High Throughput Modulus Measurements of Soft Polymer Networks

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INTRODUCTION

Soft polymer systems such as hydrogels present a considerable challenge to existing mechanical testing techniques. One of the most important considerations in the evaluation of hydrogels for biomedical applications is the elastic modulus. The elastic modulus is related to several important factors including flexibility, adhesion, swelling behavior, and the potential for cell proliferation and growth.[1] Current methods for assessing the moduli of hydrogels are typically oriented towards the measurement of single specimens in a non-automated manner. The increasing pace of research and development of such products demands that measurements occur in a high-throughput manner.

In response to these challenges, we are producing a platform for high-throughput measurement of the modulus of soft polymer materials and products. This platform draws on a high-throughput metrology[2] we developed for measuring the elastic modulus of thin films and coatings. This methodology leverages an elastic buckling instability that occurs upon compression of a stiff upper film adhered to a soft elastic substrate. The periodicity of the buckling pattern is primarily dependent on the modulus ratio between the film and substrate as well as the thickness of the upper film:

$$\frac{E_f}{(1-\nu_f^2)} = \frac{3E_s}{(1-\nu_s^2)}\left(\frac{d}{2\pi h}\right)^3 \quad (1)$$

where E is the elastic modulus, ν is Poisson's ratio, h is the thickness of the film, and d is the wavelength of the instability (subscripts f and s denote the film and substrate, respectively). In our validation studies[2], the upper film was the unknown to be measured (all else being known or constant). We propose in this study to invert the experimental design by using a sensor film of known modulus and thickness, thus rearranging Eq. 1 as follows:

$$\frac{E_s}{(1-\nu_s^2)} = \frac{E_f}{3(1-\nu_f^2)}\left(\frac{2\pi h}{d}\right)^3 \quad (2)$$

Here, the unknown to be determined is the modulus of the soft elastic substrate, E_s. The thickness of the sensor film is chosen such that the wavelength of the buckling instability can be measured by small angle light scattering (SALS), thus enabling high-throughput measurement of the substrate modulus.

EXPERIMENTAL[3]

Poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Chemical) was chosen as the elastic foundation since it is optically transparent, it approximates an ideal elastomer, and its modulus can be tuned by the mixing ratio of base to curing agent ($E_s \approx$ (0.1 to 2) MPa). Polystyrene (PS) was employed as the sensor film having a measured modulus of 3.5 GPa.[2] Solutions of PS in toluene were spin coated onto silicon wafers to the desired thickness. Sensor films were transferred to the surface of pre-strained PDMS as described previously.[2] A compressive stress was applied to the film by slowly releasing the applied strain until buckling occurred. The wavelength of the buckling pattern was measured using a custom-designed SALS apparatus equipped with a computer-controlled *x-y* translation stage. The translation stage enables rastering of the sample across the laser beam, transforming the SALS apparatus into a high-throughput measurement platform.

DISCUSSION

Before employing this metrology, we need to gauge the sensitivity of the buckling wavelength (the measurable) on the substrate modulus over the range of moduli anticipated for soft gels and networks. This exercise will also provide guidance as to the thickness of the sensor film needed to provide sufficient sensitivity. Figure 1 plots the wavelength as a function of substrate modulus and sensor film thickness. For a given film thickness, the highest sensitivity (largest slope, $\delta y/\delta x$) is for substrate moduli less than approximately 2 MPa. The sensitivity increases with sensor film thickness, but practical aspects such as adhesion of the sensor film to the substrate may prove prohibitive for film thickness $h \geq 200$ nm. As a result, the sensor film thickness should be in the range 100 nm < h < 200 nm.

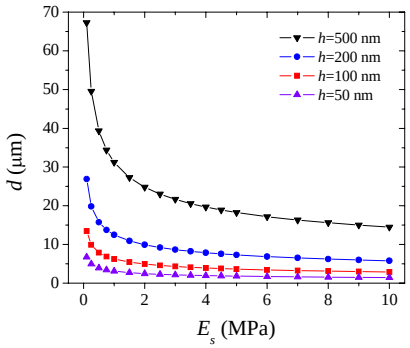

Figure 1. Predicted sensitivity of buckling wavelength (d) on the substrate modulus (E_s) as a function of probe film thickness (h). The modulus of the sensor film (E_f) is taken as 3.5 GPa, the measured value for polystyrene.

Another metrological question is what depth into the substrate material are we probing with this metrology? Due to specific material processing issues (*e.g.*, surface enrichment of low molecular weight materials, attenuation of light in a UV curing system, etc), the surface modulus of some materials could be either higher or lower than the bulk modulus of that material. We are answering this depth sensitivity question by employing Finite Element Analysis (FEA). The depth of deformation in the substrate is expected to be a function of both the buckling wavelength and the buckling amplitude, each of which can be further related to the material properties of both the sensor film and substrate, the thickness of the sensor film, and the applied strain. FEA is a powerful tool to deduce these relationships due to its flexibility regarding material properties and boundary functions. Based on such knowledge, high-throughput experiments could be designed to probe the depth-dependent modulus of various substrate materials.

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3. Equipment and instruments or materials are identified in the paper in order to adequately specify the experimental details. Such identification does not imply recommendation by NIST, nor does it imply the materials are necessarily the best available for the purpose.