EXTRACTING VISCOELASTIC PROPERTIES OF SOFT POLYMERS FROM DYNAMIC NANOINDENTATION USING AN IMPROVED MODEL

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ABSTRACT

Recently there is an increasing interest in using polydimethylsiloxane (PDMS)-based micropillars as bio-transducers for cellular forces measurements. Cells often produce cyclic motion, in which case the viscoelastic properties in the frequency domain are needed for force calculation. In this work, continuing on our prior time domain study, we measured the complex modulus of PDMS using a dynamic nanoindentation technique (DNT). An improved model for complex modulus extraction was developed for the flat punch indenter. The complex modulus of PDMS measured at small scale will allow for more accurate cellular force measurements in the frequency domain.

KEYWORDS

PDMS; Micropillar; Cellular force; Transducer; Viscoelastic; Complex modulus; Dynamic nanoindentation.

INTRODUCTION

Cellular force plays critical roles in various physiological developments such as division, growth, migration and signal transductions. Polydimethylsiloxane (PDMS)-based micropillar transducers have been employed extensively to measure cellular contractile forces during the last decade (Figure 1) [1-3]. The basic sensing principle relies on converting lateral deflections to corresponding reaction forces using appropriate beam theory. In most previous studies, the polymer materials were assumed to behave as linear elastic materials. However, PDMS has an inherent viscoelastic behavior [4, 5], i.e. time- or frequency-dependent modulus which violates the linear elastic assumption. Neglecting this behavior will compromise the accuracy of these devices in measuring the cellular contractile forces for different cell force sensing applications, resulting in a false interpretation of the cell mechanics.

In cellular contraction, oscillatory motion is often involved, in which case the mechanical response of micropillars in the frequency domain needs to be understood for interpretation of the complex cellular contraction behavior [2]. For a linear viscoelastic material, the viscoelastic properties can be represented by complex functions in the frequency domain. With the development of both instrumented nanoindentation and the associated analysis, dynamic nanoindentation has recently been used to characterize the viscoelastic properties of soft materials in the frequency domain [6-9]. However, the accuracy of this measurement technique is highly dependent upon the accurate characterization of the dynamic response of the measurement system, the nanoindenter tip geometry, and an appropriate model for extracting the viscoelastic properties of a material. In addition, the extreme mechanical compliance of PDMS poses a challenge to probing its viscoelastic properties at the micro/nano scales.

In this work, we developed a method to measure the complex modulus of soft polymers using dynamic nanoindentation with a flat punch indenter. The viscoelastic behavior under a time-harmonic loading condition was analyzed using a hereditary integral operator [6, 10]. A general formulation is given such that this approach is applicable to all linear viscoelastic materials, thus removing all the constraints imposed by the previous methods. The complex modulus of PDMS measured at the small scale will allow for more accurate cellular force measurements in the frequency domain.

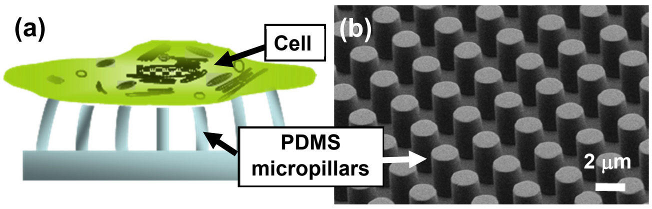

Figure 1: (a) Schematic illustration of micropillar-based cellular force transducer. (b) SEM micrographs of high density micropillars.

THEORETICAL BACKGROUND

Nanoindentation on a thick, soft material can be considered as a process of indenting a half-space with a rigid indenter. For a flat punch indenter indenting into a homogeneous, isotropic and linear elastic material, the load P is proportional to the indentation displacement h [11]:

$$P = \frac{2RE}{1-\nu^2} h \tag{1}$$

where R is the radius of indenter, and E and ν are the Young's modulus and Poisson's ratio of the test material, respectively.

The solution to the linear viscoelastic material indented by a flat punch indenter can be obtained based on the corresponding linear elastic indentation. Since the contact area between the indenter tip and the test material is constant during indentation [6], the load-displacement relationship for a viscoelastic material follows a hereditary integral:

$$P = \frac{2RE}{1-\nu^2} \int_0^t E(t-\xi) \frac{dh(\xi)}{d\xi} d\xi \tag{2}$$

where $E(t)$ is the Young's relaxation modulus.

For a load controlled indentation, from Equation 2, the displacement can be represented by the harmonic load and compliance function of material. The time domain compliance function can be converted to the frequency domain through the Fourier transform. Through several derivations [12], the complex compliance can be obtained from the magnitude and phase information of input harmonic force and output displacement

$$D'(\omega) = \frac{2R}{1-\nu^2}\frac{\Delta h_0}{\Delta P_0}\cos\phi \qquad (3)$$
$$D''(\omega) = \frac{2R}{1-\nu^2}\frac{\Delta h_0}{\Delta P_0}\sin\phi$$

where ΔP_0 is the amplitude of harmonic load, Δh_0 is the amplitude of harmonic displacement, and ϕ is the phase between the load and displacement.

Consequently, the complex modulus can readily be obtained from the complex compliance through the reciprocal relationship in the frequency domain:

$$E^*(\omega) = \frac{1}{D^*(\omega)} = \frac{1}{D'(\omega) - iD''(\omega)} = \frac{D'(\omega) + iD''(\omega)}{D'(\omega)^2 + D''(\omega)^2} \qquad (4)$$

Given that $E^*(\omega) = E'(\omega) + iE''(\omega)$, the storage modulus and loss modulus are readily obtained

$$E'(\omega) = \frac{D'(\omega)}{D'(\omega)^2 + D''(\omega)^2} = \frac{1-\nu^2}{2R}\frac{\Delta P_0}{\Delta h_0}\cos\phi \qquad (5)$$
$$E''(\omega) = \frac{D''(\omega)}{D'(\omega)^2 + D''(\omega)^2} = \frac{1-\nu^2}{2R}\frac{\Delta P_0}{\Delta h_0}\sin\phi$$

The expression essentially agrees with *Herbert et al.'s* formulas in the case of the circular flat punch indenter [8]. The advantage of our method is that there is no linear constitutive model used in derivation, therefore, the frequency-dependent viscoelastic behavior is precisely captured without assumptions.

RESULTS AND DISCUSSION

Dynamic Nanoindentation Test

The DNT tests were conducted on a G200 Nanoindenter system (Agilent), using a sapphire flat cylindrical punch indenter (Micro Star Tech.) with a diameter of 2.01 mm (Figure 2). The "G-Series XP CSM Flat Punch Complex Modulus" method was used. The frequencies of the harmonic load were in the range of 1~45 Hz. The harmonic load was controlled such that the resulting amplitude of oscillatory displacement was maintained at 50 nm. The complex modulus and loss factor as a function of frequency were obtained from the model described in previous section.

Since a flat punch indenter tip was used in this work, the measurement results are sensitive to the mounting conditions associated with the small angle between the tip end and the sample surface. Therefore, it is important to identify the full contact region. It is seen that pre-compression depth has a strong effect on the storage modulus. At small depths (2.5 - 20 μm), the partial contact due to the tip tilting results in the lower modulus; at larger depths (70 - 100 μm), the increase is most likely

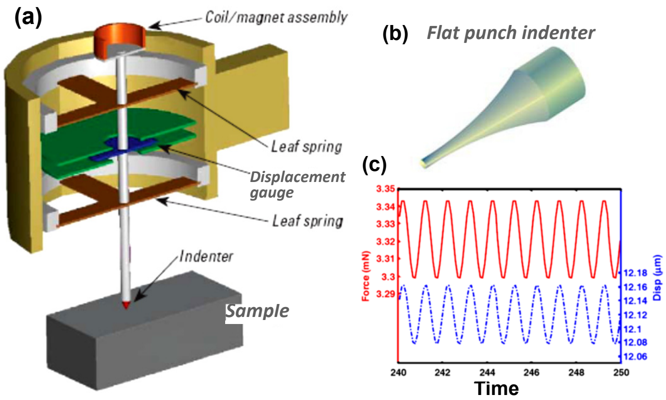

Figure 2: (a) Schematic of the "head" of the Agilent G200 Nanoindenter system. (b) The sapphire flat-ended cylindrical punch tip with a diameter of 2.01 mm. (c) Representative harmonic displacement and force curves at 1 Hz.

induced by the large strain applied on the PDMS which

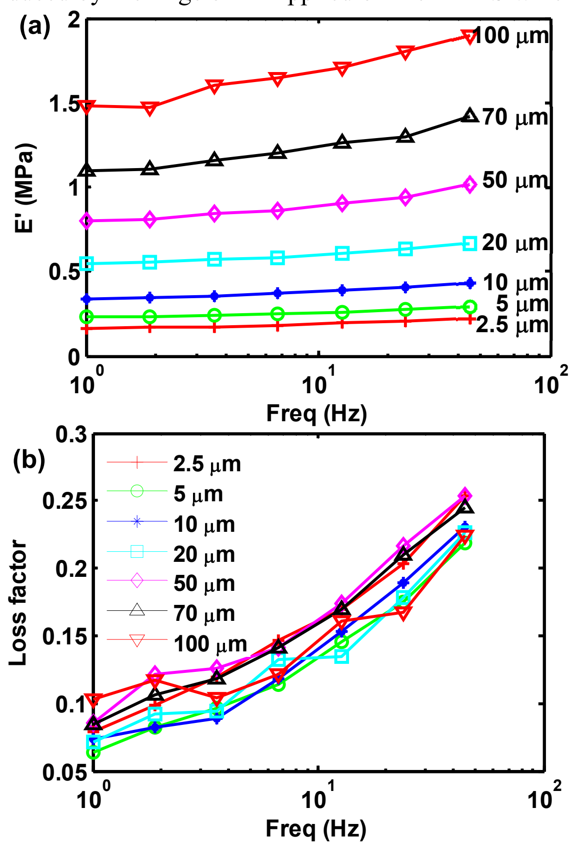

Figure 3: Frequency-dependent (a) storage modulus and (b) loss factor of PDMS under various pre-compressions.

violates the small deformation assumption in linear viscoelasticity. The modulus in the vicinity of 50 μm depth is comparable to that previously reported by *Conte and Jardret* [13], as well as our own measurement in the time domain [4]. Therefore we conclude that this is the "full contact" region for the 2.01 mm diameter flat punch indenter tip.

White et al. reported a thorough summary of the complex modulus of PDMS measured by various techniques, including nanoindentation, solids analyzer, shear rheometer, and the Johnson-Kendall-Roberts (JKR) adhesion test [7]. Good agreement was found among all the tests, with their nanoindentation data using a Berkovich tip remaining a factor of 2 higher than those of the bulk methods. In our experiments, the flat punch indenter ensures the constant contact area during the indentation process and, therefore, our results are more accurate than those obtained using Berkovich nanoindentation.

Generalized Maxwell Model

The complex modulus data measured at discrete frequencies can be interpolated to a frequency dependent function using the generalized Maxwell model

$$E(t) = E_\infty + \sum_{j=1}^{N} E_j e^{-\lambda_j t} \tag{6}$$

where E_∞ and E_j are relaxation coefficients, λ_j are the reciprocals of relaxation times (τ_j) and N is the number of exponential terms in the Prony series. Using the half-sided Fourier transform, the complex modulus $E(\omega)$ can be obtained from the relaxation modulus $E(t)$

$$E(\omega) = i\omega \int_0^\infty E(t) e^{-i\omega t} dt$$
$$= \left(E_\infty + \sum_{j=1}^{N} \frac{E_j \omega^2}{\lambda_j^2 + \omega^2}\right) + i\left(\sum_{j=1}^{N} \frac{E_j \lambda_j \omega}{\lambda_j^2 + \omega^2}\right) \tag{7}$$

A nonlinear least squares curve fitting method was performed to obtain the coefficients and relaxation times using both the storage modulus and loss factor (ratio of loss modulus to storage modulus). The fitting results are plotted in Figure 4.

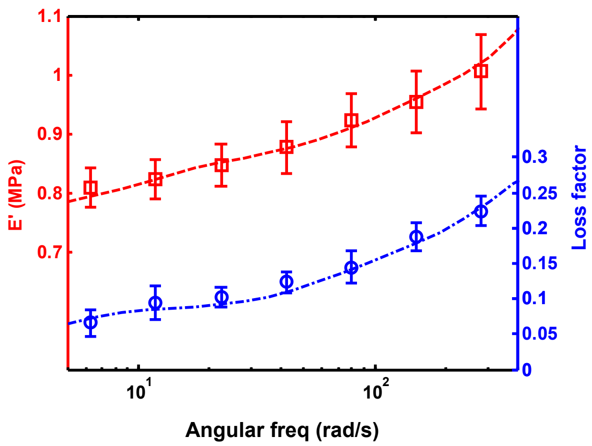

Figure 4: The experimental data (marker with error bar) and generalized Maxwell model fitting (dashed lines) for both the storage modulus and loss factor.

Application

The viscoelastic property of PDMS can be further applied to calculate the cellular contractile force. Herein the cardiac myocyte contraction tests from Zhao and Zhang's previous report was used as the study case [2]. Two states were chosen, 3-min and 7-min after the isoproterenol stimulation, respectively. The cellular force was then calculated by finite element analysis (FEA) using ABAQUS. The enlarged root and notched sidewall of the micropillar was modeled using 3D elements C3D10. The Fourier series of displacement and complex modulus from the previous analysis were incorporated into the FEA model. The force responses follow the similar cyclic patterns as the contraction displacements. The magnitudes of forces for 3-min and 7-min cases are 15.9 nN and 10.8 nN, respectively. These values are significantly less (approximately 75%) than those calculated from Zhao and Zhang's report. Based on these results, it is seen that the effects of viscoelastic properties and the use of an appropriate beam model are critical to the accurate calculation of cellular contraction forces using PDMS micropillar sensor arrays.

CONCLUSIONS

The viscoelastic properties of PDMS in the frequency domain were measured by a dynamic nanoindentation technique. An improved model was developed to extract the complex modulus with the use of a flat punch indenter. The frequency-dependent modulus function was obtained using least squares curve fitting of a generalized Maxwell model. The DNT is extremely useful for soft polymeric materials for which the dynamic mechanical properties are a challenge to characterize at small scales.

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