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Review

Analysis and modeling for time-dependent behavior of polymers exhibited in nanoindentation tests

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ABSTRACT

Through the arrangement of the applied load, experimental nanoindentation results of polymethylmethacrylate (PMMA) and polyurethane (PU) employed to establish a mechanical model. The proposed model consists of irreversible delayed plastic (viscoplastic) deformation, irreversible viscous deformation, and reversible delayed elastic (viscoelastic) deformations. The phase lag exhibited between the responding depth and the oscillating load is found to be linear proportional to frequency in the range of 1–50 Hz. The residual cavity profile of the PMMA scanned by an atomic force microscope gives a validity of accommodation assumption applied in the present model. The effects of overshooting, which occurred in the dwelling process, are also discussed.

1. Introduction

A commonly used method for addressing the viscoelastic properties of polymers during nanoindentation is to hold the indenter at the maximum load for a period of time [1–4]. The creep effects led by the loading-hold segment are useful for observation of viscoelastic properties; however, it depends on the holding time, holding load, and rise time of the loading process [5–7]. In addition, the error caused by the drift is often significant in very long duration tests even though the correction according to the measurement before or after the tests is used. Therefore, the drift noise is one of the difficulties faced in very long creep tests.

The beginning of the creep increases when decreasing the rise time of the loading process, therefore, it is reasonable to believe that the viscoplastic, viscoelastic properties dominate the initial parts of creeps. According to the VEP model proposed by Oyen and Cook [1], the unloading behaviors of polymers depend upon both the viscous and elastic properties. However, the study developed by Zhang et al. [2–3] reported that the viscous effect would vanish after the first dwelling. According to the observations of our experiments, the plastic and viscous deformations of polymers are irreversible. However, the unloading behaviors, after a long dwelling, showed a viscoelastic response, not elastic. Based on these observations, a mechanical analog describing the relation between applied load and penetration depth of polymers is proposed under indentation tests with a Berkovich indenter. Both creep and oscillation responses are emphasized to investigate the deformation exhibited in polymers. The mechanical properties of hardness and modulus are evaluated by extracting the plastic and elastic responses from the experimental results. Finally, the issue of overshooting dwells is also discussed.

2. Experiments and modeling

2.1. Kelvin model with quadratic elements

For indentation tests based on an indenter with geometric similarity, the indentation load P and the indentation depth h in the loading process satisfy the following quadratic relation [8–9]:

$$P = G \cdot h^2, \qquad (1)$$

where the G coefficient is dependent upon the indenter's geometry, elastic and plastic properties of the specimen. The deformation due to the viscous effect is reasonable to express as a linear function of

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the representative stress σ and the representative strain rate $\dot{\varepsilon}$. Since the representative stress is linearly proportional to P/h^2 and the representative strain rate has the relation of $\dot{\varepsilon} \sim \dot{h}/h$ ($\dot{h} = \mathrm{d}h/\mathrm{d}t$) [10], the linear form of $\sigma \sim \dot{\varepsilon}$ will lead $P/h^2 \sim \dot{h}/h$ or $P \sim \dot{h} \cdot h$. Therefore, the deformation, due to the viscous effect, is reasonably expressed as form:

$$P_\mathrm{v} = Q \cdot \mathrm{d}(h_\mathrm{v}^2)/\mathrm{d}t, \tag{2}$$

where the Q coefficient is dependent on the geometry of the indenter and the viscous properties of the specimen. The behaviors of Eqs. (1) and (2) can be modeled by the quadratic elements of spring and dashpot, respectively, as Fig. 1a and b show. Since the quadratic relations of Eqs. (1) and (2) are considered, the Kelvin model in quadratic form is also proposed in order to describe the viscoelastic deformation behavior exhibited in the indentation tests. As Fig. 1c shows, the indentation load and the square of indentation depth, expressed in the quadratic Kelvin model, are written as

$$P_\mathrm{ve} = P_\mathrm{e/ve} + P_\mathrm{v/ve} \tag{3.a}$$

$$h_\mathrm{ve}^2 = h_\mathrm{e/ve}^2 = h_\mathrm{v/ve}^2 \tag{3.b}$$

where the subscripts, ve, e/ve, and v/ve, denote the total, the spring and the dashpot quantities in the Kelvin model, respectively.

For the quadratic Kelvin model, as mentioned above, depth solutions can be obtained according to the applied load. During the loading process with a constant loading rate C_L the applied load can be expressed as $P_\mathrm{L} = C_\mathrm{L} \cdot t$, and the corresponding deformation can be solved as

$$h_\mathrm{L}^2 = \frac{C_\mathrm{L} \cdot t}{K} + \frac{C_\mathrm{L} \cdot M}{K^2} \cdot \left(e^{\frac{-t \cdot K}{M}} - 1\right). \tag{4}$$

The solution in the dwelling process, after the constant-loading-rate process, shown in Fig. 2a, can be obtained by time-shifted function. The solution is expressed as

$$h_\mathrm{L-H}^2 = \frac{C_\mathrm{L} \cdot M}{K^2} \cdot \left[e^{\frac{-t \cdot K}{M}} - e^{\frac{-(t-t_1) \cdot K}{M}}\right] + \frac{C_\mathrm{L} \cdot t_1}{K}. \tag{5}$$

Similarly, the depth solution corresponding to the sinusoidal load $P_\mathrm{OS} = P_\mathrm{O} \cdot \sin(\omega \cdot t)$, as Fig. 2b shows, can be obtained as

$$h_\mathrm{OS}^2 = \frac{P_\mathrm{O}/K}{\sqrt{(\omega \cdot M/K)^2 + 1}} \cdot \sin[\omega \cdot t - \theta] + \frac{P_\mathrm{O}}{\omega^2 + (K/M)^2} \cdot \frac{\omega}{M} \cdot e^{\frac{-K \cdot t}{M}}, \tag{6}$$

where ω denotes the angular velocity of the oscillating load, and θ denotes the phase lag, $\theta = \tan^{-1}(\omega \cdot M/K)$.

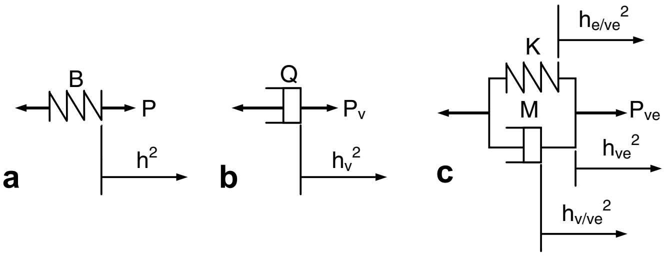

Fig. 1. The quadratic elements of (a) spring, (b) dashpot, and (c) the Kelvin model.

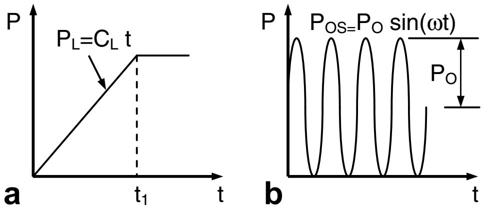

Fig. 2. The load conditions for (a) the loading process with a constant loading rate C_L and followed by a dwell process, (b) the oscillating process with a sinusoidal load.

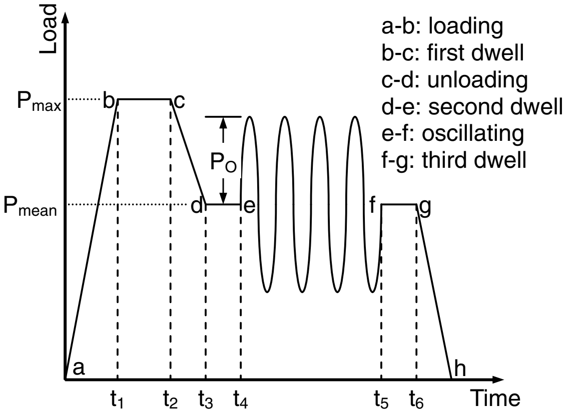

Fig. 3. The arrangement of load conditions applied in this study; the load in the b–c segment is maximum.

2.2. Experimental details

In this study, the polymers of polymethylmethacrylate (PMMA) and polyurethane (PU) were chosen as tested materials. The specimens were annealed at a temperature 5 °C above their glass transition temperature (PMMA: 145 °C, PU: 42 °C). Then, they were cooled down to room temperature at a cooling rate of approximately 5 °C/h. Samples were stored in an enclosed desiccator with approximately 50% relative humidity and controlled by dehumidifier. All specimens had ageing times of almost 72 h, and were placed on steel holders during testing. All indentation tests were performed by a TriboScope (Hysitron, US) system, and a Berkovich indenter made of diamond was used. The load conditions used in the indentation tests, as Fig. 3 shows, involve following subregions: the loading process with a constant loading rate (a–b), the first dwell after the loading process (b–c), the constant-rate-unloading

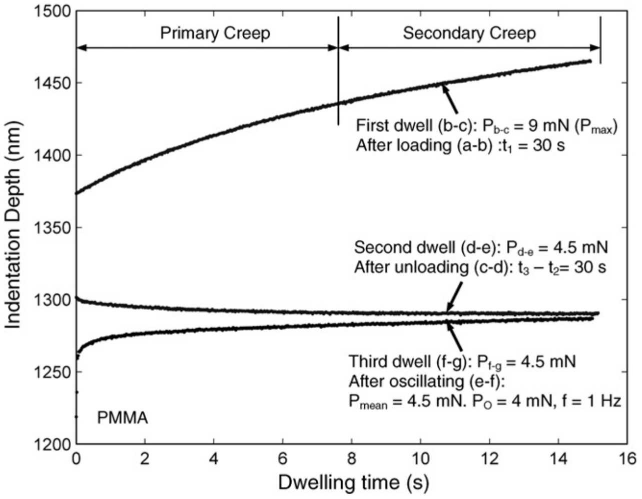

Fig. 4. The experimental results of depth vary with time in the b–c, d–e, and f–g segments.