Elastic Moduli of Polymer Thin Films: A High-throughput Metrology

Thin polymer films are playing an increasing role in technological applications such as lithographic resist layers, barrier layers, electronic packaging, and optical coatings. As a result, it is becoming apparent that confined polymers can display subtle or even dramatic differences in their physical properties when compared to the same polymers in the bulk state. Understanding these differences is critical to the performance and stability of these devices and systems. In particular, the mechanical properties of thin films are of paramount importance since these properties often impact many of the reliability issues encountered while integrating thin polymer films into new devices. Thus, there is a growing need for measurement techniques that probe the mechanical properties of these materials, not in the bulk state, but rather in their application form, that is, in thin film geometries. This article highlights an innovative high-throughput (HT) method by which the elastic moduli of thin polymer films/coatings can be measured both rapidly and quantitatively. This platform is ideally suited for integration into combinatorial and high-throughput (C&HT) workflows that utilize gradient specimens to generate two-dimensional maps of the mechanical properties of polymer films that vary spatially. Results on several model systems are reviewed that demonstrate the broad applicability of this technique to a wide range of film thickness (30 nm to 50 μm) and modulus (5 MPa to 10 GPa).

1. Thin Film Mechanical Properties

There exist a limited number of techniques to measure the mechanical properties of polymer thin films. The most prominent of these methods are based on instrumented indentation (VanLandingham 2003), where a point load is applied to a substrate-supported film and the load–penetration depth curve is recorded over a loading/unloading cycle. From the load–penetration depth curve, the hardness and the Young's modulus of the film can be determined. This measurement technology has enjoyed great success in several fields of materials science, primarily in metals and ceramics, and recent advances in instrumented indentation have enabled more quantitative measurements to be made on relatively soft, polymeric materials. Instrumented indentation has evolved to include micro-/nanoindentation (Asif et al. 1999, VanLandingham et al. 2001) as well as nanomechanical testing based on atomic force microscopy (AFM) (Kovalev et al. 2004).

Despite the success of instrumented indentation, there continue to be a number of technical issues impeding accurate indentation measurements on thin polymer films, the most notable being the so-called substrate effect. While performing indentation on soft polymer films, the presence of the stiff substrate (e.g., silicon or glass) inevitably affects the measurement. To avoid any contributions from the substrate, it is commonly estimated that the indentation depth be less than 10% of the total film thickness. Such shallow indentation depths become increasingly impractical or difficult as the film thickness approaches 100 nm or below. Another unresolved issue in indentation is the uncertainty in probe size and shape, and thus the indented area. This is particularly problematic in AFM experiments since the indented region is typically imaged with the same AFM tip that was used to indent; therefore, the resolution of the image used to quantify the tip shape and the indent area is self-limited.

In addition to instrumented indentation, there are surface acoustic/guided wave methods for probing the near-surface mechanical properties of polymer thin films (Every 2002). Common methods for measuring the elastic modulus of thin films include Brillouin light scattering (BLS) (Forrest et al. 1998) and surface acoustic wave spectroscopy (SAWS) (Flannery et al. 2002). These techniques are noncontact and nondestructive and thus are ideally suited for in-line quality control applications. BLS also has the advantage that it can be performed on free-standing films.

Each of these techniques (indentation, AFM, BLS, SAWS) has distinct advantages and notable disadvantages when applied to studying polymer thin film mechanical properties. In addition, these methodologies are not amenable or adaptable to C&HT measurement strategies, which are proving to be pivotal in an increasingly fast-paced research environment. C&HT methods combine experiment design, instrument automation, and computing tools to increase the pace of scientific discovery. Over the past few decades, C&HT approaches have enjoyed success in the pharmaceutical industry, where they provide a platform for the accelerated discovery and screening of new drug candidates. (Gordon and Kerwin 1998) More recently, C&HT concepts are being adapted to study problems in materials science. However, the C&HT methods developed for the pharmaceutical industry often cannot be applied directly to materials research since methods for generating materials libraries and measuring properties rapidly, especially mechanical properties, are often lacking. C&HT materials research requires new sets of tools that enable the fabrication of materials-relevant libraries and characterization techniques that measure materials properties in an HT manner. Highlighted here is an innovative buckling-based metrology that shows profound potential to address numerous questions posed regarding the mechanical response of confined polymer thin films. This new metrology is uniquely positioned as a viable HT technique to measure the elastic moduli of polymer thin films.

2. History of Surface Buckling

The study of buckling in struts and columns can be traced back to the pioneering work of Leonhard Euler. His detailed analysis of column buckling revealed that there is a critical load above which the column becomes unstable and undergoes a lateral displacement away from the centerline axis. It was determined that the critical load is a function of the flexural rigidity of the column and inversely proportional to its length. This analysis was later applied to laminates in the form of sandwich panels, the simplest of which is comprised of two relatively thin, stiff sheets of material (face) confined to either surface of a thick, low-density material or foam (core). The core material acts to inhibit large wavelength deformations of the laminate and sustains most of the shear forces. The text by H.G. Allen (1969) provides a thorough review of the mechanics pertaining to structural sandwich panels. One of the primary modes of failure of a sandwich panel is local (surface) buckling or wrinkling of the laminate when subjected to compressive stress σ_f. It is this buckling mode (see Fig. 1) that will be the focus of this article.

Recently, surface buckling has reemerged in the literature with regard to the buckling of stiff films adhered to soft, elastomeric substrates. Bowden *et al.* (1998) demonstrated the formation of buckles on the surface of poly(dimethylsiloxane) (PDMS) that was coated with 50 nm of gold. It was deduced that a buckling instability was induced by the thermal expansion of the PDMS during evaporation of the gold capping layer, followed by subsequent contraction of the laminate upon cooling to ambient temperature. Since the compressive stresses that evolve during this thermal cycling are isotropic, the resulting buckling patterns were isotropic, but ordered patterns were observed near the edges of relief structures in PDMS. The authors also noted that the wrinkling which occurred in this geometry was highly periodic with wavelengths ranging from 20 μm to 50 μm and peak-to-valley amplitudes of 1.5 μm to 3.9 μm.

The dependence of the buckling wavelength and amplitude on the system properties and experimental conditions has been previously determined for the case of buckling of stiff plates (face) coupled to soft substrates (core) when subjected to a compression
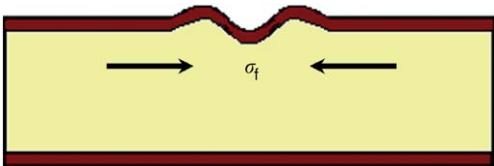

Figure 1
Schematic of face wrinkling that can occur in laminates and structural sandwich panels.

strain (Volynskii *et al.* 2000, Groenewold 2001, Huang 2004). In this derivation, the energy required to bend the plate is balanced against the energy required to deform the core/substrate, resulting in suppression of large wavelengths (due to the unfavorably large deformations of the core) and short wavelengths (due to the large energy required to bend the plate). By minimizing the total energy of the system upon application of a compressive stress, a relationship between the wavelength of the buckles and the material properties of both face and core can be obtained (Eqn. (1)):

$$\frac{E_f}{(1 - v_f^2)} = \frac{3E_c}{(1 - v_c^2)}\left(\frac{d}{2\pi h}\right)^3 \tag{1}$$

E_f and E_c are the elastic moduli of the face and core, respectively; v_f and v_c are the Poisson's ratio of the face and core, respectively; d is the wavelength of the buckles; and h is the thickness of the face. This solution is valid given the following conditions: (a) low strain ($\varepsilon \ll 10\%$), (b) $E_f/E_c \gg 1$, (c) the core is much thicker than the face, and (d) the amplitude of the wrinkles is much smaller than their wavelength. The significance of this analysis is that the buckling of stiff plates on elastic media provides an invaluable tool for gaining insight into the mechanical properties of thin films.

3. A Buckling-based Metrology

Inspection of Eqn. (1) leads to a very intriguing conclusion: if a polymer film of unknown modulus is laminated onto a substrate whose elastic properties are known, the modulus of the polymer film can be calculated simply by compressing the laminate and measuring the periodicity or wavelength of the resulting buckling pattern. This exercise also assumes that the thickness of the polymer film is known. This value can be accurately measured by any of a variety of existing techniques (e.g., ellipsometry, interferometery, X-ray reflectivity). Utilizing this concept, NIST has developed a simple metrology by which the mechanical properties of thin polymer films can be realized. This metrology has been denoted strain induced elastic buckling instability for mechanical measurements (SIEBIMM). In this geometry, a highly periodic buckling instability arises from a mismatch of the elastic moduli of a relatively stiff polymer coating applied to a soft silicone substrate (see Fig. 2). The buckling wavelength can be ascertained by several conventional techniques. If the buckles have periods of 1 μm up to 50 μm, the wavelength can be rapidly measured by laser light diffraction (see Figs. 3 and 4(a)). Larger wavelengths can be captured using an optical microscope (see Fig. 4(b)). Ripples with periods less than 1 μm can be imaged via AFM (see Fig. 4(c)). Light diffraction and optical
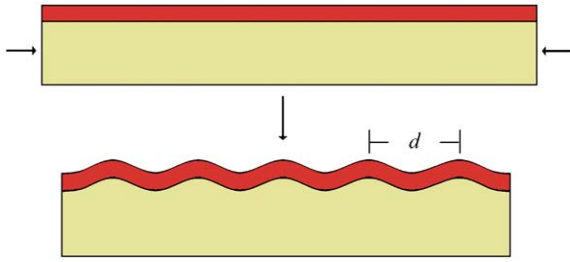
Figure 2
Compression of stiff film (red) supported on a soft substrate (yellow) leads to buckling with a well-defined wavelength, *d*.
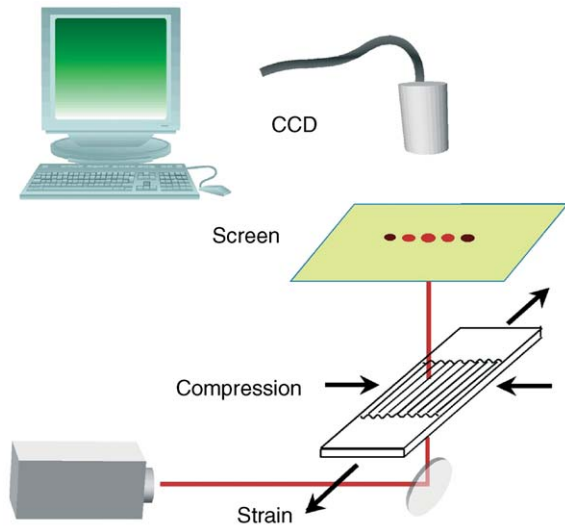

Figure 3
Experimental light scattering setup designed for the rapid measurement of buckling wavelength as a function of spatial position on the sample.

microscopy are best for HT workflows, since data acquisition and image analysis can be automated, providing single point modulus measurements in less than 5 s. Accordingly, this technique enables the rapid characterization of multivariate combinatorial film libraries. Acquiring images by AFM is inherently slower, but image analysis can also be automated to increase throughput.

For most of the work presented here, laser light diffraction was the method of choice for ascertaining the buckling wavelength. Using light scattering data, a simple image analysis algorithm is constructed to determine the scattering angle of the diffraction peaks, which is then converted to *d*-spacing (wavelength)

using Eqn. (2)

$$q_0 = \frac{2\pi}{d} \approx \frac{4\pi}{\lambda} \sin \theta \qquad (2)$$

where 2θ is the diffraction angle of the first-order peak. This wavelength is substituted into Eqn. (1) to determine the modulus of the film. HT measurements are achieved by rastering the sample across the beam using a computer-controlled translation stage in order to map out the properties of the gradient film. If the sample is comprised of a uniform film, a multitude of images can be acquired to generate acceptable statistics. Since this technique has a small footprint (beam diameter ≈ 1 mm), it is well suited for measurements of combinatorial libraries with spatially varying properties that can be prepared by existing methodologies.

4. Sample Preparation

Sample fabrication is a critical step in applying this buckling technique. For polymer materials, film specimens can be prepared on a separate substrate (silicon wafer, glass slide, polished salt plate) by spin coating, dip coating, solvent casting, doctor blading, or spray coating. While using silicon or glass, the substrates are pretreated with UV/ozone for 20 min to render the surface of the silicon oxide hydrophilic ($\theta_{\text{water}} \approx 0°$). Films are then transferred onto an elastic substrate (crosslinked PDMS) by employing a water-immersion technique similar to floating films on water, producing a laminate or bilayer structure. Obviously, water-soluble polymers cannot be transferred this way, though they may be spin-coated directly onto the PDMS substrates. PDMS was chosen as a substrate because it behaves like an ideal elastomer, with $v_c \approx 0.5$ and little or no viscoelasticity, and is optically transparent. Unfortunately, PDMS swells in most organic solvents, so direct deposition of a polymer film onto PDMS is problematic unless a solventless technique is employed. One strip of PDMS per batch is retained for measuring the modulus of the substrate by traditional methods (e.g., stress–strain), immediately prior to performing a buckling measurement.

If the polymer film does not easily release from the silicon wafer or the film is to be annealed prior to transfer, the polymer can be cast onto polished salt plates and transferred to PDMS by dissolving away the salt plate. This method requires identical samples to be cast in parallel onto silicon substrates for accurate film thickness measurements. The thickness *h* of each film is measured extensively by conventional interferometry or ellipsometry.

To generate strain in the bilayer, the PDMS is uniaxially strained using a custom-built linear strain stage. The disparity in Poisson's ratio (*v*) between the PDMS ($v_c \approx 0.5$) and the polymer film ($v \approx 0.3$) results in a net compressive strain on the film in the
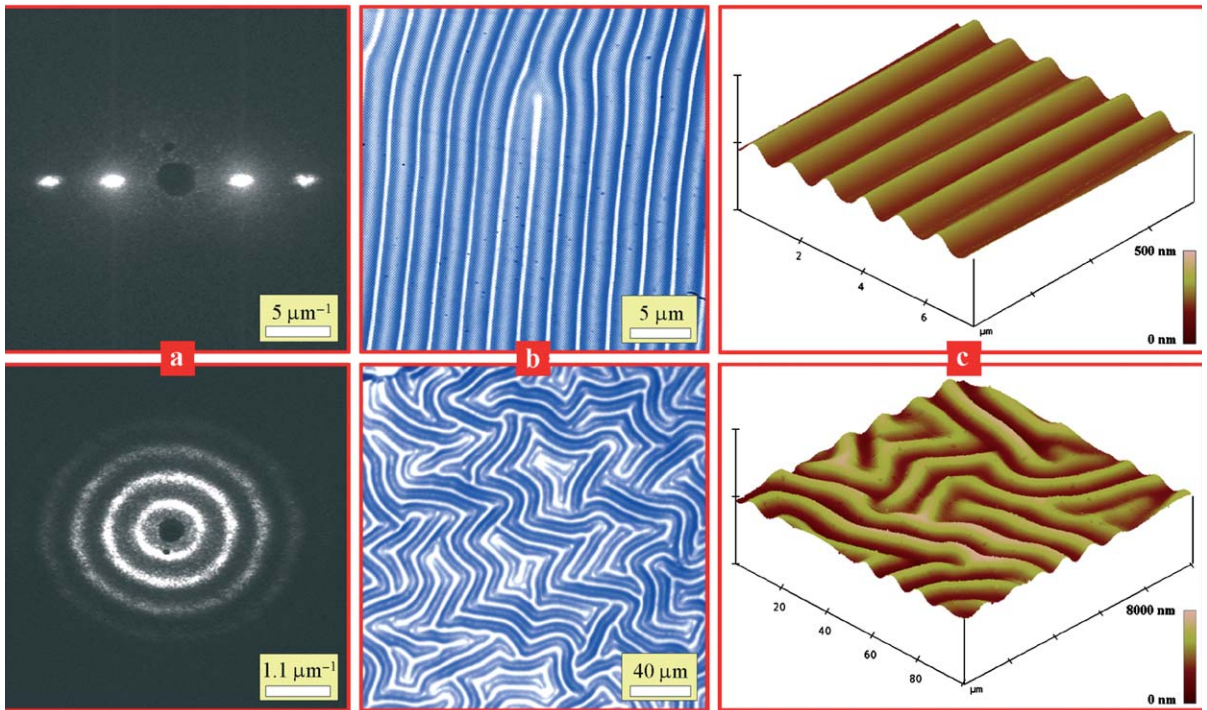
Figure 4

Methods for ascertaining the buckling wavelength: (a) laser light diffraction, (b) optical microscopy (colorized micrograph), and (c) AFM. The top row of images corresponds to oriented buckling whereas the bottom row corresponds to isotropic buckling.

direction orthogonal to stretching. One major drawback of applying tension is that each unit of strain applied, ε_x, results in a compression strain of $\varepsilon_y = \frac{1}{2}\varepsilon_x$, given that the Poisson's ratio of PDMS is $v_c \approx 0.5$. Conversely, prestraining the PDMS prior to film transfer and then releasing the strain in a controlled manner until the onset of buckling provides a means to directly apply compressional strain to the film. The latter geometry also provides a route by which a permanently wrinkled surface is obtained after removal of the sample from the strain stage and allowing the PDMS to completely relax back to its original length.

5.   Applications

As a demonstration of the SIEBIMM technique, measurements were made on a common glassy polymer, polystyrene (PS). A thin film of PS ($h \approx 100\,\text{nm}$) was spin-coated onto a silicon wafer and transferred to a prestrained PDMS strip (strain was applied uniaxially), and subsequently compressed to induce buckling. Since the buckling wavelength was several micrometers, the specimen could be imaged using optical microscopy. Movie clip 1 is a video demonstrating the onset of wrinkling induced by the compression of the PS/PDMS bilayer. In this video micrograph, the strain direction is from left to right. The amount of compression is gradually increasing as a function of time, and as a demonstration of reversibility, the compression is then gradually decreased to recover the original, smooth laminate structure. This movie also illustrates the occurrence of a critical strain below which it is energetically more favorable to compress, rather than buckle, the specimen. Above this critical strain, highly periodic buckles appear that are perpendicular to the compression direction. The buckling is completely reversible in the limit of low strain such that macroscopic damage of the film does not occur (e.g., fracture, yielding, delamination).

Conversely, the wrinkling can be tracked by light scattering to ascertain the dominant wavelength of the system. Since the applied strain is uniaxial, the buckling patterns are anisotropic (aligned) and the scattering from the samples results in spots, orthogonal to wrinkles. This is shown as a video in Movie clip 2. The buckling pattern is sufficiently periodic to produce several orders of diffraction spots in the image.

Another significant point is that the wavelength of the buckles does not change as a function of strain.

Increasing strain = Increasing amplitude
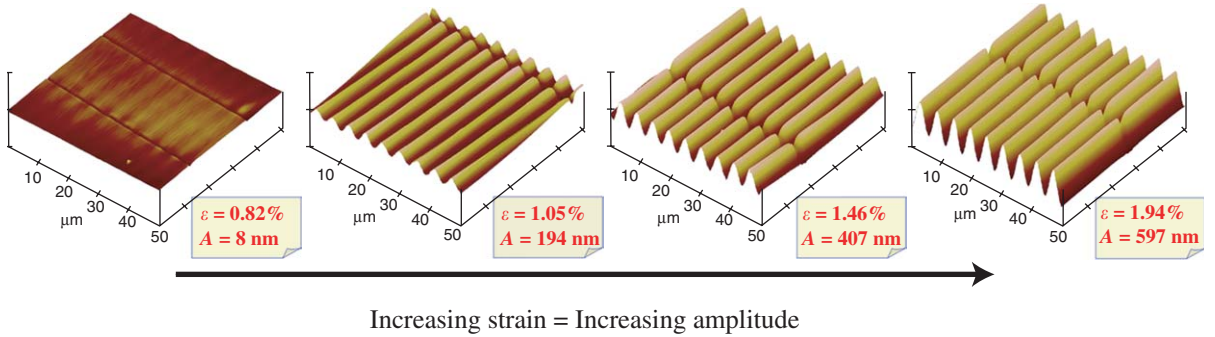
Figure 5
AFM images showing, from left to right, the increase in amplitude *A* of the wrinkles with increasing strain. The film is PS having a thickness of 83.2 nm $\pm$ 0.8 nm. All of the AFM images are 50 μm $\times$ 50 μm scans with a height scale of 800 nm. Cracks in the film can be seen traversing perpendicularly to the wrinkles, but do not alter the observed wavelength.

Rather, the amplitude of the buckles increases with increasing strain, as shown in Fig. 5. All images contain approximately nine periods of the buckling pattern in an identical scan area (50 μm $\times$ 50 μm), but the amplitude of the buckles increases as a function of the applied strain. The benefit of this is that a measurement of the exact compressive strain applied to the film is not essential for determining the modulus of the film, as long as macroscopic damage of the sample is minimized.

SIEBIMM was validated as a quantitative HT measurement technique through the use of a PS film that exhibited a gradient in film thickness. The PS specimen spanned a thickness range from 140 nm to 280 nm. Rearranging Eqn. (1) reveals that the buckling wavelength should be directly proportional to the thickness of the upper film for a film of constant modulus, E_f (see Eqn. (3)):

$$d = 2\pi h \left[\frac{(1 - v_s^2) E_f}{3(1 - v_f^2) E_s} \right]^{1/3} \qquad (3)$$

Figure 6 demonstrates this relationship. As the film thickness increases by a factor of 2, the buckling wavelength also increases by a factor of 2 as measured by both optical microscopy and light scattering. Through Eqn. (1), the modulus of the PS film is calculated to be $E_f = 3.4$ GPa ± 0.1 GPa for the entire range of thickness, in excellent agreement with reported bulk values for PS (Brandrup *et al.* 1999).

Several other model systems have been studied in order to gauge the applicability of this technique to a broad range of materials and film thicknesses. For example, PS films that were plasticized with a common plasticizer, dioctyl phthalate, displayed a sigmoidal decrease in modulus from 3.4 GPa ± 0.1 GPa down to 0.4 GPa ± 0.01 GPa for 40% mass fraction of plasticizer in PS. The shape of this curve is markedly similar to data obtained for conventional plasticized systems such as bulk poly(vinyl chloride) specimens (Sears and Darby 1982). Higher plasticizer concentrations could not be studied since the spin-coated film dewet the silicon wafer before the film could be transferred to the PDMS substrate. An issue that one must be cognizant of is the potential for the PDMS to absorb low molecular weight components, such as a plasticizer, from the overlying film being studied. This would cause a minor change in the surface modulus of the PDMS substrate, but more importantly, it would decrease the predicted mass fraction of plasticizer in the film to lower concentrations, thus leading to an unexpected drift in the measured values of the modulus.

Another application of this technique is probing the aging processes in polymer films. For example, a PS film was transferred to a PDMS substrate and strained to induce buckling. The buckling wavelength *d* was ascertained by laser light diffraction, and Eqn. (1) was used to calculate the apparent modulus. The applied strain was removed and the buckled surface reverted to a smooth, supported film. This process was repeated as a function of the amount of time the sample was exposed to ambient light and temperature. Figure 7 shows the results of the aging experiment. The measured modulus gradually increased as a function of time before reaching a plateau value of $E_f \approx 3.7$ GPa, or $\sim 9\%$ of the original value. The observed increase in modulus is most likely due to minor oxidation of the near surface of the PS film as a result of prolonged exposure to ambient light and oxygen.

To demonstrate the ability to measure soft-structured materials, two triblock copolymers comprised of styrene–isoprene–styrene (P(S–I–S)) were blended over a range of composition, where the modulus of the film was tuned by the ratio of each component in the film. For these triblock copolymers, PS (glassy)
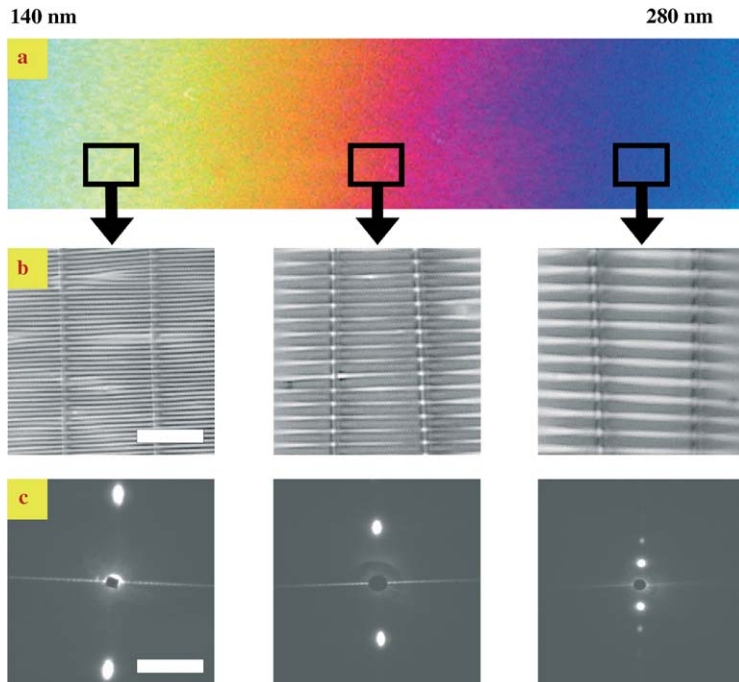
Figure 6
(a) Optical image of a thickness gradient of PS, (b) optical images of the buckling pattern as a function of film thickness (scale bar is 50 μm), and (c) light diffraction patterns from the periodic wrinkles shown in (b) (scale bar is 0.88 μm^{-1}). Cracks can be seen running perpendicular to the wrinkles in the optical micrographs and show up again in the light scattering images as a faint equatorial line.
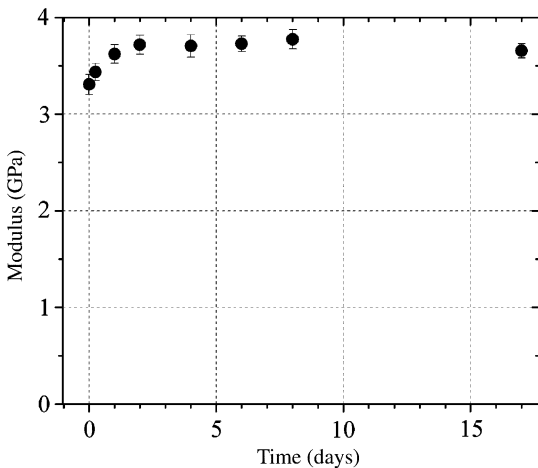

Figure 7
Modulus of a PS film ($h = 102.3$ nm ± 0.5 nm) as a function of time exposed to ambient conditions in the laboratory. The error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement. Some error bars are smaller than the symbols.

was the minor component and polyisoprene (rubbery) the major one. This system displayed a monotonic increase in elastic modulus with increasing mass fraction of PS in the film. For the highest concentration of PS (0.44 mass fraction), the measured modulus was 89 MPa ± 5 MPa. The lowest concentration of PS (0.30 mass fraction) exhibited a modulus of 5.0 MPa ± 0.4 MPa. These results compare well with traditional mechanical testing on bulk samples of these polymers (Hefner 2001).

6.   Summary and Future Directions

The mechanical properties of thin films are paramount for their effective utilization in next-generation devices and multilayer laminates. A new HT technique, SIEBIMM, that allows the rapid and quantitative determination of elastic moduli of polymer thin films, has been discussed. The measurement itself takes only a few seconds per location on the sample, and thus an entire sample can be scanned in just a few minutes. The entire workflow (i.e., sample preparation, thickness measurement, film transfer, image collection, and analysis) takes less than 1 h, thereby

allowing testing of many samples within a day. The method is also inexpensive to implement, requiring only off-the-shelf PDMS, an optical microscope or laser, and a film of interest. This technique has been demonstrated on films with thickness ranging from several microns to 20 nm, and films with a range of moduli from several GPa to 5 MPa. SIEBIMM has been partnered with well-established combinatorial technologies, such as flow coating, to make a powerful HT measurement strategy. Research is continuing in the areas of nanoporous low-*k* films for next-generation semiconductor applications, UV-curable coatings and adhesives, and metal and ceramic thin films. Metal and ceramic thin films would provide a rigorous test of the upper limits and capabilities of the measurement method. In general, this method will certainly find broad applicability in addressing a variety of measurement issues in thin films and structured materials as well as providing a unique pathway for micron-scale manipulation of surface topography.

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