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Determining the Young's Modulus of Polyelectrolyte Multilayer Films via Stress-Induced Mechanical Buckling Instabilities

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Polyelectrolyte multilayer (PEM) deposition is a technique whereby two or more oppositely charged water-soluble polymers are alternately adsorbed onto a substrate. This method has become increasingly popular as a means of creating thin polymer films with a wide range of physical properties and potential applications, making the mechanical strength and stability of these films an important factor in evaluating the practicality of their use. This is especially true, for example, in the biomaterials area, where the mechanical properties of a surface have been shown to dramatically affect the attachment and growth of cells.[1] Though a number of different techniques have been pursued in the literature,[1−32] PEMs continue to present a considerable challenge for those wishing to investigate their mechanical stiffness, as they usually exist only as ultrathin films. Previous attempts to measure the modulus of PEMs, for example, have required assembly of films into hollow capsules followed by mechanical-[4,5,16−21,32] or chemical-driven[9,10,15,31] probing of the capsule stiffness or have utilized specialized equipment that typically requires films to be of micron-scale thickness, as in the case of nanoindentation.[1,6,7,23−26] Not all multilayer systems have proven amenable to microcapsule assembly,[33] however, and building films microns thick can be prohibitively time-consuming with certain polyelectrolyte systems that may exhibit thickness increments of less than 1 nm/bilayer.[34] In this study, a recently reported buckling-based technique[35] (termed "strain-induced elastic buckling instability for mechanical measurements", or SIEBIMM for short) is used to measure the modulus of PEM assemblies in both the wet and dry states. It is demonstrated that SIEBIMM is a simple and easy to implement method that solves many of the problems associated with previous attempts to measure the modulus of these materials.

SIEBIMM analysis exploits the fact that a thin, higher modulus material bonded to a semiinfinite, lower modulus substrate will buckle when subjected to compressive planar forces in order to relieve the strain energy in the system. To minimize this energy, buckling takes place at a characteristic wavelength, λ, given by[35,36]

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

where d is the film thickness, and E_f, ν_f, E_s, and ν_s are the Young's moduli and Poisson's ratios of the film and substrate, respectively.

In this study, polyelectrolyte multilayer films were grown directly on substrates of poly(dimethylsiloxane) (PDMS) elastomer. Films consisting of poly(allylamine hydrochloride) (PAH) and poly(styrenesulfonate) (PSS) were chosen for testing. This system has been well studied in the literature,[2,4,5,8,9,11,12,15−21,30−32] allowing measurements obtained via SIEBIMM to be compared against the results obtained from other techniques. Multilayers were constructed in the usual manner[37] of dipping the substrate back and forth between dilute (0.01 M by repeat unit in Milli-Q water with added 0.1 M NaCl) PAH and PSS baths (both baths pH 3.0, adjusted with 1 M HCl), with triplicate rinse steps following each immersion in a polymer bath. Assembled films were deformed by applying a lateral compressive strain with a pair of tweezers while examining the film under an optical microscope. The buckling transition is a critical phenomenon, and the wavelength is therefore expected to be strain-independent in the limit of small deformations. Some researchers have reported slight decreases in the expected buckling wavelength for high strains (10%);[38] the strains in this study were only a few percent and were therefore assumed to not measurably change the buckling wavelength from its critical value. The buckling wavelength was obtained via Fourier transform of optical microscope images. Film thicknesses were measured via spectroscopic ellipsometry, and the modulus values of the PDMS substrates (typically 1.7−1.9 MPa) were determined by uniaxial compression testing. A Poisson's ratio of 0.33 was assumed for dry-state multilayers, and a value of 0.5 was assumed for wet-state multilayers and the elastomeric PDMS substrate. During dry-state experiments, the relative humidity was in the range of 20−32%.

To determine the modulus of the PEM films, a method of accurately measuring the PEM film thickness was required. Although ellipsometry is typically used with highly reflective substrates such as silicon, we developed a measurement method whereby spectroscopic (multiple wavelength) ellipsometry is performed directly on the PEM-coated PDMS system.[39] The significant refractive index mismatch between the PEMs ($n \sim 1.55$) and PDMS ($n \sim 1.41$) allowed calculation of the film thickness through modeling of the ellipsometric data. In all, 25 samples created in three separate batches with different numbers of bilayers were assembled in order to evaluate the SIEBIMM method at a variety of film thicknesses. The thickness vs number of bilayers plot generated from these samples is displayed in Figure 1.

A linear regression performed on the data indicated a thickness increment of 1.76 nm/bilayer with an R^2 value of 0.999. These results show that PAH/PSS multilayers exhibit a reproducible, linear growth profile on PDMS over the entire range of thicknesses (11−100 bilayers) that were tested. The thickness increment reported here is slightly higher than previous results obtained by growing PAH/PSS multilayers on weak polyelectrolyte platforms on glass substrates.[37]

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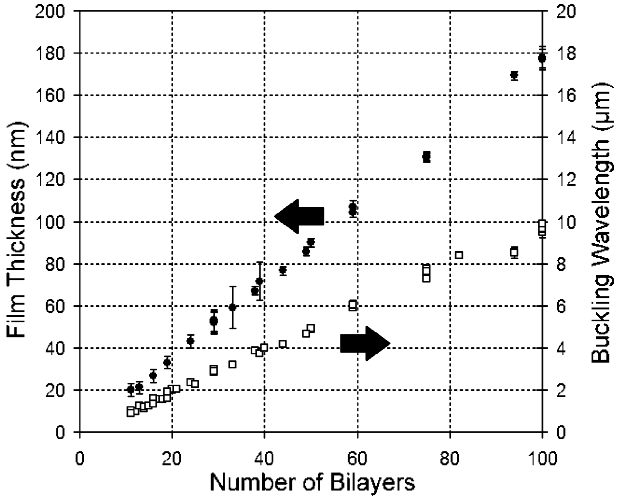

Figure 1. Thickness of PAH/PSS films vs number of bilayers deposited on PDMS. Thicknesses were determined by spectroscopic ellipsometry. The corresponding buckling wavelengths of the samples are also given.

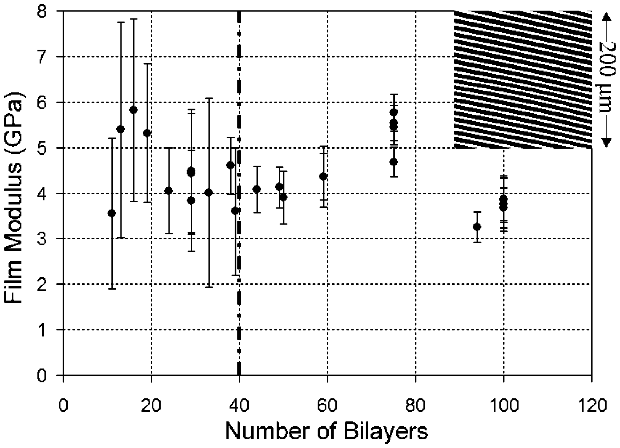

Figure 2. Young's modulus vs number of bilayers for PAH/PSS films. Error bars indicate the estimated measurement error. Larger errors are associated with the data points left of the dotted line (<40 bilayers). The inset image is an optical micrograph (200 μm square) of a 100-bilayer film undergoing buckling.

When subjected to a lateral strain, all films exhibited uniform buckling over the entire sample surface, except for regions where the occasional crack would locally relax planar stresses. The buckling wavelength was observed to increase linearly with thickness (see Figure 1), as would be expected from eq 1 for a PEM Young's modulus which does not change with increasing film thickness. Figure 2 shows the Young's modulus measured using the SIEBIMM method for films with different numbers of bilayers. Also shown is an optical microscopy image of a film undergoing buckling (inset).

The modulus values of films ranging from 20 nm (11 bilayers) to 180 nm (100 bilayers) thick were measured, and error bars were calculated by propagation of the uncertainties in the PEM thicknesses, the buckling wavelengths, and the Young's modulus of the PDMS substrate. Averaging the data yields a value of 4.4 ± 0.7 GPa for the Young's modulus of PAH/PSS multilayers.

The accuracy of the SIEBIMM technique is limited primarily by measurements of the PEM film thickness. This is especially true for very thin films, where the data indicate higher uncertainties for films less than ≈70 nm (40 bilayers) thick. Despite such uncertainties, SIEBIMM proved to be remarkably sensitive to the PEM modulus, even in very thin films. This was evidenced in two additional batches of samples that were prepared, which were identical to the previous samples except that the PDMS substrates had been soaked in DI water for ≈6 h before beginning multilayer deposition. The modulus values determined from these samples are displayed in Figure 3.

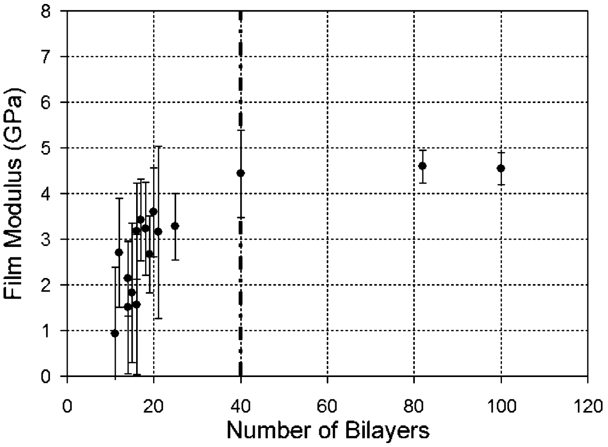

Figure 3. Effect of substrate treatment on the Young's modulus of PAH/PSS films. PDMS substrates were treated by soaking in DI water for ≈6 h prior to multilayer deposition.

The PEM films deposited on the water-treated PDMS show lower modulus values at small bilayer numbers. The modulus then rises rapidly with increasing film thickness, eventually reaching a plateau at 4.5 GPa, essentially the same modulus value observed for PEMs on untreated PDMS. Correspondingly, the bilayer thickness increment was observed to be only 1.56 nm/bilayer for films with less than 40 bilayers, with an R^2 value of 0.823, indicating less linearity in the data. Soaking the PDMS in water most likely causes surface reconstruction, allowing the initial adsorbing layers to adopt a different chain configuration compared to what is obtained without pretreatment in water. As more bilayers are deposited, the effect of the substrate treatment on the growth behavior diminishes, and the mechanical properties of the thin region of initially adsorbed layers are less influential in determining the overall film properties. These observations are consistent with the notion that in the region near the substrate a PEM film can possess physical properties and growth behavior different from that of the interior region of the film.[40] The above observations lead to two important conclusions: First, SIEBIMM measurements are sensitive enough to respond to the modulus difference resulting from substrate-dependent morphologies in PEM films. Second, films must be built to an adequate thickness to avoid measuring a modulus influenced by substrate-induced effects in very thin films as well as to minimize film thickness measuring errors. For the PAH/PSS system on PDMS as explored here, building films thicker than 70 nm is recommended.

Given the potential of PEMs for use as biomaterials,[1,3,6,26,33] an important question was whether SIEBIMM could be used to measure the wet-state modulus of PEM assemblies. For this task two samples assembled on untreated PDMS were utilized. Samples were immersed in either DI water or a 1 M solution of NaCl and allowed to equilibrate for ≈1 h before testing. Upon compression, buckling was observed over the

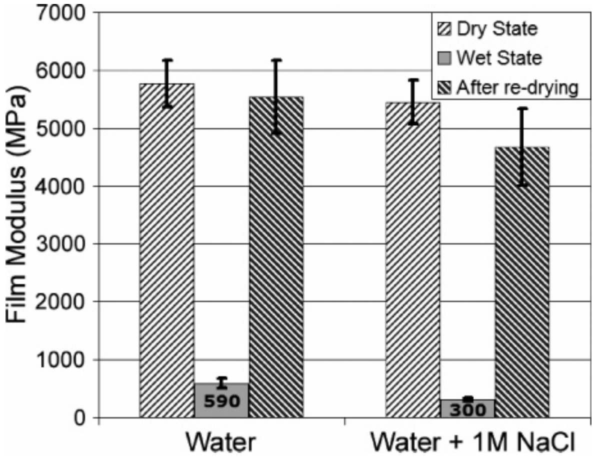

Figure 4. Dry- and wet-state modulus values of PAH/PSS films. Samples with 75 bilayers were tested in both DI water and 1 M NaCl solution. Modulus values of the films following drying of the swollen samples are also shown.

entire sample surface, and the images obtained looked similar to films buckling in the dry state (see inset, Figure 2), except for a decrease in contrast as a result of the smaller refractive index difference between the sample and the water environment. It was thus concluded that the PEM films remained well bonded to the PDMS in solution, as achieving the buckling state relies upon good adhesion of the film to the substrate. In-situ spectroscopic ellipsometry[41] was performed to determine the PEM wet-state thicknesses. After wet-state measurements, the samples were dried, and the modulus values were remeasured. The results are shown in Figure 4:

The sample immersed in DI water exhibited a decrease in modulus from 5.8 ± 0.4 GPa to 590 ± 90 MPa. The sample immersed in 1 M NaCl showed an even greater reduction in modulus, from 5.4 ± 0.4 GPa when dry to 300 ± 30 MPa in solution. The films showed corresponding thickness increases when wet, swelling 28% in water and 48% in the NaCl solution. These swollen film thicknesses are comparable with the results of previous work on this system.[41−43] Water is an excellent solvent for PEM films, inducing large reductions in modulus due to higher chain mobility in the swollen film and the possibility of breaking and re-forming electrostatic cross-links. The high salt concentration increases this effect by allowing charge screening of the electrostatic cross-linking groups. In addition, salt solutions can cause reorganization of the film structure to take place.[43] This latter effect is evidenced by the fact that upon drying the film swollen in water returned to a thickness of 136 nm, close to its original thickness of 130 nm, while the film swollen in salt returned to a thickness of 166 nm, a value still considerably higher than its original 130 nm thickness. Upon drying, the film that had been immersed in water returned to a modulus that was 96% of its original value, while the film swollen in NaCl solution only regained 86% of its original stiffness.

The values of 590 ± 90 MPa (water) and 300 ± 30 MPa (1 M NaCl) measured for PAH/PSS multilayers in the wet state fall within the range of values given so far in the literature. Vinogradova et al., using AFM deformation[16−21] and osmotic swelling[15,31] of PAH/PSS capsules, have reported an estimated modulus of 100−200 MPa. On the other hand, Gau et al., utilizing the osmotic-driven collapse of PAH/PSS capsules[9] (using different assumptions), report a higher value on the order of 1.5−2.0 GPa. Similarly high numbers (1.3−1.9 GPa) were obtained from PAH/PSS capsules by Dubreuil et al. using AFM and reflection interference contrast microscopy.[4,5] Most recently, Heuvingh et al. have reported a modulus of ≈400 ± 200 MPa for PAH/PSS capsules in 1 M NaCl solution.[32] This latter number is notably close to our reported value of 300 ± 30 MPa. To our knowledge, only one other group has previously reported a dry-state modulus for PAH/PSS multilayers. Hsieh et al., using PEM-coated Lycra yarns, estimated the modulus of PAH/PSS multilayers to be between 1 and 9 GPa;[11,12] the value of 4.4 GPa reported here falls within that range.

In conclusion, the Young's modulus of PAH/PSS PEM films was determined successfully by the SIEBIMM method in both the dry and wet states. To reduce the amount of uncertainty in the modulus, it is suggested that PEMs be grown to an adequate thickness to minimize film thickness measuring errors. In addition, measuring the modulus as a function of the number of bilayers deposited can provide information about how the stiffness changes with film thickness, which can help guard against measuring a modulus influenced by substrate-induced effects in very thin films.

Upcoming work will focus on using SIEBIMM to test the mechanical properties of weak polyelectrolyte assemblies, which offer the possibility of tuning the mechanical properties of PEM films through pH control of the polycation and polyanion deposition solutions.[23,24] In addition, previous work from our group[37] has confirmed the possibility of creating complex physical property gradients throughout the depth of the multilayer film. Such structures offer the chance of creating PEM-based thin films with enhanced mechanical properties, such as increased resistance to indentation and sliding contact damage.[44]

Numerous applications suggested in the literature clearly point to the need for a fast, accurate, and flexible way to measure the mechanical properties of very thin films in both the dry and wet states. The technique outlined in this study meets these demands and suggests that anyone conducting layer-by-layer assembly by conventional methods may wish simply to include a PDMS substrate and use it to determine the stiffness of the multilayer films in that batch of samples, making it a routine characterization technique similar to film thickness or surface roughness measurements. This work demonstrates that the SIEBIMM method is positioned to become an extremely useful tool in the field of polyelectrolyte multilayer mechanical property characterization.

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Supporting Information Available: Description of the spectroscopic ellipsometry technique. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Thompson, M. T.; Berg, M. C.; Tobias, I. S.; Rubner, M. F.; Van Vliet, K. J. *Biomaterials*, in press.

(2) Baumler, H.; Artmann, G.; Voigt, A.; Mitlohner, R.; Neu, B.; Kiesewetter, H. *J. Microencapsulation* **2000**, *17*, 651−655.

(3) Collin, D.; Lavalle, P.; Garza, J. M.; Voegel, J. C.; Schaaf, P.; Martinoty, P. *Macromolecules* **2004**, *37*, 10195−10198.

(4) Dubreuil, F.; Elsner, N.; Fery, A. *Eur. Phys. J. E* **2003**, *12*, 215−221.

(5) Dubreuil, F.; Shchukin, D. G.; Sukhorukov, G. B.; Fery, A. *Macromol. Rapid Commun.* **2004**, *25*, 1078−1081.

(6) Engler, A. J.; Richert, L.; Wong, J. Y.; Picart, C.; Discher, D. E. *Surf. Sci.* **2004**, *570*, 142−154.

(7) Fan, X. W.; Park, M. K.; Xia, C. J.; Advincula, R. *J. Mater. Res.* **2002**, *17*, 1622−1633.

(8) Fery, A.; Dubreuil, F.; Mohwald, H. *New J. Phys.* **2004**, *6*, 1−13.

(9) Gao, C.; Donath, E.; Moya, S.; Dudnik, V.; Mohwald, H. *Eur. Phys. J. E* **2001**, *5*, 21−27.

(10) Gao, C. Y.; Leporatti, S.; Moya, S.; Donath, E.; Mohwald, H. *Langmuir* **2001**, *17*, 3491−3495.

(11) Hsieh, M. C. Ph.D. Thesis. University of Massachusetts Amherst, Amherst, MA, 1999.

(12) Hsieh, M. C.; Farris, R. J.; McCarthy, T. J. *Abstr. Pap., Am. Chem. Soc.* **1999**, *218*, U620−U620.

(13) Jiang, C. Y.; Markutsya, S.; Pikus, Y.; Tsukruk, V. V. *Nat. Mater.* **2004**, *3*, 721−728.

(14) Jiang, C. Y.; Markutsya, S.; Tsukruk, V. V. *Adv. Mater.* **2004**, *16*, 157−161.

(15) Kim, B. S.; Vinogradova, O. I. *J. Phys. Chem. B* **2004**, *108*, 8161−8165.

(16) Lebedeva, O. V.; Kim, L. S.; Vinogradova, O. I. *Langmuir* **2004**, *20*, 10685−10690.

(17) Lulevich, V. V.; Andrienko, D.; Vinogradova, O. I. *J. Chem. Phys.* **2004**, *120*, 3822−3826.

(18) Lulevich, V. V.; Nordschild, S.; Vinogradova, O. I. *Macromolecules* **2004**, *37*, 7736−7741.

(19) Lulevich, V. V.; Radtchenko, I. L.; Sukhorukov, G. B.; Vinogradova, O. I. *Macromolecules* **2003**, *36*, 2832−2837.

(20) Lulevich, V. V.; Radtchenko, I. L.; Sukhorukov, G. B.; Vinogradova, O. I. *J. Phys. Chem. B* **2003**, *107*, 2735−2740.

(21) Lulevich, V. V.; Vinogradova, O. I. *Langmuir* **2004**, *20*, 2874−2878.

(22) Mamedov, A. A.; Kotov, N. A.; Prato, M.; Guldi, D. M.; Wicksted, J. P.; Hirsch, A. *Nat. Mater.* **2002**, *1*, 190−194.

(23) Mermut, O.; Lefebvre, J.; Gray, D. G.; Barrett, C. J. *Macromolecules* **2003**, *36*, 8819−8824.

(24) Pavoor, P. V.; Bellare, A.; Strom, A.; Yang, D. H.; Cohen, R. E. *Macromolecules* **2004**, *37*, 4865−4871.

(25) Pavoor, P. V.; Gearing, B. P.; Gorga, R. E.; Bellare, A.; Cohen, R. E. *J. Appl. Polym. Sci.* **2004**, *92*, 439−448.

(26) Richert, L.; Engler, A. J.; Discher, D. E.; Picart, C. *Biomacromolecules* **2004**, *5*, 1908−1916.

(27) Salomaki, M.; Laiho, T.; Kankare, J. *Macromolecules* **2004**, *37*, 9585−9590.

(28) Salomaki, M.; Loikas, K.; Kankare, J. *Anal. Chem.* **2003**, *75*, 5895−5904.

(29) Tang, Z. Y.; Kotov, N. A.; Magonov, S.; Ozturk, B. *Nat. Mater.* **2003**, *2*, 413−U418.

(30) Vinogradova, O. I. *J. Phys.: Condens. Matter* **2004**, *16*, R1105−R1134.

(31) Vinogradova, O. I.; Andrienko, D.; Lulevich, V. V.; Nordschild, S.; Sukhorukov, G. B. *Macromolecules* **2004**, *37*, 1113−1117.

(32) Heuvingh, J.; Zappa, M.; Fery, A. *Langmuir* **2005**, *21*, 3165−3171.

(33) Yang, S. Y.; Lee, D.; Cohen, R. E.; Rubner, M. F. *Langmuir* **2004**, *20*, 5978−5981.

(34) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213−4219.

(35) 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.

(36) Volynskii, A. L.; Bazhenov, S.; Lebedeva, O. V.; Bakeev, N. F. *J. Mater. Sci.* **2000**, *35*, 547−554.

(37) Nolte, A. J.; Rubner, M. F.; Cohen, R. E. *Langmuir* **2004**, *20*, 3304−3310.

(38) Harrison, C.; Stafford, C. M.; Zhang, W. H.; Karim, A. *Appl. Phys. Lett.* **2004**, *85*, 4016−4018.

(39) See Supporting Information.

(40) Ladam, G.; Schaad, P.; Voegel, J. C.; Schaaf, P.; Decher, G.; Cuisinier, F. *Langmuir* **2000**, *16*, 1249−1255.

(41) Itano, K.; Choi, J.; Rubner, M. F. *Macromolecules* **2005**, *38*, 3450−3460.

(42) Hiller, J.; Rubner, M. F. *Macromolecules* **2003**, *36*, 4078−4083.

(43) Dubas, S. T.; Schlenoff, J. B. *Langmuir* **2001**, *17*, 7725−7727.

(44) Suresh, S. *Science (Washington, D.C.)* **2001**, *292*, 2447−2451.

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