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Research paper

Modified flat-punch model for hyperelastic polymeric and biological materials in nanoindentation

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ABSTRACT

Nanoindentation can characterize in-situ elastic modulus E of an object by pressing an indenter into the sample surface and fitting the detected data to a contact equation. In this work, we found the conventional contact-mechanism theory resulted in a high uncertainty of E for the hyperelastic materials, including some polymers and biological cells. The evaluated E displayed an exponential decrease with increasing indent distance when fitting to Hertz model and caused high E variance as a function of indent depth. To obtain a reliable E of those specimens, a new equation for E computation directly adopting the mechanical behavior of the sample was proposed. Indenting on hyperelastic polydimethylsiloxane (PDMS), we observed linear force-displacement curves and used its power-law for the selection of the correct equation. The flat-punch model was thus chosen and showed constant E independent of the indent size, which meant the indent depth in this paper. After eliminating the depth effect on E, we referred the nanoindentation results to the bulk E of PDMS for the revision of the flat-punch model. A new equation was generated and displayed the improvement on not only the precision (remove depth effect) but also the accuracy (compare to compression test) of E for PDMS. The suitability of the modified flat-punch model for hyperelastic material implied the practical deformational mechanism different from the general idea. Applied on microbial samples, our new equation characterized two bacteria and showed consistent results with their membrane structures. In conclusion, we suggest the modified flat-punch model improves the description of mechanical behaviors and derived the correct E for hyperelastic materials.

Introduction

The elastic modulus (E) represents the resistance of a material under elastic deformation, and serves as the reference for the prediction of the mechanical performance of an object. The traditional methods to measure E include tensile and compression tests, which record the relation of stress and strain and calculate E from the linear part of the stress-strain curves, but the application of these models is limited by the feature size of the specimen. For smaller samples, such as electronic devices, thin films, and biological materials, a process of nanoindentation, usually conducted with an atomic force microscope (AFM) and nanoindentor (NI), detects the mechanical responses of a material's surface from a micro/nanoscale indenter and this approach has been widely used. Because the indenter is smaller than the specimen and is pressed into sample surface, the tip geometry is therefore taken into account for the presentation of the contact mechanism between these two objects. Considering the tip as a sphere with radius R, Hertz described the relation of applied force F, indent depth δ, tip radius R, and E, from which E can be derived, and the model is widely used with AFM nanoindentation (Hertz, 1881). When using a sharp indenter, which has conical and pyramidal tips, Sneddon replaced the term R in the Hertz model with the half open angle of tip α to present the indenter, which is known as the Sneddon model (Sneddon, 1965). Although they have been used for a variety of materials, these popular models are not suitable for the hyperelastic materials, and will produce a high deviation in the value of E as a function of indent depth, and thus fail to predict the correct E.

Hyperelastic materials, such as rubber, have incompressible and rheological properties, and perform only elastic deformation under small strain, so the conventional theories for calculating E using nanoindentation are not suitable (Mark et al., 2005). In addition to hyperelastic polymers, some biological materials, such as fatty tissue, have also been characterized as being hyperelastic while most of the E analysis carried out via AFM still used the Hertz and Sneddon models, which could thus lead to high deviations in the value of E (Samani and Plewes, 2004; Kaster et al., 2011). Several solutions have been proposed to obtain the correct E of elastic solids: some researchers took the surface adhesion of the specimen into account and claimed that the E

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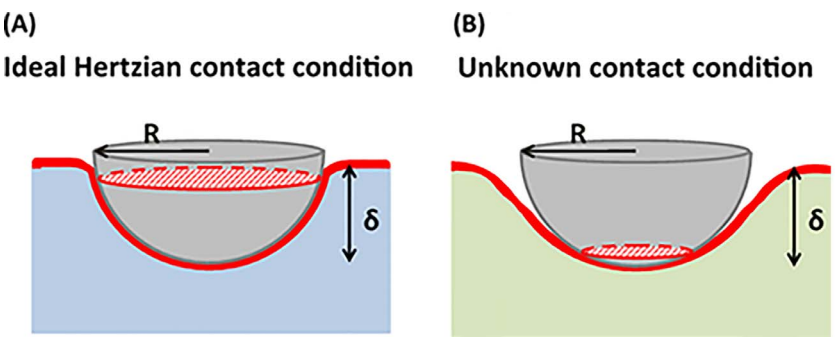

Fig. 1. The schematic graphic of nanoindentation on two materials possessing different deformational mechanisms. The contact area between tip and sample depends on (A) tip shape and (B) sample intrinsic properties.

computed via nanoindentation would be comparable to that measured in the bulk material (Dokukin and Sokolov, 2012). The commonly-used adhesion-adapted models include the Johnson, Kendall, Robert (JKR), Derjaguin, Mullar, Toporov (DMT), and Maugis models, which all are basically derived from Hertz's theory (Chang et al., 2016; Carrillo et al., 2005; Sun et al., 2004). Other models use the hyperelastic strain energy functions, which describe the stored energy in materials under deformation, to predict the E of rubber-like materials by the common hyperelastic models, such as polynomial and Ogden theories (Kaster et al., 2011; Lin et al., 2009; Ogden, 1972). However, when compared to the bulk E of material, the adhesion-adapted equations obtain similar E only in some cases and the hyperelastic models are suitable for the condition with high sample deformation rather than the shallow nanoindentation. In this experiment, we characterized the mechanical performance of *Staphylococcus aureus* cells, and found that it was similar to that of hyperelastic polydimethylsiloxane (PDMS). The conventional indenter-dependent contact mechanism theory (Fig. 1A) for computing E was found to result in high levels of uncertainty, because these materials have different deformational behaviors (Fig. 1B) from metals and ceramics. A flat-punch equation that has similar power-law of force-displacement curve with PDMS was chosen for the improvement of the E precision that would be independent of other experimental factors and be specific to each specimen. To obtain accurate E, we revised the formula by connecting the bulk E of the PDMS to that measured by nanoindentation and subsequently, the new equation was derived. The practical application of nanoindentation with the new equation in the microbial field successfully characterized the E of Gram-positive *S. aureus* and Gram-negative *Pseudomonas aeruginosa*, where the results could be linked to their differences in membrane structures. Based on knowledge of the force curve and the unusual indents left on the PDMS surface, we not only suggested the suitability of the new equation for the E evaluation for the hyperelastic matters but also proposed a different deformational mechanism for those materials during nanoindentation.

Materials and methods

Specimens

The polydimethylsiloxane (PDMS) (SIL-MORE INDUSTRIAL LTD., Taiwan) network consisted of the elastomer base and curing agent at a ratio of 5:1. After degassing in a vacuum, the mixture was poured into a petri dish and cured at 65 °C for 12 h.

Two microbe species, Gram-positive *Staphylococcus aureus* and Gram-negative *Pseudomonas aeruginosa*, were selected in this study. Both microorganisms were inoculated from the stock to the agar plates, which were Mannitol salt agar and cetrimide agar, respectively, and cultivated in ambient atmosphere at 37 °C. A colony was then selected and spread onto the glass substrate for the AFM nanoindentation.

AFM nanoindentation tests

The AFM system (Dimension Icon, Bruker, USA) and probe-I with a spring constant k of the cantilever of 6.83 N/m, tip radius R of 58 nm, and half open angle α of 40°, were used for the nanoindentation tests on both *S. aureus* and PDMS specimens. The other five probes, whose k and R were 0.25 N/m and 36 nm for probe-II, 0.25 N/m and 107 nm for probe-III, 0.15 N/m and 24 nm for probe-IV, 60.9 N/m and 534 nm for probe-V, and 58.6 N/m and 239 nm for probe-VI, were indented on PDMS for the examination and establishment of the new contact-mechanism model. The collected force-depth curves were fitted to the standard Hertz theory, as shown in Eq. (1), and the deviations of E as a function of indent depth were correlated with the suitability of model-selection (Hertz, 1881; Sneddon, 1965).

$$E_H = \frac{3F(1-\nu^2)}{4\sqrt{R}\delta^{3/2}} \quad (1)$$

where E_H refers to the Hertz modulus, F is the applied force, δ is the indent depth, R is tip radius, and ν is Poisson's ratio of the specimen. $\nu = 0.5$, described previously, was used for both PDMS and microbial cells in this work (Johnston et al., 2014; Costa, 2004; Liu et al., 2013).

After the nanoindentation tests, all the probes were cleaned by immersing in acetone, ethanol, and distilled water to remove any possible pollution on the tip. The probes were then air-dried and kept in the damp-proof case.

Compression tests

Three PDMS samples were examined using compression tests (SHIMADZU AG-10kNX, Japan) at a strain rate of 20 mm/min at room temperature. The length, width, and thickness of the specimens were 10 mm, 10 mm, and 1.53 mm, and thus the stress as a function of strain could be plotted. The linear part in the strain range of 0.2–0.4 was considered as the elastic deformation of PDMS, and the slope of stress/strain was the bulk modulus of PDMS (Johnston et al., 2014).

Results

Our previous work suggested that the specimen-dependent selection of the indent size should be 10 times greater than the surface roughness and less than 10% of the thickness, so that the influences of both roughness and thickness of sample on E evaluation become negligible. (Chang et al., 2016). The surface roughness and thickness of the PDMS specimen were respectively 1.64 nm and 1.53 mm, and thus a δ ranging from 16.40 nm to 153 μm was used in the experiment.

AFM nanoindentation on both S. aureus and PDMS

Using probe-I with the maximum indent depth of 40 nm, the force curves of *S. aureus* cells and PDMS were found to be nearly linear but with different slopes, which were 1.23 N/m for bacterial cells and 0.58 N/m for PDMS, as shown in Fig. 2. The linear force curves were