Supplementary Materials

Accurate measurement of elastic modulus and hardness via a rate-jump method

In this method, the elastic modulus and hardness are evaluated at the onset of an unloading stage. Such an onset point for unloading is a rate-jump point, the true elastic modulus $S_e$ can be calculated from the data just before and after the unloading point using equation (1) [1],

$$\frac{1}{S_e - K} = \frac{1}{S} - \frac{h\text{'}}{P_u} \left( \frac{P_{\text{u}}}{1 - P_{\text{u}}} \right)$$

(1)

$$S_e = 2aE_r = \frac{2E_r}{1 - v^2} - \frac{2a}{1 - 0.3^2} = 2.2Ea$$

(2)

where $S$ is the apparent tip–sample contact stiffness at the onset of unload and equals to $dP/dh$, $P$ is force and $h$ is displacement. $h\text{'}$ is the displacement rate just before the unload, $P_{\text{h}}$ and $P_{\text{u}}$ are the loading and unloading rate, respectively. $K$ is the fitting parameter and equals to zero when the indentation is performed in air condition. Following the Sneddon relation [2,3] we can have equation (2), where $E_r$ and $E$ are the reduce modulus and the elastic modulus of the tested materials, $v$ is the poission ratio, ($v = 0.3$ for glass-ionomer cement, [4]). $a$ is the radius of the contact area. The contact size $a$ can be estimated from a pre-calibrated shape function $f(h_c) = \pi a^2$ of the tip. The contact depth $h_c$ is obtainable using the Oliver–Pharr relation [5] with the true contact stiffness $S_e$, as shown in equation (3).

$$h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S_e} = h_{\text{max}} - 0.75 \frac{P_{\text{max}}}{S_e}$$

(3)

Where $h_{\text{max}}$ and $P_{\text{max}}$ are the maximum indenter displacement at the onset of unloading and the load before unloading, respectively. $\varepsilon$ is a constant ($\varepsilon = 0.75$ for Berkovich tip). And the hardness can be measured by equation (4),

$$H = \frac{P_{\text{max}}}{A_c}$$

(4)

All the raw data collected from the nanoindentor were read and calculated via Matlab R2014a software. Here we show how the results of one set data were calculated.

**Sample 1:**

Since samples are tested in air testing condition, $K=0$,

$$\frac{1}{S_e} = \frac{1}{S} - \frac{h\text{'}}{P_u} \left( \frac{1}{1 - P_{\text{u}}} \right) = \frac{1}{17543} - \frac{257.6 \times 10^{-9}}{-9.993 \times 10^{-3}} \left( \frac{1}{1 - 7.342 \times 10^{-3}} \right)$$

The true elastic stiffness $S_e = 2.1 \times 10^4$ N/m;

The contact depth $h_c = h_{\text{max}} - 0.75 \frac{P_{\text{max}}}{S_e} = 5700 \times 10^{-9} - 0.75 \times \frac{100 \times 10^{-3}}{2.1 \times 10^4} = 2.13 \times 10^{-6}$ m

The contact size $A_c = 1.11 \times 10^{-10}$ m$^2$

The contact radius $a = 5.95 \times 10^{-6}$ m

The true elastic modulus $E = \frac{S_e}{2.2a} = 1.16 \times 10^9$ Pa = 1.16 GPa

The hardness $H = \frac{P_{\text{max}}}{A_c} = \frac{100 \times 10^{-3}}{1.11 \times 10^{-10}} \times 9.01 \times 10^9$ Pa = 0.9 GPa

**References**
