s 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 min at 85 °C. Finally, the PDMS/silicon wafer was cut into chips of ~20 × 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 was not perfectly circular; therefore the deformation field of the specimen may not have been axisymmetric. Choi et al. [1] performed finite-element analysis to investigate 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 <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 could be obtained from the experimental data. However, the Nano Indenter® XP provides basically load-controlled experiments. Therefore, we describe the method for extracting 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 0.2 mN in 4 s and then F_{Raw} was held constant for 3000 s, followed by unloading in 15 s. The "raw displacement", $U_{\mathrm{Raw}}(t)$, 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 with 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 the actual force, $F(t)$, on the specimen is calculated by

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

Most of the raw displacement, $U_{\mathrm{Raw}}(t)$, 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

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

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; we call this 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 for 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 $\alpha(v, h/a)$, defined in Eq. (10) of Choi et al. [1] and plotted in Figure 2 therein. Here, v and h are Poisson's ratio and the thickness of the elastic film, respectively, and a is the radius of indenter tip. Poisson's ratio is assumed to be independent of time, as is the parameter $\alpha(v, h/a)$. 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 $\alpha(v, h/a)$. Since, for 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

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

or, equivalently,

$$\delta(t) = \frac{1-v}{4a\alpha(v, h/a)}\int_0^t J(t-\tau)\frac{\mathrm{d}F(\tau)}{\mathrm{d}\tau}\mathrm{d}\tau \tag{4}$$

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 $\bar{J}(s) = [s^2\bar{\mu}(s)]^{-1}$, where the overbar represents the Laplace transformed function and s is the transform variable. Eqs. (3) and (4) above are the applied force–penetration depth relation for the flat indentation of a viscoelastic film on a rigid substrate.

With the force–depth relation of Eq. (4), the relaxation modulus and Poisson's ratio can be obtained from experimental data. Figure 2 shows the depth–time, force–time and force–depth curves of indentation experiments with a flat-ended diamond tip of radius $a = 12.7$ μm on a 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 to depth δ_0. Then, Eq. (4) provides us with

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

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