A Two-Plate Buckling Technique for Thin Film Modulus Measurements: Applications to Polyelectrolyte Multilayers

Adam J. Nolte,[†] **Robert E. Cohen,***[,‡] **and Michael F. Rubner***[,†]

Departments of Materials Science and Engineering and Chemical Engineering, and the Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received March 21, 2006; Revised Manuscript Received May 4, 2006

ABSTRACT: We present a modified version of a strain-induced buckling instability technique that relies on the analysis of a two-plate composite film deposited on an elastomeric poly(dimethylsiloxane) (PDMS) substrate. We have previously shown that the "strain-induced elastic buckling instability for mechanical measurements" (SIEBIMM) technique is suitable for testing polyelectrolyte multilayers (PEMs) that are amenable to deposition directly on the testing substrate. The method presented in this paper broadens the applicability of the SIEBIMM technique through the transfer of a thin layer of polystyrene (PS) to the PDMS surface prior to film deposition, which creates a deposition surface that can be treated to promote adhesion of films not amenable to transfer or assembly directly onto PDMS. Multilayers assembled onto the PS-coated PDMS substrates yield thin two-plate PS−PEM composite films on the surface of the PDMS substrates that buckle like their homogeneous counterparts. The mechanical contribution of the PS layer is mathematically deconvoluted from the behavior of the composite film to arrive at a Young's modulus value for the PEM part of the two-plate film. We test the new method by comparing results from two systems evaluated with both conventional SIEBIMM and the two-plate technique. Following this, we use the two-plate method to perform measurements on two PEM assemblies comprised of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) that could not be measured by the conventional SIEBIMM approach. In addition to confirming the accuracy of the two-plate approach, our results yield new insights into the mechanical properties of PEM films. We find that the dry-state stiffness of PEM films is affected primarily by the choice of polyelectrolytes and the ambient humidity and secondarily by assembly conditions. In addition, films assembled from PAH and PAA have moduli on the order of 10 GPa at low (20%) ambient humidities, an unusually high value for a nonreinforced cross-linked polymer network.

Introduction

Current interest in thin film materials is motivated by a number of factors such as the desire to advance microelectronics by moving to smaller device sizes, the need for protective or functional coatings, and the high degree of promise for thin films as actuator and sensor devices.[1] Knowledge of the mechanical properties of the film is often of fundamental interest for many of these applications. Traditional mechanical testing methods have generally relied upon macroscale manipulation of samples; however, thin films can often exhibit properties very different from their bulk values, and some very promising thin film materials exist for which there is no easily obtainable bulk counterpart. Such considerations have led to the development of a number of novel methods for thin film mechanical property measurements, including the recent "strain-induced elastic buckling instability for mechanical measurements" (SIEBIMM) technique.[2]

SIEBIMM presents many advantages among the various thin film characterization techniques, including its straightforward and fast implementation as well as its ability to do rapid combinatorial material screening without requiring expensive or specialized equipment. In its current form, however, SIEBIMM is limited to testing thin film materials that can be transferred or assembled onto a hydrophobic poly(dimethylsiloxane) (PDMS) substrate. We have previously demonstrated the use of SIEBIMM to measure the Young's modulus of polyelectrolyte multilayer (PEM) thin films comprised of poly(allylamine hydrochloride) (PAH) and poly(styrenesulfonate) (PSS).[3] In that case, PEM assembly onto the neutral, hydrophobic PDMS substrate was successful; however, we found that later attempts to assemble specific multilayer systems comprised of PAH and poly(acrylic acid) (PAA) resulted in cloudy films that exhibited a very high surface roughness when deposited at certain values of pH. Our initial failed attempts at assembling these systems motivated us to consider possible ways of generalizing the SIEBIMM method to make it amenable to a wider variety of materials.

The basic principle behind SIEBIMM is that a thin, stiff film deposited on an elastomeric substrate will undergo a buckling instability when subjected to planar compressive forces. Measurement of the wavelength of buckling (λ), combined with knowledge of the film thickness (d_f) and the substrate Young's modulus (E_s), allows one to calculate the unknown Young's modulus (E_f) of the thin film via eq 1:[2]

$$\frac{E_f}{1-\nu_f^{\,2}} = \frac{3E_s}{1-\nu_s^{\,2}}\left(\frac{\lambda}{2\pi d_f}\right)^3 \qquad (1)$$

where ν_f and ν_s are the Poisson's ratios of the film and substrate and are typically assumed to be 0.33 in the case of glassy polymeric films and 0.5 for the rubbery substrate.[2,3]

Any suitably compliant elastomeric material could be used as the substrate, but PDMS is considered an ideal choice for such an application due to its optical transparency, ease of processing, easily tunable mechanical properties, and elasticity over large temperature ranges. SIEBIMM requires both compat-

---

* To whom correspondence may be addressed. E-mail: recohen@mit.edu (R.E.C.); rubner@mit.edu (M.F.R.).

[†] Department of Materials Science and Engineering.

[‡] Department of Chemical Engineering.

10.1021/ma0606298 CCC: $33.50

ibility between the testing material and the substrate for successful film transfer or deposition as well as good adhesion between the film and substrate to prevent the buckled film from immediately relaxing. This suggests that a suitable method of modifying the PDMS surface is needed. Many studies have explored this topic, with plasma, corona discharge, and UV/ozone treatments being the most popular techniques used to create a hydrophilic surface on normally hydrophobic PDMS.[4,5] Because of the chemical nature of the siloxane backbone, however, such surface modification methods result in the growth of a brittle, silica-like layer on the surface of the PDMS.[6] This layer leads to an increase in the local surface modulus[4] and can actually lead to buckling on the treated PDMS surface as the thin, brittle silica layer becomes compressed under thermally induced strains.[7] Furthermore, it has been suggested that the low glass transition temperature of PDMS (−123 °C) allows it to quickly bury high-energy surface functionalities into the bulk,[6] a fact that might be problematic even if one could find a suitable carbon-based elastomer substitute. One possible solution to the preceding difficulties would be the deposition of a thin, glassy polymeric layer on the surface of the PDMS. If correctly chosen, such a layer would exhibit good adhesion to the PDMS, while presenting a deposition surface that could be easily modified by plasma techniques and not prone to the above-mentioned difficulties facing direct modification of the PDMS surface.

In the current work, we report on a modified buckling technique that involves the deposition of PEMs onto a thin layer of polystyrene (PS) that has been previously transferred to the PDMS substrate.[2] Plasma modification permits tuning of the wetting properties of the PS surface, enabling the assembly of polyelectrolyte systems not amenable to deposition on hydrophobic substrates. The resulting system consists of a two-plate composite of PS and PEM instead of a single, homogeneous PEM film. These PDMS−PS−PEM systems give rise to buckling exactly like their homogeneous counterparts, a fact that has been reported in other composite film systems as well.[8] We explain how the SIEBIMM equation can be modified to account for the presence of a two-plate composite film and how, by measuring the thickness and buckling wavelength of the PS layer prior to the PEM deposition, one can deconvolute its effects from the buckling of the composite film to yield a value for the Young's modulus of the PEM. We demonstrate the reliability of this technique by measuring the modulus values for two separate PEM systems with both the standard SIEBIMM technique and the two-plate method and find very close agreement. We also provide results from testing two polyelectrolyte multilayer systems that cannot be evaluated by the conventional SIEBIMM approach, requiring measurement via the two-plate methodology.

Experimental Section

PS pellets (Styron 663 W, Dow Chemical Co.) were dissolved in toluene (Mallinckrodt Chemicals) to create solutions for spin-coating. Polished, single-crystal silicon wafers (p-type, WaferNet) were used as substrates. Wafers were cut into approximately 2 cm × 3 cm pieces and treated for 5 min at high power (100 W) in an air-plasma (Harrick Scientific PDC-32G plasma cleaner/sterilizer) operated at a pressure of 400 mTorr. Spin-coating (PWM32, Headway Research) was carried out for 20 s at 2000 rpm with a ramp of 300 rpm/s. A series of concentrations were initially spin-coated to find the dependence of PS thickness on solution concentration. Subsequently, solutions with concentrations of 3.6 and 9.0 g/L were prepared in order to create films with thicknesses of approximately 20 and 70 nm, respectively. Pure toluene was spun onto each wafer surface immediately prior to spinning the PS solutions. PS-coated silicon samples were annealed under vacuum for ≈1 h at 75 °C and then removed from the oven and allowed to cool to room temperature before further processing.

PDMS (Sylgard 184, Dow Corning) was prepared by mixing the cross-linker and base compound in a 1:10 w/w ratio. The mixture was cast into a tray to a thickness of ≈3 mm and allowed to degas at atmospheric conditions for 45 min−1 h, after which it was baked at atmospheric pressure for 45 min at 80 °C. After cooling to room temperature, the PDMS was cut into 2 cm × 6 cm pieces.

Transfer of PS films from the wafer to the PDMS was carried out according to the method described by Stafford et al.[2,8] Briefly, the PS-coated side of the spin-coated sample was placed onto a piece of PDMS. Good contact between the PDMS and the PS was confirmed by observing the elimination of the PDMS−PS air gap. The samples were then immersed under deionized water, and the wafer was slowly pulled from the PDMS, leaving the PS film adhered to the PDMS.

In cases where the experiment called for hydrophilic modification of the PS, the samples were treated for 30 s in air plasma under the same conditions given above for wafer cleaning. In the case of the (PAH4.0/PAA4.0) system, an additional 10 s treatment was used immediately prior to deposition due to some hydrophobic recovery of the PS surface.[9]

PAH ($M_w = 70\,000$, Sigma-Aldrich), PSS (sodium form, $M_w = 70\,000$, Sigma-Aldrich), and PAA (25% aqueous solution, $M_w = 90\,000$, Polysciences) were used without further purification to create polymer solutions of 0.01 M concentration by repeat unit. When PAH and PSS solutions were used together to construct multilayers, 0.1 M NaCl (Mallinckrodt Chemicals) was added to each polyelectrolyte solution as previously described.[3,10] Milli-Q deionized water (Millipore) with a resistivity of 18.2 MΩ cm was used for all procedures and preparations. Solutions were adjusted to the appropriate pH with 1.0 M HCl or NaOH immediately prior to PEM assembly.

Assembly of PEMs onto PDMS, PDMS−PS, and plasma-treated PDMS−PS substrates was performed by an automated programmable slide stainer (HMS slide stainer, Zeiss). Substrates were first immersed in the polycation (PAH) for 15 min, followed by three 1 min rinse steps. The samples were then immersed in the polyanion (PAA or PSS) for 15 min, followed again by three 1 min rinses. This completed the deposition of one bilayer, which is defined as an adsorption step of polycation followed by an adsorption step of polyanion. This process was cycled until the desired number of bilayers were deposited. If more than 10 bilayers were deposited, the immersion time in the polyelectrolyte baths was decreased to 5 min for the 11th and all subsequent bilayers. For the remainder of this paper PEM systems will be referred to as ("polycation name"X/"polyanion name"Y)$_Z$, where X and Y are the pH values of the polycation and polyanion baths, respectively, and Z is the number of bilayers assembled. For example, (PAH3.0/PSS3.0)$_{48}$ refers to a sample constructed from 48 bilayers of PAH and PSS, with the pH of both baths adjusted to 3.0 immediately prior to assembly. When the number of bilayers is reported as a half-integer, for example (PAH4.0/PAA4.0)$_{10.5}$, an additional polycation adsorption step has been employed so that the polycation appears next to both the substrate and air interfaces. Following the completion of PEM assembly, samples were allowed to air-dry. Samples were stored in air at ambient conditions and tested within a few days of PEM assembly.

Modulus measurements were obtained by applying planar compressive strains (1−2%) on each sample with a pair of tweezers while taking photographs of the buckled surface with an optical microscope (Axioplan 2, Zeiss). Optical micrographs were subjected to Fourier analysis[3] to determine the average wavelength of buckling, λ. Spectroscopic ellipsometry (M-2000D, J.A. Woollam Co.) was performed according to a method we have previously described to obtain the thicknesses of the PS (d_{PS}) and PEM (d_{PEM}) regions of the film.[3] Except where otherwise indicated, the relative humidity was 50 ± 4% during testing of the (PAH3.0/PSS3.0) and (PAH7.5/PAA3.5) systems and 20 ± 4% during testing of the (PAH3.5/PAA3.5) and (PAH4.0/PAA4.0) samples. Compression

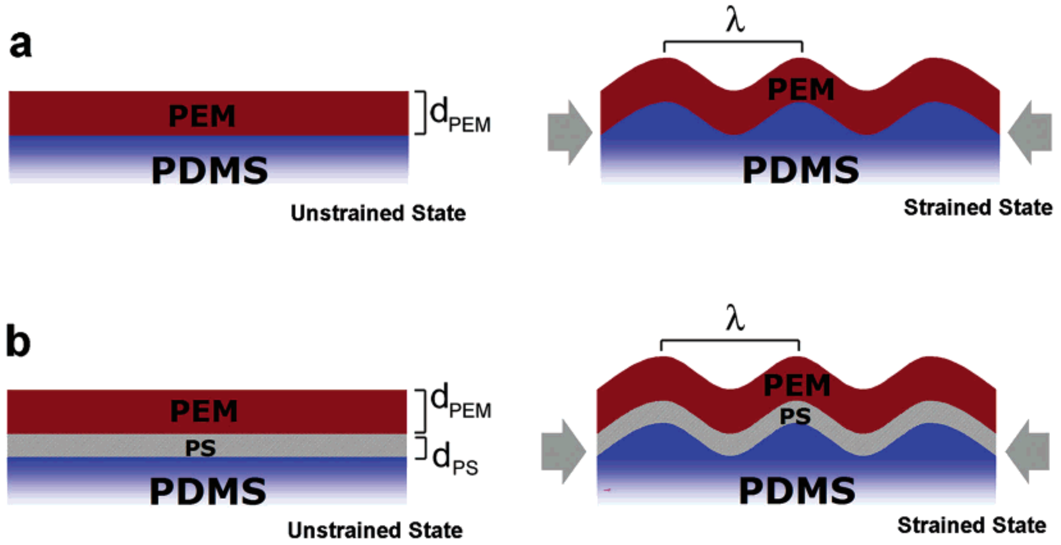

Figure 1. Cross-sectional illustrations showing both the unstrained and strained (undergoing buckling) states for (a) the conventional SIEBIMM technique with a PEM film and (b) the two-plate method with a PS−PEM composite film.

testing (model Z010, Zwick/Roell) of $^1/_2$ in. diameter cylindrical samples cut from the PDMS substrates was performed to find the Young's modulus of the substrate (E_s). Samples were compressed at a strain rate of ≈0.02 s^{-1}, and the modulus values were taken as the slopes of the stress−strain curves in the linear, small strain portions of the data. The results from testing at least eight different samples were averaged to yield E_s for a particular batch of PDMS.

Young's modulus values were calculated using either eq 1 (conventional SIEBIMM) or eqs 4 and 5 (two-plate method) as reported in the text. All errors represent standard deviations in the averaged modulus values.

Results and Discussion

For the case of a uniform PEM deposited directly on PDMS (Figure 1a), the mechanical stiffness and thickness of the film dictate the wavelength at which the buckling instability will occur. The relationship between these quantities can be written as[9,11]

$$\bar{E}_{PEM}I_{PEM} = \frac{\bar{E}_s w}{4}\left(\frac{\lambda}{2\pi}\right)^3 \qquad (2)$$

In eq 2 and in the following the symbols are the same as in eq 1, except that the subscript f has now been replaced with PEM and the quantity I_{PEM} represents the second moment of area of the PEM film (with width w) about its neutral bending axis. The overbars indicate reduced modulus values, where for any material $\bar{E} = E/(1 - \nu^2)$, with E being the Young's modulus and ν the Poisson's ratio. The quantity on the left in eq 2 is known as the *flexural rigidity*,[12] and it provides a measure of the resistance of a material to bending based not only on the material's stiffness but also on its distribution in space. Because the neutral axis is located directly in the middle of a homogeneous film, in the case where the PDMS is coated with a PEM, $I_{PEM} = wd_{PEM}{}^3/12$, and eq 2 reduces to eq 1.

In the two-plate scenario (Figure 1b), the PEM is deposited on a thin layer of PS. When the composite film is buckled, both the PS and PEM undergo buckling together, and total resistance to this buckling is given by the sum of their individual flexural rigidities:[13]

$$\bar{E}_{PEM}I_{PEM} + \bar{E}_{PS}I_{PS} = \frac{\bar{E}_s w}{4}\left(\frac{\lambda}{2\pi}\right)^3 \qquad (3)$$

I_{PEM} and I_{PS} are not found as easily in this case because the location of the neutral axis must be determined in light of both the thicknesses and Young's moduli of the PEM and PS.[12] When these values are found and inserted into eq 3, the resulting equation can be solved *implicitly* for the Young's modulus of the PEM to yield the following relationships:[9]

$$\bar{E}_{PEM} = \frac{\dfrac{\bar{E}_{eff}}{4} - \bar{E}_{PS}\left[\left(\phi_{PS} - \dfrac{\kappa}{2}\right)^3 + \left(\dfrac{\kappa}{2}\right)^3\right]}{\left(1 - \dfrac{\kappa}{2}\right)^3 - \left(\phi_{PS} - \dfrac{\kappa}{2}\right)^3} \qquad (4)$$

$$\bar{E}_{eff} = 3\bar{E}_s\left(\frac{\lambda}{2\pi d_t}\right)^3; \quad \kappa = \frac{1 + \phi_{PS}{}^2\left(\dfrac{\bar{E}_{PS}}{\bar{E}_{PEM}} - 1\right)}{1 + \phi_{PS}\left(\dfrac{\bar{E}_{PS}}{\bar{E}_{PEM}} - 1\right)} \qquad (5)$$

In eq 4 and eq 5, d_t is the combined thickness of the PEM and PS films (i.e., $d_{PEM} + d_{PS}$) and ϕ_{PS} is the height fraction of PS (i.e., d_{PS}/d_t). In the current work we have derived eq 4 specifically to solve for the unknown value of $\bar{E}_{PEM}$. Stafford et al. have discussed a related problem and have also provided an equation giving $\bar{E}_{eff}$ when the modulus of both materials is known.[8] The two equations appear quite different on first inspection, but we have confirmed that they are algebraically identical. Thus, two different approaches to solving this problem give identical results. The quantity $\bar{E}_{eff}$ in eq 4 is referred to as the *effective modulus*, and it represents the calculated modulus of the two-plate composite as if it were a homogeneous film with thickness d_t.

Because eq 4 is solved for $\bar{E}_{PEM}$ only implicitly, an initial value of $\bar{E}_{PEM} = \bar{E}_{PS}$ was assumed, which set $\kappa = 1$ (see eq 5). Equation 4 then yielded a refined value of $\bar{E}_{PEM}$, which was used to calculate a new κ, and the process was iterated until $\bar{E}_{PEM}$ no longer changed. Equation 4 converged rapidly—all the results that follow required no more than four iterations, at which point $\bar{E}_{PEM}$ was unchanging to at least the third decimal point. Actual (not reduced) Young's modulus values are reported according to the assumed Poisson's ratios given in the Introduction. Except where otherwise noted, samples appeared transparent and displayed uniform buckling across the film surface upon compression. Optical micrographs of buckled films are not

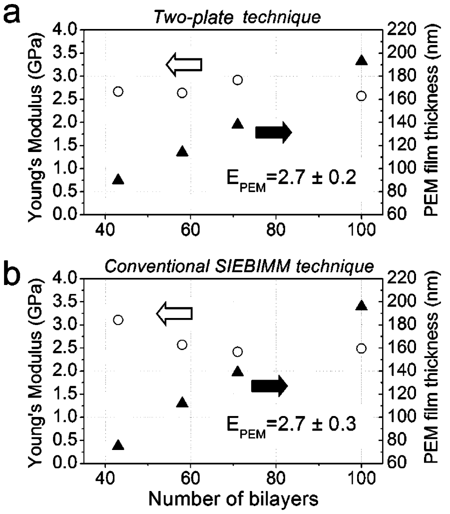

Figure 2. (PAH3.0/PSS3.0) film thickness (filled triangles) and Young's modulus (open circles) vs number of bilayers using the (a) two-plate and (b) conventional SIEBIMM techniques. The average modulus for each technique is displayed in each graph pane. The relative humidity was 50 ± 4%.

reproduced here, as they appeared very similar to those previously published.[3]

Our initial task was to test the validity of eq 4 using two polyelectrolyte systems that were amenable to deposition on both untreated PDMS and PS. Our first choice was to assemble (PAH3.0/PSS3.0) in the presence of 0.1 M NaCl. In total, eight samples were used for dipping—four PDMS substrates as prepared and four with ≈20 nm PS layers transferred to their surface (the precise thickness of each sample's PS layer was determined before PEM deposition). After measuring the buckling wavelength of the four PS-coated PDMS samples, all eight substrates were coated with multilayers of (PAH3.0/PSS3.0). Two samples were removed during assembly (one PS-coated substrate, one uncoated) following the deposition of 43, 58, 71, and 100 bilayers. For all samples, the PEM thickness, buckling wavelength, and the PDMS stiffness were measured, and the PEM Young's modulus was calculated using eq 1 (for PDMS−PEM samples) and eqs 4 and 5 (for PDMS−PS−PEM samples). PEM thickness and modulus data found from both the conventional and the two-plate technique are graphed vs number of bilayers in Figure 2.

(PAH3.0/PSS3.0) multilayers grown on the PDMS−PS platform (Figure 2a) and directly on PDMS (Figure 2b) displayed linear growth, with thickness increments of 1.8 and 2.1 nm/bilayer, respectively. *R*-squared values were >0.997 in both cases. Figure 2 illustrates that the PEM modulus as measured by both techniques remains basically constant as the film thickness increases, in agreement with our previous results.[3] In addition, there is excellent agreement between the two methods, both giving an average Young's modulus of 2.7 ± 0.3 GPa for the (PAH3.0/PSS3.0) system.

Figure 3 provides a closer examination of the (PAH3.0/PSS3.0) two-plate modulus data that appear in Figure 2a, but now plotted alongside the effective modulus (see eq 5) of the entire PS−PEM assembly. The similarity between the effective modulus and the PEM modulus values as well as the lack of a rising or decreasing trend in the effective modulus with the decreasing fraction of PS in the film (also displayed in Figure 3) indicates a very close match in modulus between the (PAH3.0/PSS3.0) layers and the PS. Indeed, SIEBIMM testing on the uncoated PS films prior to deposition established an average modulus of 2.3 ± 0.2 GPa, very close to the 2.7 ± 0.3 GPa value measured for the PEM.

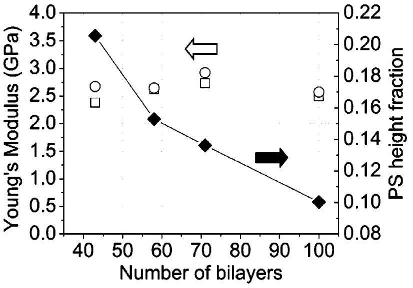

Figure 3. Young's modulus of (PAH3.0/PSS3.0) PEM multilayers (open circles) and the effective Young's modulus of the entire PS−PEM assembly (open squares) graphed vs the number of bilayers. The fraction of the total film thickness taken up by the PS is also displayed (filled diamonds). The relative humidity was 50 ± 4%.

We note that 2.7 ± 0.3 GPa (measured at 50% relative humidity) is lower than the value of 4.4 ± 0.2 GPa that we have previously reported for this system.[3] Our earlier results were obtained under humidity conditions that varied from approximately 20% to 30%. Suspecting that the higher relative humidity was the cause of the lower modulus values in the present work, we tested the exact same films at a later date when the ambient humidity had decreased to less than 20%. The average modulus during this second test was 5.6 ± 0.3 GPa, consistent with the notion that lower relative humidity values lead to stiffer PEM films.[14] This is not surprising, given that films measured in water, a good solvent for the (PAH3.0/PSS3.0) multilayers, can display modulus values an order of magnitude lower than the dry-state films.[3] Previous studies of PAH/PSS-coated fibers and free-standing spin-assisted PAH/PSS multilayer films embedded with gold nanoparticles have yielded dry-state modulus values comparable to the numbers reported here.[15−17] Our results, however, also show that the stiffness of dry-state films can be significantly affected by the humidity conditions, emphasizing the importance of including humidity measurements with any report of Young's modulus for PEMs.

A second system that was amenable to deposition both on the untreated PDMS and on the PS-coated PDMS substrates was the (PAH7.5/PAA3.5) system. For this system, nine substrates were dipped—four PDMS and five PS-coated PDMS. One substrate of each type was removed during the dipping process, similar to the case with (PAH3.0/PSS3.0), after the completion of 9.5, 11.5, 13.5, and 16.5 bilayers (the extra PDMS−PS sample was also removed at 16.5). The results from two-plate and conventional SIEBIMM analysis are displayed in Figure 4.

Linear growth was again observed for both sample types, with PEM thickness increments of 15.7 nm/bilayer (*R*-squared > 0.999) measured for both PDMS and PDMS−PS substrates. A Young's modulus of 6.6 ± 0.1 GPa was found for (PAH7.5/PAA3.5) multilayers using the two-plate technique. Conventional SIEBIMM yielded a value of 7.0 ± 0.2 GPa, again confirming good agreement between the results from the two techniques, both of which were carried out at 50% relative humidity. In addition, Pavoor et al. have previously measured a value of 7.1 ± 1.0 GPa for the Young's modulus of the (PAH7.5/PAA3.5) system via nanoindentation at approximately the same humidity,[18] in very close agreement with the results given here. A subsequent test of the same (PAH7.5/PAA3.5) samples at 20% humidity revealed an increase in the average Young's modulus to a value of 10.5 ± 0.5 GPa, again

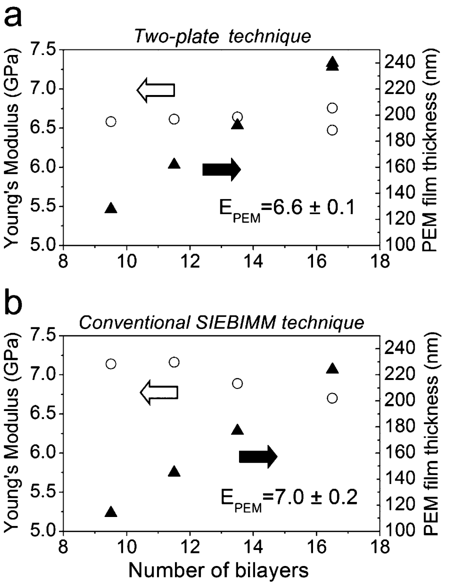

Figure 4. (PAH7.5/PAA3.5) film thickness (filled triangles) and Young's modulus (open circles) vs number of bilayers using the (a) two-plate and (b) conventional SIEBIMM techniques. The average modulus for each technique is displayed in each graph pane. The relative humidity was 50 ± 4%.

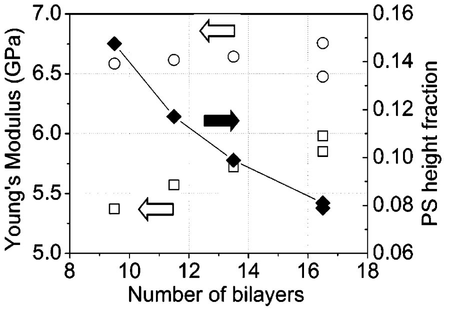

Figure 5. Young's modulus of (PAH7.5/PAA3.5) PEM multilayers (open circles) and the effective Young's modulus of the entire PS−PEM assembly (open squares) graphed vs the number of bilayers. The fraction of the total film thickness taken up by the PS is also displayed (filled diamonds). The relative humidity was 50 ± 4%.

demonstrating that the ambient humidity has a significant influence on the stiffness of these systems.

In Figure 5 the PEM modulus data measured using the two-plate technique are plotted along with the effective modulus of the entire PS−PEM assembly and the height fraction of PS in the film. In contrast to the situation previously described where (PAH3.0/PSS3.0) multilayers displayed a modulus very closely matched to that of the PS, the (PAH7.5/PAA3.5) system is more than twice as stiff as the PS on which it is deposited. As a result, the effective modulus of the PS−PEM assembly rises as the number of bilayers of PEM increases, as is evident from Figure 5. The measured modulus of the PEM, however, remains essentially constant, providing evidence that eq 4 is able to successfully extract the mechanical stiffness of the PEM from the PS−PEM composite film.

Modulus measurements on the (PAH3.0/PSS3.0) and (PAH7.5/PAA3.5) systems allowed us to confirm the validity of eqs 4 and 5. Following this, we focused our attention on two more systems that required a hydrophilic surface for uniform PEM film growth. Plasma treatment of the PS-coated PDMS substrates was used to make the substrates amenable to PEM deposition. In addition to introducing charge and polar surface groups that render the surface hydrophilic, plasma treatment can lead to modulus enhancements in polymeric materials by introducing cross-linking.[19] Consequently, we chose to monitor the effects of the plasma treatment on the PS films via spectroscopic ellipsometry, contact angle measurements, and SIEBIMM analysis. In the results that follow, measurements of the PS thickness and buckling wavelength were made following plasma treatment and immediately preceding PEM deposition. This was done in order to account for plasma-induced changes in the PS, which for 70 nm thick films typically included only a slight reduction in film thickness but an increase in modulus of up to 40%.[9]

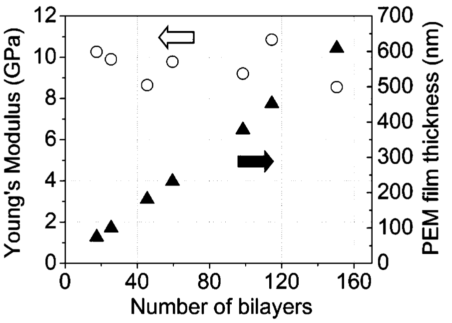

Figure 6. (PAH3.5/PAA3.5) film thickness (filled triangles) and Young's modulus (open circles) vs number of bilayers as measured via the two-plate SIEBIMM technique. The average Young's modulus is 9.6 ± 0.8 GPa. The relative humidity was 20 ± 4%.

The first system assembled on the plasma treated PDMS−PS substrates was (PAH3.5/PAA3.5). This system was chosen because we had difficulty assembling PAH and PAA at this pH onto untreated PDMS, and, as with the case of the (PAH7.5/PAA3.5) system, results from previous nanoindentation studies were available for comparison.[18] Similar to previous experiments, substrates were removed during dipping to obtain samples with differing PEM film thicknesses. In the case of (PAH3.5/PAA3.5), samples were collected following the deposition of 17.5, 25.5, 45.5, 59.5, 98.5, 144.5, and 150.5 bilayers. The PEM thickness and Young's modulus, as determined via the two-plate analysis (eq 4), are graphed in Figure 6.

As for the previous systems, the film thickness of (PAH3.5/PAA3.5) multilayers showed very precise linear growth, with a calculated thickness increment of 4.0 nm/bilayer (*R*-squared = 0.999). The PEM Young's modulus, which again remained constant with increasing film thickness, was 9.6 ± 0.8 GPa. Our value of 9.6 ± 0.8 GPa was obtained at a relative humidity of 20%; previous nanoindentation studies of this multilayer system conducted at a relative humidity of ~50% provided a value of 16.1 ± 2.8 GPa, higher than the value given here.[18] Thus, under more humid conditions, nanoindentation suggests an even higher modulus value. Given the considerable differences between the buckling technique and nanoindentation, especially in the nature of the sample deformations, agreement in the absolute value of the modulus for any given system is not necessarily expected; however, the two techniques also reveal different trends in the modulus values when comparing films at the same humidity.

Our next choice of system for testing was the (PAH4.0/PAA4.0) system, which also required a hydrophilic substrate for good multilayer growth. Although the deposition pH of the (PAH4.0/PAA4.0) system is very close to that of the (PAH3.5/PAA3.5) system, it is well-known that weak polyelectrolyte film thickness, chain organization, and network structure can change dramatically over very small changes in deposition conditions.[20] In addition, there has been recent interest in (PAH4.0/PAA4.0) PEMs as candidate platforms for controlling cell growth, leading

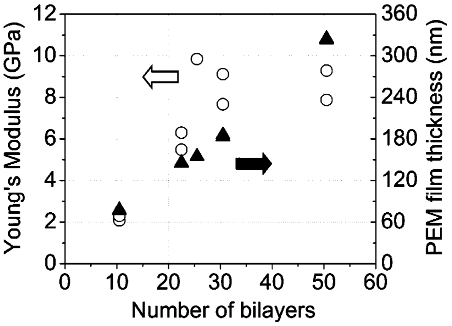

Figure 7. (PAH4.0/PAA4.0) film thickness (filled triangles) and Young's modulus (open circles) vs number of bilayers as measured via the two-plate SIEBIMM technique. The average modulus of films with 25.5 or more bilayers is 8.8 ± 0.9 GPa. The relative humidity was 20 ± 4%.

to nanoindentation studies of the wet-state mechanical properties of this system;[21] there is no information, however, on the dry-state mechanical properties.

During the deposition of (PAH4.0/PAA4.0), samples were removed after completion of 10.5, 22.5, 25.5, 30.5, and 50.5 bilayers. The PEM thickness and Young's modulus for this system, as determined via the two-plate analysis, are graphed in Figure 7.

It is evident from Figure 7 that the Young's modulus of the (PAH4.0/PAA4.0) samples displays a very different trend from that measured for the (PAH3.5/PAA3.5) system. Linear regression of the data revealed a thickness increment of 6.2 nm/bilayer, a value ~50% higher than the value of 4.0 nm/bilayer obtained for the (PAH3.5/PAA3.5) system. In addition, though the thickness data are still linear with the number of bilayers deposited, the *R*-squared value was 0.994, which was lower than those of the previous systems, implying less uniformity in the growth rate. The modulus rises from a value of ≈2 GPa for 10.5 bilayer samples and levels off at an average value of 8.8 ± 0.9 GPa for samples with 25.5 or more bilayers.

The trend in modulus data for the (PAH4.0/PAA4.0) system is very similar to that observed in our previous work for (PAH3.0/PSS3.0) multilayers deposited on PDMS substrates that had been pretreated by soaking in water prior to film deposition. In that case we concluded that the layers near the PDMS surface assumed a different chain conformation due to interactions with the water-treated surface. In our previous work, the average modulus value at which the (PAH3.0/PSS3.0) modulus leveled off was very close to the average modulus measured on nontreated substrates.[3] In the case of the (PAH4.0/PAA4.0) multilayers, the asymptotic value of Young's modulus of 8.8 ± 0.9 GPa obtained from averaging samples with 25.5 or more bilayers is close to the value of 9.6 ± 0.8 GPa obtained for the (PAH3.5/PAA3.5) system. The proximity of these two values leads us to conclude that for films of sufficient number of bilayers the stiffness of PAH and PAA multilayers does not change dramatically when the deposition pH is changed from 3.5 to 4.0. The decrease in mechanical stiffness at low bilayer numbers, however, confirms our earlier suggestion that it is advisable to monitor the Young's modulus as a function of thickness if one wishes to obtain a reliable measurement for a thin PEM film.[3]

The modulus values of the (PAH7.5/PAA3.5), (PAH3.5/PAA3.5), and (PAH4.0/PAA4.0) films at 20% humidity were found to be 10.5 ± 0.5, 9.6 ± 0.8, and 8.8 ± 0.9 GPa, respectively. These values do not reveal a significant dependence of stiffness on the pH assembly conditions of PAH and PAA, even though different chain organizations are expected for each system.[20] In comparison, these values are all significantly higher than the modulus of 5.6 ± 0.3 GPa measured for (PAH3.0/PSS3.0) at the same humidity. Thus, our results indicate that polyelectrolyte type and the ambient humidity are the most significant factors in determining the dry-state modulus of a PEM film. The pH of deposition, at least for the weak polyelectrolyte systems that we have tested, appears to be a less important factor. These same considerations do not apply to films in the wet state, however. Given that deposition pH controls both the internal structure and the cross-link density of films assembled using weak polyelectrolytes such as PAH and PAA, films swollen underwater have been shown to display significant differences in stiffness that correspond to the amount of electrostatic bonding present in the multilayer.[21]

A Young's modulus on the order of 10 GPa for (PAH/PAA) films at low ambient humidity is approximately 2−3 times larger than is typically reported for cross-linked polymer resins.[22] Previous work (using nanoindentation and assuming a Poisson's ratio of 0.33) found values of 8.47 ± 0.25 and 1.20 ± 0.52 GPa for the PAA and PAH homopolymers, respectively, and suggested that the interchain ionic cross-linking present in multilayer films of (PAH/PAA) contributed to enhancing PEM stiffnesses to values greater than either homopolymer.[18] The present work has shown, however, that absolute modulus values from buckling and nanoindentation are not always directly comparable. Thus, more investigation is needed to formulate a full explanation of the high modulus values exhibited by certain PEM films.

Conclusions and Future Work

In conclusion, we have introduced a two-plate buckling instability technique to make the SIEBIMM technique applicable to a wide variety of thin film systems. Because of the difficultly in obtaining a stable, hydrophilic surface through direct modification of PDMS without interfering with the mechanical properties of its surface, we have introduced a thin PS layer whose surface can be easily modified to control wettability. We have further demonstrated using PEMs that thin film systems not otherwise amenable to deposition on untreated PDMS can be successfully assembled and tested on this new platform over a wide range of thicknesses, creating PS−PEM two-plate composite films that undergo buckling instabilities like their homogeneous counterparts. By using the proper mechanical analysis, the unknown Young's modulus of the PEM layer can be extracted from the overall mechanical properties of the two-plate composite film.

The technique introduced in this work should prove especially useful for the polyelectrolyte multilayer community, where properties such as the surface wettability and film thickness growth increment can vary widely from system to system. The two-plate method, like conventional SIEBIMM, allows measurements to be performed in both the dry and wet states. We are currently investigating implementation of the two-plate method under controlled humidity conditions and in aqueous solutions, and our future work will focus on using mechanical measurements to elucidate properties of PEMs such as film morphology, cross-link density, and the effects of controlled incorporation of pores[23] or nanoparticles[10] into the PEM matrix. Although we have demonstrated the two-plate technique by testing multilayer films of polyelectrolytes, the method should be applicable to other types of materials systems as well. This could be an important consideration as thin film mechanical property measurements become increasingly important in a wide variety of fields.

Acknowledgment. The authors thank Dr. Christopher M. Stafford of NIST and Prof. Krystyn van Vliet of MIT for valuable discussions. This work was supported primarily by the MRSEC Program of the National Science Foundation under Award DMR 02-13282 and made use of equipment at the MIT Institute for Soldier Nanotechnologies.

Supporting Information Available: Detailed derivation of the two-plate buckling equation and the effects of plasma treatment on PS. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Freund, L. B.; Suresh, S. In *Thin Film Materials*; Cambridge University Press: Cambridge, UK, 2003.
(2) Stafford, C. M.; Harrison, C.; Beers, K. L.; Karim, A.; Amis, E. J.; Vanlandingham, M. R.; Kim, H. C.; Volksen, W.; Miller, R. D.; Simonyi, E. E. *Nat. Mater.* **2004**, *3*, 545−550.
(3) Nolte, A. J.; Rubner, M. F.; Cohen, R. E. *Macromolecules* **2005**, *38*, 5367−5370.
(4) Hillborg, H.; Tomczak, N.; Olah, A.; Schonherr, H.; Vancso, G. J. *Langmuir* **2004**, *20*, 785−794.
(5) Olah, A.; Hillborg, H.; Vancso, G. J. *Appl. Surf. Sci.* **2005**, *239*, 410−423.
(6) Hillborg, H.; Gedde, U. W. *Polymer* **1998**, *39*, 1991−1998.
(7) Chua, D. B. H.; Ng, H. T.; Li, S. F. Y. *Appl. Phys. Lett.* **2000**, *76*, 721−723.
(8) Stafford, C. M.; Guo, S.; Harrison, C.; Chiang, M. Y. M. *Rev. Sci. Instrum.* **2005**, *76*, 062207.
(9) See Supporting Information.
(10) Nolte, A. J.; Rubner, M. F.; Cohen, R. E. *Langmuir* **2004**, *20*, 3304−3310.
(11) Volynskii, A. L.; Bazhenov, S.; Lebedeva, O. V.; Bakeev, N. F. *J. Mater. Sci.* **2000**, *35*, 547−554.
(12) Beer, F. P.; E. Russel Johnston, J. In *Mechanics of Materials*, 2nd ed.; McGraw-Hill: New York, 1992.
(13) Allen, H. G. In *Analysis and Design of Structural Sandwich Panels*; Pergamon Press Ltd.: Oxford, 1969.
(14) Tang, Z. Y.; Kotov, N. A.; Magonov, S.; Ozturk, B. *Nat. Mater.* **2003**, *2*, 413−418.
(15) Hsieh, M. C. *Polyelectrolyte Multilayer Assemblies*; University of Massachusetts: Amherst, 1999.
(16) Hsieh, M. C.; Farris, R. J.; McCarthy, T. J. *Abstr. Pap. Am. Chem. Soc.* **1999**, *218*, U620−U620.
(17) Jiang, C. Y.; Kommireddy, D. S.; Tsukruk, V. V. *Adv. Funct. Mater.* **2006**, *16*, 27−32.
(18) Pavoor, P. V.; Bellare, A.; Strom, A.; Yang, D. H.; Cohen, R. E. *Macromolecules* **2004**, *37*, 4865−4871.
(19) Li, J. W.; Oh, K. H.; Yu, H. *Chin. J. Polym. Sci.* **2005**, *23*, 187−196.
(20) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213−4219.
(21) Thompson, M. T.; Berg, M. C.; Tobias, I. S.; Rubner, M. F.; Van Vliet, K. J. *Biomaterials* **2005**, *26*, 6836−6845.
(22) Hollaway, L. *Handbook of Polymer Composites for Engineers*; Woodhead Publishing Ltd.: Cambridge, UK, 1994.
(23) Zhai, L.; Nolte, A. J.; Cohen, R. E.; Rubner, M. F. *Macromolecules* **2004**, *37*, 6113−6123.

MA0606298