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Effect of Relative Humidity on the Young's Modulus of Polyelectrolyte Multilayer Films and Related Nonionic Polymers

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ABSTRACT: We have measured the Young's modulus and thickness of ultrathin polyelectrolyte multilayer (PEM), polystyrene (PS), and poly(methyl methacrylate) (PMMA) films as a function of relative humidity. We demonstrate that PEMs undergo substantial swelling and plasticization in the presence of ambient water and that both the choice of polyelectrolytes and the pH of the deposition baths influence the response of a PEM film to changes in humidity. These responses were roughly linear in two of the PEM systems tested; however, a third system demonstrated evidence of antiplasticization and an abrupt swelling transition at intermediate humidity. This behavior is attributed to an internal structure rich in hydrogen-bonding sites. Overall, our results suggest that the chemical composition and molecular architecture of PEMs are responsible for differences in the environmental responsiveness of these materials. Both PS and PMMA films exhibited comparatively small but measurable swelling and plasticization in the presence of water; these effects were more pronounced in the case of the more hydrophilic PMMA. Our results offer insight into the material structure and internal chemical interactions that determine the properties and responsiveness of PEM systems.

Introduction

The layer-by-layer (LbL) assembly of polyelectrolyte multilayer films (PEMs) represents an area of sustained interest in surface science. PEM materials are distinguished from common nonelectrolyte polymer thin films such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) by their unique preparation via aqueous-based alternating adsorption of polycations and polyanions, a process which allows their molecular organization and chemistry to be readily tuned through control of the depositing polymer type and solution pH and ionic strength. Since their introduction in the early 1990s,[1] the combined chemical tunability and water responsiveness of PEMs has led to a broad spectrum of potential utility for these materials, including applications in biology,[2–4] medicine,[5,6] sensing,[7–9] tribology,[10] and optics.[11,12]

Much of the previous research dedicated to examining how a PEM responds to ambient water focused on measuring thickness changes in response to changes in relative humidity (RH). Early work focused on strong polyelectrolyte systems (chains fully charged upon deposition) comprised of poly(styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH). Lösche et al. demonstrated using neutron reflectometry that PAH/PSS PEMs can contain up to 40 vol % water when incubated at 100% RH.[13] Kügler and co-workers subsequently measured film thickness as a function of relative humidity for the PAH/PSS system; their work suggested that multiple hours were required to attain equilibrium swelling in these systems.[14] To our knowledge, the most recent report examining humidity-driven swelling in the PAH/PSS system is from Wong et al., who used in-situ ellipsometry to study the influence of humidity and last adsorbed layer (i.e., whether PAH or PSS is present at the air interface) on the film thickness.[15] These researchers reported data in overall good agreement with the study by Kügler; however, Wong reported that equilibrium swelling for their films was attained on a time scale of minutes, not hours. This latter work has also recently been examined in the context of understanding the internal structure and hydration properties of polyelectrolyte multilayer assemblies in review articles by von Klitzing[16] and Schönhoff et al.[17]

In contrast to strong polyelectrolyte systems such as PAH/PSS, weak polyelectrolytes have a pH-tunable degree of ionization in solution, allowing for control of the PEM chemistry and molecular architecture through changes in the deposition pH.[18] Tanchak et al. have demonstrated that PEMs assembled from PAH and poly(acrylic acid) (PAA) can exhibit equilibrium swelling times in aqueous solution differing by orders of magnitude depending upon the pH at which they were assembled.[19] These researchers have suggested that water clustering mediated by the internal film chemistry is at least partially responsible for this phenomenon, a hypothesis that seems to be supported by their recent neutron scattering study of water distribution in PAH/PAA films.[20]

The response of PEMs to ambient water is evidently a complex phenomenon that remains only partially understood. Nevertheless, the success of many PEM-based applications clearly relies in a large part on the measurement and control of the film thickness as well as on other physical properties such as the Young's modulus which have until recently been more difficult to quantify for these ultrathin materials. These particular film attributes, for example, can govern important biological functions such as cell attachment and spreading.[2,4,21,22] In this paper we present a systematic study of both the thickness and Young's modulus of PEM films as a function of relative humidity. We demonstrate that these combined controlled humidity measurements, enabled by in-situ spectroscopic ellipsometry and elastic buckling on poly(dimethylsiloxane) (PDMS) substrates,[23–25] provide significant insight into the chemical and structural properties of the films and reveal dramatic differences between PEM responsiveness as a function of polyelectrolyte type and assembly conditions. Additionally, we provide humidity-dependent measurements of thin films of PS and PMMA and compare the behavior of these systems to PEMs. Our results provide a comprehensive look at the response of ultrathin polymer films to ambient humidity and highlight

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the importance of understanding the influence of humidity on properties that are critically important to many environmentally sensitive applications.

Experimental Details

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)[46] were used without further purification to create polymer solutions of 0.01 M concentration by repeat unit. In addition, 0.1 M NaCl (Mallinckrodt Chemicals) was added to the deposition baths when PAH and PSS were being assembled. Solutions were prepared using Milli-Q deionized water (Millipore) with a resistivity of 18.2 MΩ cm and were pH adjusted using either 1.0 M HCl or NaOH immediately prior to PEM assembly.

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, allowed to degas at atmospheric conditions for 45 min−1 h, and then baked for 45 min at 80 °C. After cooling, the PDMS was cut into 2 cm × 6 cm pieces. These pieces were used as substrates without further cleaning or preparation.

A programmable slide stainer (HMS Slide Stainer, Zeiss) was used to assemble PEMs onto PDMS substrates. The first 10 bilayers of a film were assembled using 15 min immersions in each polyelectrolyte (films always began with PAH deposition), followed by three 1 min rinse steps with gentle agitation. If a film recipe called for more than 10 bilayers, the immersion time in the polyelectrolyte baths was reduced to 5 min. Addition adsorption time was allowed for the first 10 bilayers of the film to ensure maximum coverage of the initially adsorbed layers on the PDMS surface. Samples were allowed to air-dry and were stored at ambient conditions.

The nomenclature for PEM films follows the convention ("polycation"X/"polyanion"Y)$_Z$, where X and Y represent the pH of the respective polyelectrolyte solutions during assembly and Z is the total number of bilayers (polycation−polyanion) deposited. A half-integer value of Z indicates that the PEM was finished with a polycation deposition step.

PS (Styron 663 W, Dow Chemical Co., $M_w \sim$ 300 000) and PMMA (Scientific Polymer Products, M_w = 35 000) were dissolved in toluene. To create films of each polymer with thicknesses of approximately 40 and 80 nm, polymer solutions were prepared at concentrations of 4.1 and 6.3 g/L (PS) and 10 and 20 g/L (PMMA). Spin-coating (PWM32, Headway Reseach) was conducted for 20 s at 2000 rpm with a 300 rpm/s ramp onto ~2 cm × 3 cm pieces of single-crystal polished silicon wafers (p-type, 1−50 MΩ cm, [100] orientation, WaferNet). Prior to spin-coating, the silicon was treated for 5 min at 100 W power in an air plasma (Harrick Scientific PDC-32G plasma cleaner/sterilizer) operated at 400 mTorr. The silicon was rinsed with pure toluene immediately before spin-coating each film.

PS and PMMA films were transferred to PDMS substrates using the water transfer technique described in previous publications.[23,24] Although PS films were able to be transferred immediately upon immersion in water, PMMA films necessitated an overnight soak to ensure film transfer.

Measurements of the buckling wavelength were conducted by performing He−Ne laser (Research Electro-Optics, 0.5 mW at 632.8 nm) diffraction measurements on a strained sample in a controlled-humidity glovebox (Electro-Tech Systems, Inc.). Photographs of the diffracted beam were taken using a digital camera against a calibrated screen (see Supporting Information). Before measuring the humidity-dependent mechanical properties of the PEMs, the samples were first allowed to equilibrate for at least 1 week in a desiccator containing LiCl (11.3% RH at 25 °C)[26] before being moved to the humidity chamber, which was maintained at 12% RH. After taking diffraction measurements of the buckling wavelength, samples were hermetically sealed into a quartz cell and transferred to a spectroscopic ellipsometer for thickness characterization using a previously described technique.[25] The samples were then returned to the humidity chamber, after which the humidity was increased to the next value and the film was allowed to re-equilibrate. Reported equilibrium swelling times for PEM films exposed to changes in relative humidity have varied anywhere from minutes to several hours;[14,15,27] we therefore chose to let our films equilibrate for ≈ 1 day following each increase in humidity. A photograph of the experimental setup and an image of a film being subjected to laser diffraction are shown in Figure 1.

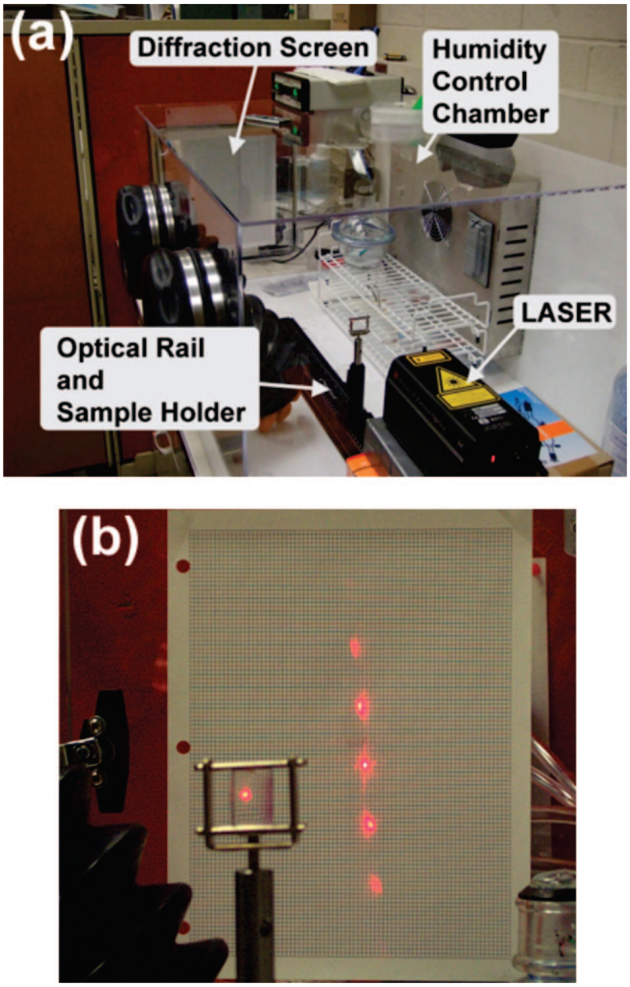

Figure 1. Experimental setup for humidity-controlled laser diffraction measurements of the buckling wavelength. (a) A photograph of the humidity control chamber and laser diffraction setup. (b) Photograph of the diffracted laser beam from a (PAH3.0/PSS3.0) sample undergoing buckling at 12% RH. Two diffracted orders of the beam can be seen.

Following the buckling and humidity measurements, compression testing was performed as previously described to obtain the needed value of Young's modulus for the PDMS substrate.[24,25] Errors bars in all reported data were found by propagating the estimated uncertainty in each measurement step (see Supporting Information). The temperature in the humidity chamber remained in the range of 25−28 °C during all experiments, and the estimated uncertainty in all humidity measurements is ±4% RH.

Results and Discussion

The SIEBIMM buckling instability method[23] was used in tandem with in-situ spectroscopic ellipsometry to measure the Young's modulus of the polymer films in this study. This technique relies on the fact that the compression-induced wrinkling of a thin, stiff film on an elastomeric substrate (here PDMS) adopts a periodic wavelength. Combined knowledge of the observed wavelength of the wrinkled pattern (λ), the film thickness (d), the PDMS Young's modulus, and its Poisson's

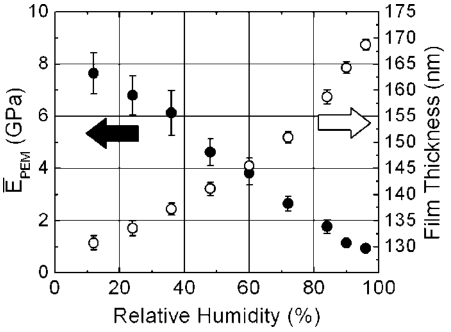

Figure 2. Plane strain Young's modulus (solid circles) and film thickness (hollow cirlces) as a function of humidity for $(PAH3.0/PSS3.0)_{75}$ multilayer films. Samples were allowed to equilibrate ~24 h at each humidity value before measurements were taken.

ratio allows for calculation of the thin film Young's modulus using[23]

$$\overline{E}_{\mathrm{f}} = \frac{E_{\mathrm{f}}}{1-\nu_{\mathrm{f}}^{2}} = 3\frac{E_{\mathrm{PDMS}}}{1-\nu_{\mathrm{PDMS}}^{2}}\left(\frac{\lambda}{2\pi d}\right)^{3} \qquad (1)$$

where E and ν represent the Young's moduli and Poisson's ratios of the film and the PDMS. Plane strain values of E (designated by the overbar) are reported in this paper to due to the difficulty of knowing the Poisson's ratio of the PEM at various relative humidity values, particularly in the case of PEM films whose behavior transitions from glassy to rubbery with increasing humidity. We have previously assumed a value of 0.33 for dry-state PEM films and 0.5 for PEM films immersed in water.[25] We assume a Poisson's ratio of 0.5 for the PDMS at all humidity values.

Probing the Young's modulus of thin films at controlled relative humidity levels necessitated modifications to the scheme we had previously used for buckling experiments.[25] In this study we employed a controlled humidity chamber to house the samples and perform laser diffraction measurements of the compression-induced buckling wavelength (see Figure 1). In the following, we present the results from examining the effect of relative humidity on the thickness and Young's modulus of PEM systems as well as thin films of PS and PMMA.

Characterization of PEM Films. We chose three different PEM assemblies for study: PAH3.0/PSS3.0, PAH7.5/PAA3.5, and PAH2.5/PAA2.5. We had previously tested the PAH3.0/PSS3.0 and PAH7.5/PAA3.5 systems at particular relative humidity values;[24,25] systematically studying the effect of humidity on the same systems thus allowed us to check the consistency of our new measurements with our previous work. The study of PAH2.5/PAA2.5 films allowed for examination of the effects of changing the deposition pH on the modulus of the PAH/PAA system. We expected this system in particular to display a greater sensitivity to humidity effects due to the fact that PAH2.5/PAA2.5 films are quite hydrophilic due to an abundance of free carboxylic acid groups distributed throughout the multilayer.[18,28]

Increases in relative humidity resulted in decreases in Young's modulus and increases in the film thickness for all three PEM systems. These results are consistent with our previous findings in which water was shown to be a good solvent for these films[24,25] and with the notion that in a polymer gel the relative humidity determines the concentration of water in the material, and this in turn controls the degree of plasticization. The range of values for these parameters and the trends in the data revealed interesting differences between systems, however. These will be discussed individually in more detail.

The plot of plane strain Young's modulus and film thickness as a function of the relative humidity is shown in Figure 2 for the $(PAH3.0/PSS3.0)_{75}$ system. We have previously measured $\overline{E}$ values of 6.3 ± 0.3 and 3.0 ± 0.3 GPa for the PAH3.0/PSS3.0 system at 20% RH and 50% RH, respectively;[24] in this study we obtained comparable values of 6.8 ± 0.8 GPa (24% RH) and 4.6 ± 0.5 GPa (48% RH), demonstrating good agreement with previous results. Overall, $\overline{E}$ ranged from 7.6 ± 0.8 GPa at 12% RH to 0.93 ± 0.09 GPa at 96% RH. This latter value is quite close to our previously reported value of 0.79 ± 0.12 GPa for a fully hydrated PAH3.0/PSS3.0 film.[25] Among the three systems we tested, the PAH/PSS film exhibited the smallest modulus at 12% RH but also the largest modulus at high humidity values. In fact, PAH/PSS films were the only films to exhibit buckling at 96% RH—the two PAH/PAA systems were presumably too compliant at this humidity to sustain the buckling instability, which requires a film modulus approximately an order of magnitude higher than that of the PDMS (here $\overline{E}_{\mathrm{PDMS}} \sim 2.7 \pm 0.2$ MPa). The system with the lowest "dry" compliance was thus shown to be the most resistant to humidity-induced plasticization. This result is consistent with the film thickness data as well. Over the range of 12%—84% RH, the PAH/PSS films swelled by only 21 ± 2%, as opposed to 26 ± 3% for the PAH7.5/PAA3.5 system and 46 ± 2% for the PAH2.5/PAA2.5 system. We note that the value of 21% swelling for the PAH/PSS films over the above-indicated humidity range corresponds nearly exactly with the results of Wong[15] and Kügler,[14] both of whom have previously conducted humidity-dependent thickness studies of the PAH/PSS system. A comparison of our data with those studies also reveals that our measured values of the film thickness follow a similar trend with increasing humidity, namely, that the film swells more dramatically at higher humidity, with a transition in behavior at ~70% RH. This transition is most evident in the data of Wong et al. for PAH-capped films, which they also demonstrate to be more hydrophobic and resistant to swelling, although their data, like ours, seem to demonstrate this transition for PSS-capped films as well.[15] The films prepared by Kügler et al. were also PAH-capped and displayed similar transitional behavior.[14] These observations suggest that the hydrophobicity of the PEM system may be responsible for the swelling transition.

Although the exact reason for this "two-regime" swelling behavior is unknown, we can speculate that water entering a dry film would tend to segregate to the more hydrophilic regions in the vicinity of the electrostatic cross-links. As the humidity of the environment increases, the ion-centered water clusters would grow until they coalesce, forming a continuous water phase throughout the film resulting in enhanced swelling. This percolation hypothesis has been suggested to explain the swelling behavior of Nafion membranes.[29–31] Nafion consists of a perfluoronated polymer backbone with sulfonic acid side chains and is thus a reasonable analogue for the PAH/PSS system. Some researchers have applied Flory—Huggins theory to calculate a concentration-dependent chi parameter to quantify water—polymer interactions in such systems,[32,33] an approach which Kügler et al. took in analyzing their swelling data for PAH/PSS films.[14]

The plot of plane strain Young's modulus and film thickness as a function of the relative humidity is shown in Figure 3 for the $(PAH7.5/PAA3.5)_{10.5}$ system. Consistent with our earlier observations,[24] the PAH7.5/PAA3.5 system exhibited the highest plane strain Young's modulus, with $\overline{E}$ = 10.8 ± 1.5 GPa at 12% RH. This value decreased to 1.1 ± 0.2 GPa at 90% RH. As with the PAH/PSS system, good agreement was found with our earlier results. We previously reported $\overline{E}$ values of 11.8 ± 0.6 and 7.9 ± 0.2 GPa at 20% RH and 50% RH, respectively. Here we found values of 10.5 ± 1.3 GPa (24% RH) and 6.4 ± 0.9 GPa (48% RH).

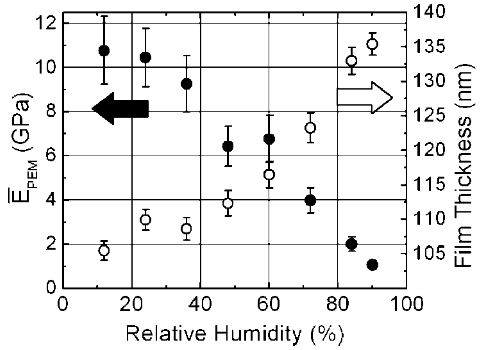

Figure 3. Plane strain Young's modulus (solid circles) and film thickness (hollow cirlces) as a function of humidity for (PAH7.5/PAA3.5)$_{10.5}$ multilayer films. Samples were allowed to equilibrate ~24 h at each humidity value before measurements were taken.

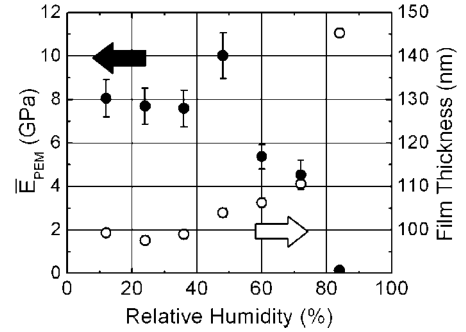

Figure 4. Plane strain Young's modulus (solid circles) and film thickness (hollow cirlces) as a function of humidity for (PAH2.5/PAA2.5)$_{20}$ multilayer films. Samples were allowed to equilibrate ~24 h at each humidity value before measurements were taken.

The PAH7.5/PAA3.5 system shows a corresponding rise in film thickness as the modulus decreases with increasing humidity. As with the PAH3.0/PSS3.0 system, the thickness change at low humidity values (12%—48% RH) is slightly less steep than what is found at higher humidity. This seems to be mirrored somewhat in the modulus data, with $\bar{E}$ appearing to plateau near ~11 GPa at low humidity.

The plot of plane strain Young's modulus and film thickness as a function of the relative humidity is shown in Figure 4 for the (PAH2.5/PAA2.5)$_{20}$ system. The behavior of this system is qualitatively different from that observed for PAH3.0/PSS3.0 and PAH7.5/PAA3.5 films (Figures 2 and 3, respectively). The PAH2.5/PAA2.5 system displays remarkable resistance to swelling and plasticization at low humidity (12%—36% RH) where $\bar{E}$ deviates only slightly from the value of 8.1 ± 0.9 GPa measured at 12% RH. The film begins to swell slightly in an intermediate regime between 48% and 72% RH where $\bar{E}$ is correspondingly observed to decrease. Between 72% and 84% RH the film undergoes an abrupt swelling transition, and $\bar{E}$ drops over an order of magnitude from 4.5 ± 0.7 to 0.14 ± 0.15 GPa. Apparently, the modulus continued to decrease substantially with increasing humidity, as no buckling was observed at either 90% or 96% RH.

The behavior of the PAH2.5/PAA2.5 system is somewhat puzzling. This system has been shown to possess an abundance of free carboxylic acid (COOH) groups, explaining the extreme hydrophilicity of the system as measured by contact angle,[34] as well the ability to bind large amounts of silver ions throughout the bulk of the film.[28] Nevertheless, the data here suggest that the PAH2.5/PAA2.5 system shows remarkable resistance to swelling for low to moderate values of the relative humidity. The likely source of this seeming contradiction of properties is cooperative hydrogen bonding among COOH moieties within the film interior. The COOH groups, present in such a high number, could feasibly create a dense physical H-bonded cross-linked network that would resist swelling at low humidity. This possibility is supported by the observation that hydrogen bonding has been demonstrated to hinder the dissolution of certain PEMs immersed in aqueous solutions.[35] With increasing humidity, however, water within the film is expected to begin disrupting hydrogen-bonding interactions and facilitating dissociation of the COOH groups, leading to abrupt swelling. This hypothetical mechanism would be similar to those proposed for explaining swelling transitions in polymer gels as a result of competing hydrogen-bonding and electrostatic interactions.[36]

We note that the humidity-dependent thickness trend for the PAH2.5/PAA2.5 system corresponds closely with the results of Chang et al., who studied water uptake in PAA homopolymer membranes.[37] This suggests that the molecular interactions within PAH2.5/PAA2.5 films are very similar to those within pure PAA, which seems reasonable given that we have previously demonstrated PAA to be the majority constituent in PAH/PAA films assembled at low pH.[18] In addition, these results parallel earlier findings from our group that the cooperative effects of COOH ionization can induce large increases in PEM thickness, with concomitant decreases in film refractive index and density.[11,38] More recently we have found that these same properties can be important in engineering cell-resistant coatings, which inhibit cell attachment due to their extreme hydration and lack of rigidity.[4,21]

Interestingly, the anomalously high value of $\bar{E}$ measured at 48% RH that appears to be an outlying data point was duplicated in a similarly prepared film (see Supporting Information), suggesting the possibility of antiplasticization of the PAH2.5/PAA2.5 system at intermediate humidity values. To our knowledge, no one has previously reported antiplasticization effects due to water in PEM systems, though the phenomenon has been well-documented for biopolymer materials such as cellulose, polysaccharides, and peat.[39–42] The observation of such effects requires the ability to carefully control the ambient water activity, as antiplasticization effects take place at relatively low concentrations of solvent, with plasticization resulting at higher concentrations.[43] Thus, such effects could not be observed by simply immersing a PEM in water—careful control of the ambient humidity is required. Humidity-induced antiplasticization is generally attributed to the association of water molecules with hydrophilic side groups on the polymer, thereby retarding chain mobility in the system. Such effects are known to hinder secondary relaxation mechanisms, thereby increasing the modulus. In our PEMs, this association of water might also lead to hydrogen bond cross-linking between chains,[39,42] also a potential source of modulus augmentation. While such mechanisms are plausible for the COOH-rich PAH2.5/PAA2.5 system, further work is needed to confirm this hypothesis.

Characterization of Thin Films of PS and PMMA. Films of PS and PMMA were prepared and subjected to humidity testing in the same manner as the PEM films discussed above. Although PMMA is more hydrophilic than PS, water is not considered a good solvent for either of these materials. Published diffusion constants for water in PMMA, however, are on the order of 10^{-8} cm^2/s and thus suggest that water should penetrate these films quickly[44] (a reliable value of the diffusion constant of water in PS could not be found). Regardless, the film thickness of these systems was purposely kept small to maximize the water uptake in each system and ensure equilibrium hydration.

The overall thickness increase for PS and PMMA films over the range of 12%—95% RH was 1.9% and 2.8%, respectively (see Supporting Information). The plot of plane strain Young's modulus and film thickness as a function of the relative humidity

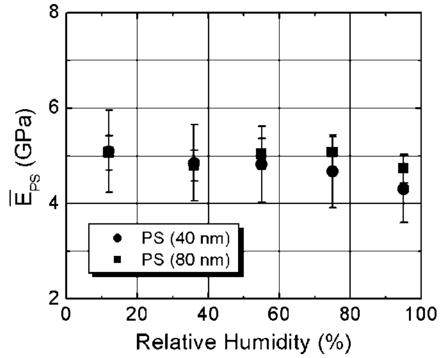

Figure 5. Plane strain Young's modulus as a function of humidity for 40 nm (solid circles) and 80 nm thick (solid squares) PS films. Samples were allowed to equilibrate ~24 h at each humidity value before measurements were taken.

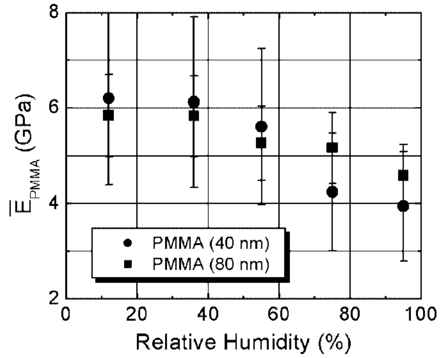

Figure 6. Plane strain Young's modulus as a function of humidity for 40 nm (solid circles) and 80 nm thick (solid squares) PMMA films. Samples were allowed to equilibrate ~24 h at each humidity value before measurements were taken.

is shown in Figure 5 for two PS films with approximate thicknesses of 40 and 80 nm.

The data in Figure 5 hint at a slight decrease in $\bar{E}$ that is more evident for the 40 nm film. Still, the values of $\bar{E}$ at 12% RH and 95% RH are all the same within error. A clearer trend is evident in the PMMA system, as shown in Figure 6. The decrease in PMMA mechanical properties with humidity is consistent with the results of Chen et al., who saw an ~15% decrease in Young's modulus at room temperature for PMMA samples soaked in water.[45] As with the PS sample, increased plasticization is observed for the thinner of the two PMMA films.

The results for PS and PMMA confirm that these polymers display significant resistance to swelling and plasticization by ambient water, as compared to the significant effects observed in PEMs, which contain a high concentration of hydrophilic ionic moieties. However, even in the two nonelectrolyte polymers studied here, a greater swelling and plasticization effect is observed in the case of PMMA, which is more hydrophilic due to the presence of the acrylate functionality. These data confirm that the presence of hydrophilic functional groups leads to increased humidity sensitivity, even in nonelectrolyte polymer systems.

Conclusions

In this paper we have presented a study of the Young's modulus and thickness of PEM films as a function of relative humidity. Humidity-dependent measurements were also conducted on spin-coated films of PS and PMMA. Our results demonstrate that while the nonelectrolyte polymer films exhibit a measurable but very minimal change in properties with humidity, the humidity responsiveness of PEMs is substantial and differs in degree and behavior based on the constituent polyelectrolytes and assembly conditions of the films. The response of PEM thickness and stiffness to increasing relative humidity can run from the more or less linear relationship observed in the PAH7.5/PAA3.5 system to the abrupt transitional swelling observed for films comprised of the same polyelectrolytes assembled at pH 2.5. The latter system also shows evidence of antiplasticization by water at intermediate humidity values, a result we found surprising given the demonstrated hydrophilicity of this system. PEMs assembled from the more hydrophobic PAH/PSS system displayed two-regime swelling behavior reminiscent of the behavior of Nafion, another polymer containing both hydrophobic and ionic functionality.

Overall, this work has demonstrated the high degree of tunability that is possible for the environmental responsiveness of PEMs and shown that humidity-dependent measurements of the thickness and Young's modulus yield new insight into the complex interactions that govern their behavior. In addition to advancing a more comprehensive fundamental understanding of polyelectrolyte multilayers, these results may yield insight into how to best utilize these functional materials in environmentally sensitive applications.

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Supporting Information Available: Buckling wavelength and error calculations from laser diffraction data, thickness data for PS and PMMA films, and supplementary results from the PAH2.5/PAA2.5 system. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) This product (catalogue no. 03326-250) has subsequently been labeled by the company as having $M_w > 200\,000$.

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