

Supporting Information

Confinement-driven Increase in Ionomer Thin-Film Modulus

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Modeling

The equations used for the modeling of effective modulus are:

$$E = E_m \frac{1 + \frac{1}{\alpha\zeta} \eta \Phi}{1 - \eta \Phi} \text{ and } \eta = \frac{E_p - E_m}{E_p + \frac{1}{\alpha\zeta} E_m} \quad (\text{S1})$$

This expression is inspired from Halpin-Tsai equations.¹ The Halpin-Tsai equations are modified to account for the role of confinement-driven aligned polymer domains in elastic modulus of the polymer. For this reason, the material parameter representing the aspect ratio of the stiffer reinforcing phase in the original expression was changed to reflect the configurational geometry of the domains in thin films. These domains, or polymer aggregates, in thin films can be interpreted as the load-bearing mechanical element controlling the mechanical behavior of the polymer.

Since eq S1 is fundamentally similar to the original Halpin-Tsai equations, the limits of the model are preserved such that limiting values of $\alpha\zeta$ lead to classical rule-of-mixture expressions:

$$\alpha\zeta \rightarrow \infty \Rightarrow \frac{1}{E} = \frac{\Phi}{E_p} + \frac{1 - \Phi}{E_m} \quad (\text{S2a})$$

$$\alpha\zeta \rightarrow 0 \Rightarrow E = \Phi E_p + (1 - \Phi) E_m \quad (\text{S2b})$$

For example, for a single PTFE chain, a theoretical maximum is reached from eq S2b, i.e. $\Phi \rightarrow 1 \Rightarrow E = E_p$, where the effective modulus becomes the modulus of a PTFE chain. For this case, the domain of interest is the CF_2 chain, such that $\alpha\zeta$ becomes irrelevant as there is no need for scaling at the molecular level. As the thickness, and therefore the scale of interest, changes from atomistic levels to nano- or mesoscales, spacing of domains as well as their distribution, or the spatial configuration, becomes more important.

The parameter ζ can be related to the number of fundamental mechanical elements in the thickness of the film and is calculated by dividing the *film thickness*, L , by some *characteristic length*, D , in the polymer,

$$\zeta = \frac{L}{D} \quad (\text{S3})$$

For Nafion membranes, we have chosen the distance between PTFE backbones. The *scaling factor*, α , accounts for fact that perturbations in material properties for polymers can often be observed at critical thicknesses (L_{cr}) many times larger than some fundamental length-scales associated with the polymer structure.

The value Φ is the fraction of *active* PTFE (i.e., backbone) domains, or fundamental mechanical elements, contributing to force transfer during deformation thus to the effective modulus of the membrane. Thus, Φ is not to be confused with the polymer fraction of hydrated membrane; within the context of this study, Φ represents the fraction of domains, i.e., mechanical elements that actively participate in force transfer during deformation. A general expression for the thickness dependence of this fraction can be written in the following form

$$\Phi(L) = \Phi_o + (1 - \Phi_o) \exp\left(-\alpha \frac{L}{D}\right) \quad (\text{S4a})$$

Because there can be significant orientation of domains, or mechanical elements, due to processing we must account separately for their contribution to the mechanical deformation. Therefore, Φ_o is the initial fraction of *active, oriented* domains that reflects alignment of domains induced through external processing (not the intrinsic confinement effects) for bulk polymer of large thickness ($L \gg D$). When the value $\alpha L/D$ is equal to 1 in eq S4a, we reach a critical thickness, L_{cr} , which controls the onset of deviation from bulk behavior as shown in **Fig. S1**. Thus, L_{cr} mathematically characterizes how deviations from critical thickness control the fraction of confinement-driven "mechanical activation" of backbone domains, and thus the thin-film modulus. Therefore, we can alternatively write

$$\Phi(L) = \Phi_o + (1 - \Phi_o) \exp\left(-\frac{L}{L_{\text{cr}}}\right) \text{ where } L_{\text{cr}} = \frac{D}{\alpha} \quad (\text{S4b})$$

Variation of the fraction with polymer thickness as used in the model is plotted in **Fig. S1** for several cases (polymers). As can be seen from the figure, a critical thickness of (50 to 150) nm is suitable for most class of polymers studied in this work. For this reason, in **Fig. 1** of main text, we used L_{cr} of 50 and 100 nm to generate an envelope that best captures the measured modulus across the various lengthscales. This range of critical thickness is in agreement with the

observations in previous Nafion thin-film studies that showed deviations from bulk behavior for water diffusion coefficient,² water uptake,²⁻⁵ ionic conductivity,^{5, 6} and activation energy.^{5, 7} Also, a recent study on Nafion thin films suggest that films confined to less than 50 nm exhibit no clear patterns from x-ray scattering, but show more mixing of smaller domains in TEM.⁶ It was also inferred from neutron reflectivity studies⁸ that domains are oriented parallel to the substrate suggesting a lamellar phase-separated nanostructure. All these findings indicate a bulk to film transition in the transport properties and nanostructure of PFSA, yet this is the first study to demonstrate such transition in mechanical properties.

It is worth noting that, thanks to the flexibility of the model, alternative descriptions for the characteristic length, D , can be used, one being the persistence length which is $l_p = (2 \text{ to } 4) \text{ nm}$ for PTFE.^{9, 10} Obviously, using the persistence length instead of PTFE inter-crystalline distance ($\approx 0.5 \text{ nm}$) would require an order-of-magnitude lower scaling factor α in order to acquire the same model predictions. This is, however, expected as the scale of interest shifts from inter-molecular distance to intra-molecular distance (i.e., persistence length). Hence, the model provides quite a flexible tool for mathematical characterization of mechanical behavior of thin films using various fundamental material elements including domain spacing, persistence length or radius of gyration.

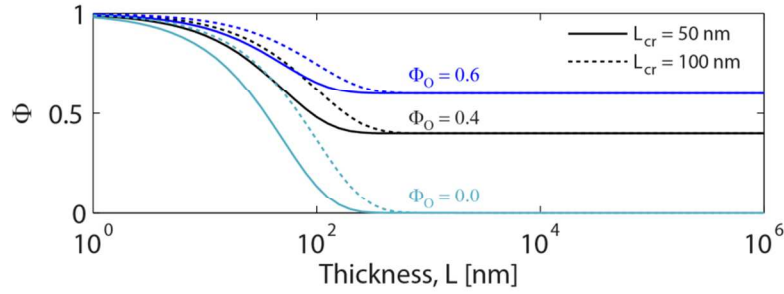


Figure S1. Thickness dependence of fraction of active domains for two critical thickness values (eq S4).

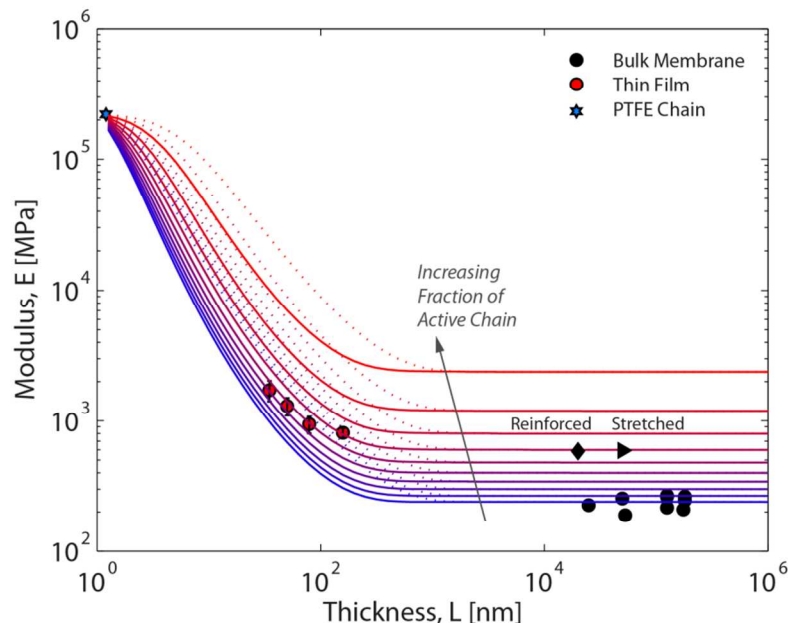


Figure S2. Model prediction for modulus generated by different fraction values (from 0 to 1, with increments of 0.1) for two critical thicknesses (solid and dotted lines).

A family of curves for the effective modulus generated by ranging Φ_0 from 0 to 1 (with increments of 0.1) are shown in **Fig. S2**. As the thickness is reduced all the curves in **Fig. S2** approach the theoretical modulus of the chain regardless of fraction, shifting the scale of interest to atomistic levels. At continuum scales, any changes in modulus of bulk polymer could be attributed to the initial non-zero values of Φ_0 that could represent the processing- and/or stretching-induced changes in modulus. Care must be taken when analyzing the model predictions for bulk polymers since an accurate physical model for stretching-induced stiffening requires a more comprehensive approach. Our objective here is to demonstrate the role of model parameters on the predicted modulus across the length-scales, not to explain the underlying origins of specific processing effects on the mechanical properties of bulk polymers, which requires a more continuum-level treatment and is not of interest in this study. However, our modeling approach is fairly adequate when it comes to the quantitative analysis of confinement-driven stiffening in thin films.

Notes on Mechanical Properties and Literature Data Used

Poisson's ratio for Nafion membranes was reported to be around 0.4 in ambient conditions.^{11, 12} Also, isotropic mechanical properties of bulk Nafion membrane can be inferred from the similarity between mechanical properties measured in the plane^{11, 13, 14} and thickness directions.^{14, 15} Similarly, nanostructure of Nafion membranes studied by SAXS indicates very small anisotropy.^{16, 17} The literature data used for the bulk modulus are taken from numerous studies on the stress-strain curves of Nafion membrane under tension^{11, 13, 14, 18, 19} and compression,²⁰ as well as pre-stretched Nafion membrane under tension²¹. Most of these

measurements were done in dry (~0 % RH) or in ambient conditions (30 % \pm 5 % RH) at which the thickness swelling for bulk membrane is much less than the swelling in fully hydrated state (5 % vs. 25 %).

Equilibrium Chemical Potential

When an ionomer membrane is in equilibrium with its external environment at a given relative humidity (RH), or water activity, a_w , and temperature, T , chemical potential of water external to the membrane can be described as²²

$$\mu_w^{\text{ext}} - \mu_{w,\text{ref}}^{\text{ext}} = RT \ln(a_w) = RT \ln\left(\frac{\text{RH}}{100}\right) \quad \text{S5}$$

Similarly, chemical potential of water in the membrane can be written in terms of concentration,

$$\mu_w - \mu_{w,\text{ref}} = RT \ln(c_w) + \bar{V}_w P, \quad \text{S6}$$

where $\mu_{w,\text{ref}}$ is the value of chemical potential at reference state, \bar{V}_w is the molar volume of water molecules (18 cm³/mol) and P is the swelling pressure developed in the ionomer in response to structural changes during hydration of polymer matrix. Swelling pressure in general can be described using the modulus and deformation of the polymer matrix, which could also be concentration dependent. However, disordered, semicrystalline nanostructure of PFSA makes it difficult to quantify the deformation of matrix due to growing water nano-domains, and studies on the mathematical formulation of swelling pressure have been limited thus far.^{23, 24} Nevertheless, a common approach in many sorption models for PFSA membranes is to describe swelling pressure as proportional to modulus of the ionomer.²³⁻²⁶ Due to lack of adequate structural information on the swollen PFSA films, and also for the sake generality, we decided to focus on the equilibrium of chemical potentials for bulk and thin film ionomer without a precise formulation for swelling pressure. In thermodynamic equilibrium, chemical potential for water external to the film (i.e., in humid air) must be equal to that for water absorbed by the ionomer film (eqs S5 and S6). Assuming that swelling pressure is proportional to the modulus of ionomer in dry state (i.e., $P \propto E$), one can investigate the thermodynamic equilibrium using the relationship between the modulus and water content in bulk and thin films.

Concentration of water can approximately related to the number of water molecules per ionic end group of the ionomer ($\lambda_{\text{H}_2\text{O}}$), which is the sulfonic acid group for PFSA

$$c_w = \frac{\lambda_{\text{H}_2\text{O}}}{1 + \lambda_{\text{H}_2\text{O}}} \quad \text{S7}$$

$\lambda_{\text{H}_2\text{O}}$ for PFSA thin-films used in this study are taken from Eastman et al.² and concentration is calculated by eq S7. Values at a relative humidity of 75 % are used for the plot in the text. We also note that, eq S7 assumes additive of molar volumes with no free volume effect, the accuracy of which is debatable for thin films. Thus, a complete model for sorption of thin-films requires a more rigorous approach, which is beyond the scope of this letter.

Evaluation of the Effect of Changing Poisson's Ratio

Below is a plot showing the modulus as a function of thickness for various values of Poisson's ratio ($\nu=0, 0.4, 0.5$). It is clear that even if the Poisson's ratio were to change dramatically, this could not account for the dramatic stiffening observed in this study.

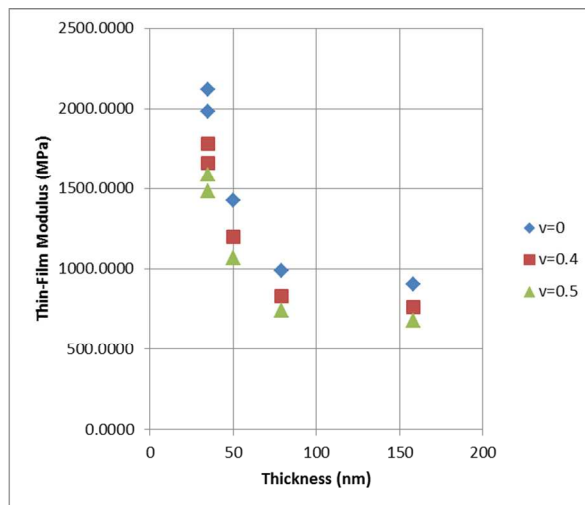


Figure S3. Plots showing the calculated value of the elastic modulus at various values for Poisson's ratio ($\nu=0, 0.4, 0.5$).

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