Supporting Information for

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

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Derivation of the Two-Plate Buckling Equation

Figure 1 from the main text is represented here as Figure S1 for clarity:

Figure S1. 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.

Volynskii gives the equation for the stress as a function of the buckling wavelength in a homogeneous rigid plate (labeled here as PEM) on an elastomeric substrate (labeled s) (Figure S1a) as:

\[
\sigma(\lambda) = \frac{4\pi^2}{wd_{\text{PEM}} \cdot \lambda^2} \left( \frac{4\pi^2}{w d_{\text{PEM}} \cdot \lambda^2} + \frac{\overline{E}_s \cdot \lambda}{4\pi d_{\text{PEM}} \cdot \overline{E}_{\text{PEM}} \cdot I_{\text{PEM}}} \right), \quad (S1)
\]
where all symbols are as described in the main text. The force, $F$, has been replaced in Equation S1 with $\sigma(\lambda) = F(\lambda)(w \cdot d_{PEM})$. The plate will buckle at the value of $\lambda$ that minimizes the stress in the plate. By taking the derivative of Equation S1 and setting it equal to 0, the governing equation for a single plate buckling on an elastomeric substrate can be found to be:

$$
\tilde{E}_{PEM} \cdot I_{PEM} = \frac{E_s \cdot w}{4} \left( \frac{\lambda}{2\pi} \right)^3, \quad (S2)
$$

which is the same as Equation 2 in the main text. The quantity $\tilde{E}_{PEM} \cdot I_{PEM}$ is known as the flexural rigidity. When two plates of equal width appear in a laminated composite structure (Figure S1b), as with a PS-PEM two-plate film, the resulting film can be treated as having an effective flexural rigidity given by the sum of the individual rigidities:

$$
\tilde{E}_{PEM} \cdot I_{PEM} + \tilde{E}_{PS} \cdot I_{PS} = \frac{E_s \cdot w}{4} \left( \frac{\lambda}{2\pi} \right)^3. \quad (S3)
$$

Thus, it is left to find $I$, the second moment of the area, for both the PS and the PEM regions. These are given by the following two expressions:

$$
I_{PS} = w \cdot \int_{0}^{d_{PS}} (y - Y)^2 \, dy \quad (S4)
$$

$$
I_{PEM} = w \cdot \int_{d_{PS}}^{(d_{PS} + d_{PEM})} (y - Y)^2 \, dy. \quad (S5)
$$

The $y$ axis is taken to be normal to the plane of the films, with its origin at the PDMS-PS interface (see Figure S1), and $Y$ is the neutral bending axis:

$$
Y = \frac{d_{PEM}^2 + 2 \cdot d_{PEM} \cdot d_{PS} + \frac{E_{PS}}{E_{PEM}} \cdot d_{PS}^2}{2 \cdot \left( d_{PEM} + \frac{E_{PS}}{E_{PEM}} \cdot d_{PS} \right)}. \quad (S6)
$$
Taking \( dt = d_{PS} + d_{PEM} \) and \( \phi_{PS} = d_{PS} / dt \), Equation S6 can be rewritten after some algebraic manipulation as:

\[
Y = \frac{d_t}{2} \frac{1 + \phi_{PS}^2 \left( \frac{E_{PS}}{E_{PEM}} - 1 \right)}{1 + \phi_{PS} \left( \frac{E_{PS}}{E_{PEM}} - 1 \right)} = \frac{d_t}{2} \kappa. \quad (S7)
\]

With the equation for \( Y \) written in the above form, \( \kappa \) represents a type of deviation factor for the neutral axis of bending. In the simplest case, where \( E_{PEM} = E_{PS} \), \( \kappa = 1 \) and the neutral axis, as expected, is located in the middle of the film. Equation S7 can be used with Equation S4 and S5 to find values for \( I_{PEM} \) and \( I_{PS} \). Plugging those values into Equation S3 yields:

\[
\bar{E}_{PEM} = \frac{\bar{E}_{eff}}{4} \bar{E}_{PS} \left[ \phi_{PS} - \frac{\kappa}{2} \right] + \left( \frac{\kappa}{2} \right)^3, \quad \bar{E}_{eff} = 3\bar{E}_s \left( \frac{\lambda}{2\pi d_t} \right)^3, \quad (S8)
\]

which is identical to Equation 4 in the main text.

It should be noted that Equation S8 assumes elastic deformation in the materials and is only valid if both the PEM and PS layers are rigid enough to support the buckled state. When one or both of the materials undergoes plastic deformation or failure, the formalism presented above fails.

**Effects of Plasma Treatment on PS Films**

The plasma treatment of PS was carried out as described in the main text. The effects of plasma treatment on typical samples are presented below for a set of 6 PS films on PDMS. All samples were spin-coated to a thickness of approximately 70 nm—the
exact thicknesses were measured by spectroscopic ellipsometry prior to all SIEBIMM measurements.

Figure S2 shows images taken during contact angle analysis of samples during 4 stages of treatment:

Figure S2. Typical side-view images of water droplets on the surface of PS films adhered to PDMS substrates. The images represent (a) the untreated PS surface shortly after film transfer, (b) the PS surface following 30 sec of plasma treatment, (c) recovery of some hydrophobicity following aging for a day at ambient conditions, and (d) a return to a very low contact angle after an additional 10 sec of plasma treatment.

An average contact angle of 105° (Fig S2a) was recorded for PS surfaces immediately following the transfer of the films from the silicon wafer spin-coating
platform to the PDMS substrates. The contact angle decreased to an average value of 26° following 30 sec of plasma treatment as described in the main text (Fig S2b). To investigate the stability of the hydrophilicity of the treated surfaces, this batch of samples was stored at ambient conditions (25° C, 20% RH) for 1 day (~ 24 hrs) and then the contact angles were re-measured. The samples recovered some of their original hydrophobicity, displaying an average contact angle of 69° (Figure S2c). Finally, samples were plasma treated once more for 10 sec. The average contact angle following this procedure was 14° (Figure S2d).

SIEBIMM was performed to monitor the effect of the plasma treatment on the PS modulus. The average modulus of the samples is graphed with the contact angle measurements in Fig S3:

![Graph showing contact angle and Young's modulus as a function of treatment](image)

*Figure S3. Average contact angle (filled triangles) and Young’s modulus (open circles) as measured via SIEBIMM for 70 nm PS films on PDMS as a function of treatment.*
The Young’s modulus rises from $3.7 \pm 0.2$ to $5.2 \pm 0.2$ following the first 30 sec plasma treatment. The modulus was not measured following the 1 day aging period, but measurements following the additional 10 sec treatment showed an even higher modulus of $5.8 \pm 0.3$. As mentioned previously, the thickness of the PS films was also measured so that accurate modulus measurements could be made. The film thickness decreased on average only $2.7 \pm 1.0\%$ following the initial 30 sec treatment. The subsequent 10 sec treatment produced no statistically significant change in the film thickness.

There is a motivation to measuring the value of the contact angle and Young’s modulus not just after the initial 30 sec treatment, but also following an addition 10 sec treatment subsequent to a hydrophobic recovery period. In general, the PDMS-PS platform is not ready for film deposition immediately following the initial treatment step, as thickness and buckling measurements are needed to obtain accurate data for the PS film for subsequent two-plate calculations. If these measurements cannot be accomplished relatively quickly, the hydrophobicity of the PS may recover to an unacceptable degree for a particular application.\(^4\) Here we demonstrate that an additional, shorter treatment can then be employed to regenerate the PS surface hydrophilicity. In addition, this treatment produces a negligible effect on film thickness (eliminating the need to re-measure the thickness), and a small increase in the PS modulus that could be determined via a quick buckling experiment.

References

