Mechanical Characterization of Polyelectrolyte Multilayers Using Quasi-Static Nanoindentation

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ABSTRACT: Polyelectrolyte multilayer (PEM) films comprised of the weak polyelectrolyte pair poly(allylamine hydrochloride)/poly(acrylic acid) were characterized in nanoindentation tests near 295 K. Film thickness in ambient air ranged from 80 to 6000 nm, and indentation depth varied from a few nanometers to 3000 nm for the thickest films tested. Elastic modulus and hardness of the films were independent of the contact depth over a range of penetration where artifacts arising from the free surface and the underlying glass substrate were insignificant. Moduli of the dry films were in the range of 10 GPa while the same films immersed in water showed modulus values about 2 orders of magnitude lower. Properties of the dry films were dependent on the selected assembly pH conditions but were insensitive to post-assembly cross-linking; both the modulus and the hardness of the hydrated films were affected significantly by the introduction of covalent cross-links into the PEM structure.

1. Introduction

The electrostatic layer-by-layer assembly of polyelectrolytes has attracted much interest over the past decade.[1] This simple methodology leads to the deposition of architectures that can be precisely tuned by manipulation of the processing conditions or polyelectrolyte pair. The resulting ultrathin polyelectrolyte multilayer (PEM) films have been investigated for a wide range of applications, including drug delivery,[2−4] tailoring cell−surface interactions,[5,6] photonic structures,[7,8] electrochemical devices,[9−11] wear-retarding coatings,[12,13] and separation membranes.[14] Critical to the success of these applications is the structural integrity and robustness of PEMs in various environments; the mechanical properties of these films have thus been heavily relied upon. Not much is known, however, about the mechanical properties of the polyelectrolyte multilayers, particularly in the dry state, and the effect of processing conditions on mechanical behavior.

One of the primary reasons for the lack of literature data on the mechanical properties of the ionically stitched multilayer systems is the small amount of material available for testing. Since these systems are deposited as thin films (incremental thicknesses[15] range from 0.5 to 14 nm per adsorbed bilayer), the elucidation of mechanical properties, independent of influences from the supporting material, is rendered difficult using conventional testing. The indirect measurement of elastic moduli of PEM films, through tensile tests on coated fibers, has been attempted.[16] These tests require the deconvolution of substrate contribution from the measurements. Atomic force microscopy (AFM) has been used to study the deformation of PEM microcapsules[17−19] filled with aqueous and organic solvents and polymer solutions. Modulus values for the walls of PEM microcapsules have been estimated from osmotic pressure induced deformations.[20,21] Plastic deformation in PEM microcapsules has been studied.[22] Recently a direct AFM study of the wet-state mechanical properties of PEMs in flat film geometry has been reported.[23]

Nanoindentation is a useful tool that allows the direct measurement of mechanical properties of thin films,[24] including polymer films[25−28] By indentation of a material to a desired force (or depth) followed by retraction of the tip, a force−displacement ($P-h$) curve, characteristic of the material being tested, is obtained. Various properties, including the elastic modulus and hardness, can be elicited by analysis of this curve. Proper use of this method facilitates the mechanical probing of thin films without a significant influence of the mechanical properties of the underlying substrate.

This paper focuses on the elucidation of mechanical behavior of PEMs through quasi-static nanoindentation. Poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) were used for film assembly. The degree of ionization of the functional groups of these weak polyelectrolytes is a function of solution pH, thus offering intricate control over the molecular organization and composition of the assembled PEM structures. The pH conditions employed in the processing of PEMs from the PAH/PAA pair govern important structural parameters like layer organization and thickness, surface roughness, and the nature of functional groups at the surface (contact angle).[15,29] The objective of this study is to examine the effect of film thickness and PAH/PAA assembly conditions on the elastic modulus and hardness of the PEMs, elicited through analyses of the $P-h$ curves. The mechanical properties of the films are compared with those of the parent polyelectrolytes and a few other commercially available polymers that have been examined in nanoindentation tests. While most of

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the results reported here were obtained on dry PEMs equilibrated in ambient air, a few hydrated PEMs were studied after immersion in pH neutral water.

2. Experimental Details

2.1. Materials. PAH ($M_W = 70\,000$) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich (Milwaukee, WI). PAA ($M_W = 90\,000$) was obtained from Polysciences (Warrington, PA). Poly(methyl methacrylate) (PMMA, $M_W = 35\,000$) from Scientific Polymer Products, Inc. (Ontario, NY) was used. All the materials were used without further purification. Deionized water (>18 MΩ cm, Millipore Milli-Q) was used for preparation of all aqueous solutions, and during rinsing procedures. Glass microscope slides from VWR Scientific, Inc. (West Chester, PA) were used in all cases as substrates for PEM assembly.

2.2. Film Assembly and Thickness Measurements. PAH/PAA PEMs were assembled on the glass substrates as previously described.[15,29] The glass slides were degreased in a detergent solution, via ultrasonication, for 15 min, followed by ultrasonication in water for 10 min. After further rinsing in water and drying in air, the substrates were subject to air−plasma treatment (5 min at 100 W−Harrick Scientific PDC-32G plasma cleaner/sterilizer). PAH and PAA aqueous solutions (0.01 M based on molecular weights of the repeat unit) were adjusted to the desired pH using 1 M NaOH or 1 M HCl. PEM films were assembled by immersing the plasma-treated slides into the PAH solution for 15 min, followed by three rinsing steps in water for 2, 1, and 1 min, respectively. They were then immersed in the PAA solution, followed by identical rinsing steps. This process built a PAH/PAA bilayer. The cycle was repeated to build PEMs of the desired thickness. The immersion and rinsing steps were automated using a Zeiss HMS programmable slide stainer.[29] Finally, the film-coated substrates were dried by flushing with air, and stored at ambient conditions for several hours before testing. The film constructions will be represented as (PAH x/PAA y)$_z$, where x and y denote the pH of the PAH and PAA solutions used for PEM assembly, and z denotes the number of PAH/PAA bilayers. Thickness of PEM films on glass substrates was measured using a Tencor P-10 surface profiler; the films were scored at 3−5 locations, and the step heights were measured.

Films of PAH, PAA, and PMMA homopolymers were prepared by spin-coating (Specialty Coating Systems, Inc.) onto glass substrates. Aqueous solutions of PAH and PAA at pH values of approximately 7.5 and 3−3.5, respectively, were used. A solution of PMMA in THF was used for spin-coating. The PAH and PAA films were dried by flushing with air and stored at ambient conditions. The spin-coated PMMA film was dried in a vacuum oven at 25−30 °C for 2−3 h. The surface profiler was used to measure film thickness in all cases.

2.3. Mechanical Characterization. Nanomechanical testing was carried out using a Triboindenter from Hysitron Inc. The instrument is a load-controlled, displacement-sensing device. NorthStar cube-corner and Berkovich diamond indenter tips were employed. The total included angle for the three-sided cube-corner indenter shape is 90°; the tip radius was 40−50 nm. The tip radius for the Berkovich indenter was in the 100−200 nm range (included angle 142.3°); this flatter indenter tip was used for films greater than 500 nm thick. A trapezoidal loading pattern consisting of a 5 s loading segment, a 2 s hold period, and a 5 s unloading segment was used for most tests. The maximum applied load was based on the thickness of the film. The hold time was incorporated to minimize the effects of specimen creep on the estimated values of modulus and hardness.[30] Prior to indentation, the tip was made to scan the specimen surface in a contact mode of engagement. This allowed the instrument to stabilize and a thermal drift rate to be estimated; the reported penetration depth readings were corrected for drift. For measurements at ambient conditions, the temperature was maintained in the 20−25 °C range; the relative humidity was approximately 50%.

The unloading segment of the $P-h$ curve was utilized for the extraction of mechanical properties, based on the method of Oliver and Pharr.[31] The effective modulus E_r, a combination of the properties of the indenter and indented materials, and the sample hardness H are defined by the following equations:

$$\frac{1}{E_r} = \frac{(1-\nu_s^{\,2})}{E_s} + \frac{(1-\nu_i^{\,2})}{E_i} = \frac{2}{S}\sqrt{\frac{A}{\pi}} \tag{1}$$

$$H = \frac{P_{\max}}{A} \tag{2}$$

A prefactor, numerically equal to 1.034 for both the Berkovich and the cube corner indentors,[24] has been neglected in eq 1. The symbols ν and E denote the Poisson's ratio and elastic modulus for the indenter material (subscript i) and the sample (subscript s). A is the projected area of contact at peak load $P_{\max}$, and S is the unloading stiffness. S is defined as the slope of the unloading curve at the maximum penetration depth $h_{\max}$. To calculate S, the unloading curve was fitted to a power law equation of the form

$$P = B(h - h_f)^m \tag{3}$$

B, h_f, and m were arbitrary fitting parameters. S is thus mathematically defined as

$$S = \frac{dP}{dh}(h_{\max}) = mB(h_{\max} - h_f)^{m-1} \tag{4}$$

The contact depth h_c, used to calculate A, is given by the equation

$$h_c = h_{\max} - \epsilon\frac{P_{\max}}{S} \tag{5}$$

The latter term accounts for the deflection of the surface at the contact perimeter.[31] The geometric constant ϵ, based on the geometry of the indenter tip,[31] was taken as 0.75. A tip calibration function was used for relating A to h_c using a polynomial expression.

$$A = C_0 h_c^{\,2} + C_1 h_c + C_2 h_c^{\,1/2} \tag{6}$$

The constants C_0, C_1, and C_2 for the cube-corner indenter were empirically determined using a fused quartz sample of known modulus and hardness.

$$C_0 = 4.397$$

$$C_1 = 158.2$$

$$C_2 = 1083.2$$

For the Berkovich tip, a value of 24.5 was used for C_0 in eq 6 based on ideal tip geometry;[31] C_1 and C_2 were taken as zero.

In this study, the indenter tip material was diamond with $E_i = 1140$ GPa and $\nu_i = 0.07$. For materials with an elastic modulus of the order of 10 GPa, the contribution of the indenter tip material to E_r (see eq 1) is negligible. Because Poisson's ratio for most polymeric materials lies in the 0.25−0.45 range, the elastic modulus (E_s) of the sample is numerically equal to 80−95% of the measured effective modulus value (E_r).

To study the behavior of PEM films in the hydrated state, water (pH adjusted to 7 using 1 M NaOH) was used as the surrounding medium. After adding a few drops of water, the film was allowed to stand for 15 min before testing. A cube-corner diamond fluid cell indenter tip was used for these measurements. P−h curves were analyzed in a manner identical to that described for measurements at ambient conditions.

3. Results

3.1. Effect of Film Thickness. To investigate the effect of film thickness on mechanical response, PEM

Table 1. Effective Modulus (E_r) and Hardness (H) Values for Various (PAH 7.5/PAA 3.5) Constructs and the Parent Polyelectrolytes

	film	appr thickness (nm)	type of indenter[a]	h_c (nm)	H (GPa)	E_r (GPa)
1	(PAH 7.5/PAA 3.5)$_8$	80	cube-corner	21.5	0.483	7.96
2	(PAH 7.5/PAA 3.5)$_{45}$	500	cube-corner	22.5	0.479	8.12
3	(PAH 7.5/PAA 3.5)$_{600}$	6000	cube-corner	21.2	0.486	7.83
4	(PAH 7.5/PAA 3.5)$_{600}$	6000	cube-corner	312.2	0.363	10.87
5	(PAH 7.5/PAA 3.5)$_{600}$[b]	6000	Berkovich	316.3 ± 9.9	0.389 ± 0.025	12.64 ± 0.47
6	(PAH 7.5/PAA 3.5)$_{600}$ heated at 150 °C, 6 h	6000	cube-corner	459.5 ± 2.8	0.432 ± 0.006	11.2 ± 0.37
7	PAH[c]	600	Berkovich	130 ± 31.5	0.036 ± 0.006	1.35 ± 0.58
8	PAA	4500	Berkovich	128.3 ± 3.8	0.35 ± 0.023	9.51 ± 0.28

[a] A trapezoidal load function with a 5 s loading segment, 2 s hold time, and 5 s unloading segment (5s−2s−5s) was used, unless otherwise specified. All measurements were made at ambient conditions. [b] Trapezoidal 33s−2s−33s loading function was used. [c] Trapezoidal 5s−4s−5s loading function was used.

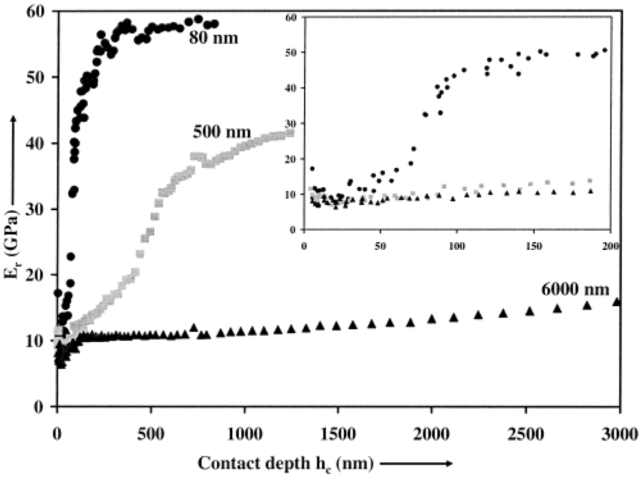

Figure 1. Effective modulus (E_r)−contact depth profile for 80 nm (8 bilayers, circles), 500 nm (45 bilayers, squares), and 6000 nm (600 bilayers, triangles) thick PEMs. Inset depicts magnified profile at lower h_c values. All films were assembled on glass at the (PAH 7.5/PAA 3.5) combination. The cube-corner indenter tip was used for these measurements at ambient conditions.

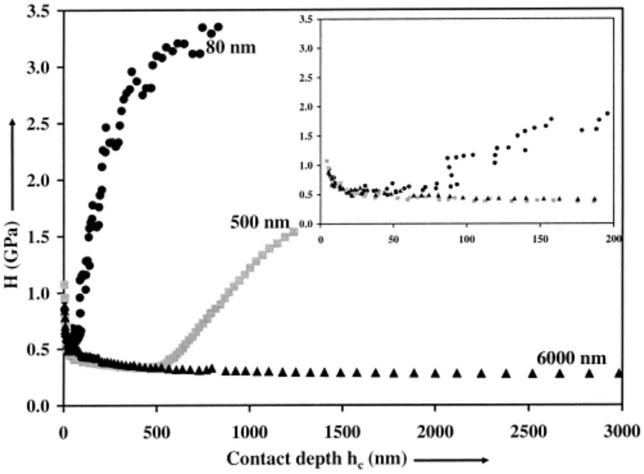

Figure 2. Hardness (H)−contact depth profile for 80 nm (8 bilayers, circles), 500 nm (45 bilayers, squares), and 6000 nm (600 bilayers, triangles) thick PEMs. Inset depicts a magnified profile at lower h_c values. All films were assembled on glass at the (PAH 7.5/PAA 3.5) combination. The cube-corner indenter tip was used for these measurements at ambient conditions.

films were subject to 80 indentations, beginning at a maximum load of 12 000 μN for the first indent; the load was decreased by 10% for each subsequent indent, reaching a value of 3 μN for the final load level. The effective modulus and hardness profiles for the approximately 80, 500, and 6000 nm thick films are depicted in Figures 1 and 2; all films were assembled at the (PAH 7.5/PAA 3.5) combination, with PAA as the last adsorbed polyelectrolyte.

For all films, the modulus and hardness profiles exhibited a U-shaped curve, with an initial decrease, a plateau region, and a subsequent rise in values as contact depths approached the film thickness; this behavior is in agreement with previously reported work on nanoindentation of thin polymer films.[25,26] The values in the plateau region are considered representative of the mechanical behavior of the sample. At values of h_c approaching the thickness of the film, the stress fields are affected by the underlying glass substrate, as reflected by an increase in the values of E_r and H; glass is associated with an elastic modulus slightly greater than 70 GPa.[31] It has been recommended in the past that indentation depths be confined to no more than 10% of the film thickness to preclude any influence of the underlying substrate on the $P-h$ curve.[24] The initial decrease in E_r and H at very low contact depth below 10 nm is attributed to surface effects and/or impurities but not to substrate influence. The modulus profiles exhibit negligible substrate effects up to contact depths approaching 20−40% of the thickness of the film; the hardness profiles, on the other hand, do not reveal significant influence from the glass substrate up to contact depths comparable with the film thickness. Table 1 compares the E_r and H values for the three films at a contact depth of 20 nm where both the surface and the substrate effects are not appreciable. To ensure that the measured mechanical properties were not an artifact of the cube-corner tip geometry and the corresponding induced stress fields, a (PAH 7.5/PAA 3.5) film was indented using a Berkovich indenter. The results, compared with data from the cube-corner indenter tip at comparable contact depths (Table 1 lines 4 and 5), reveal a 7% difference in hardness and a 16% difference in modulus values; the measurements using the Berkovich and cube-corner indenter tips were also performed on different Triboindenter machines.

The nature of the linkages between the PAH and PAA chains can be changed via thermal treatment.[32] By heating the PEMs, a fraction of the ionic attachments between the carboxyl groups of PAA and the amine groups of PAH are converted to covalent amide bonds. Table 1 (lines 4 and 6) shows that there is almost no difference in the dry state mechanical properties between the ionically stitched film and those that also contain some amide cross-links. The latter structure is associated with a marginally higher value of hardness

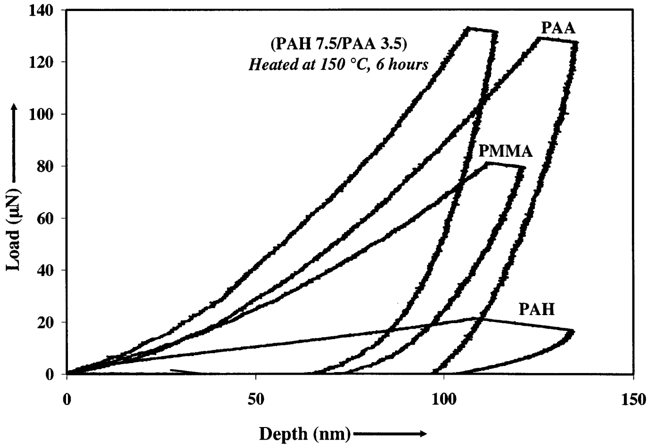

Figure 3. Sample load (P)—depth (h) curves for some thin-film specimens. A trapezoidal 5s−2s−5s loading function was used in most cases. For PAH, a hold time of 4 s was used to minimize the effects of sample creep on the unloading curve. Thickness values for the various films: (PAH 7.5/PAA 3.5) = 6000 nm, PAA = 4500 nm, PMMA = 2700 nm, PAH = 600 nm.

while the modulus values are identical within error; this observation was confirmed through dynamic nanomechanical analysis,[33] not shown here.

Table 1 also presents the mechanical properties of spin-coated films of PAH and PAA. The data of Table 1 indicate that some of the PAH/PAA PEM structures are mechanically superior to either parent polyelectrolyte. The modulus and hardness of PAA were 7−10 times the values for PAH. Some representative $P-h$ curves are depicted in Figure 3.

3.3. Effect of Assembly pH Combination. Figure 4 compares measured hardness and effective modulus values for three different PAH/PAA pH assembly combinations along with previously reported incremental thicknesses per deposited bilayer. Contact depths of 7−9 nm were employed for these 80−100 nm-thick films. Thicker films of the (PAH 3.5/PAA 3.5) combination were indented to contact depths of 50−60 nm, and values of modulus and hardness identical to those shown in Figure 4 were obtained. Similarly the results on the 6.5/6.5 PAH/PAA PEM systems were cross-checked and corroborated using dynamic nanomechanical tests.[33]

For PEMs constructed from weak polyelectrolytes like PAH and PAA, the molecular-level architectures are intimately connected with the pH of the polyelectrolyte assembly solutions, relative to their pK_a values. The pK_a values for PAH and PAA are approximately 9 and 5, respectively.[5] For the case of (PAH 6.5/PAA 6.5), the PEM films are assembled from solutions containing both polyelectrolytes in their fully charged state. The resulting film has a high density of ion-paired linkages.[15] Furthermore, at pH 6.5, both polyelectrolytes adsorb as highly charged, flattened, and extended chains, resulting in low incremental thicknesses of about 5 Å per adsorbed bilayer. The (PAH 7.5/PAA 3.5) architecture is formed by adsorption from solutions of partially charged polyelectrolytes; the selected pH values are close to the pK_a values for both PAH and PAA. The deposited layers are relatively thick and loopy (thickness per bilayer ~80 Å), and the resulting internal structure is highly interpenetrated. PAH and PAA chains are both highly ionized in the interior of the film structure. For details about the formation of these structures, see references.[15,34] Finally, the (PAH 3.5/PAA 3.5) multilayer represents the intermediate bilayer thickness regime (approximately 55 Å per adsorbed bilayer), with PAH being fully charged and PAA partially ionized at this combination.[15] To produce an approximately 100 nm thick film, 20 bilayers were required at the 3.5/3.5 pH combination, compared with 140 bilayers for the case of PAH 6.5/PAA 6.5, and 8 for the PAH 7.5/PAA 3.5 assembly conditions. In all cases in Figure 4, PAA was the last adsorbed polyelectrolyte.

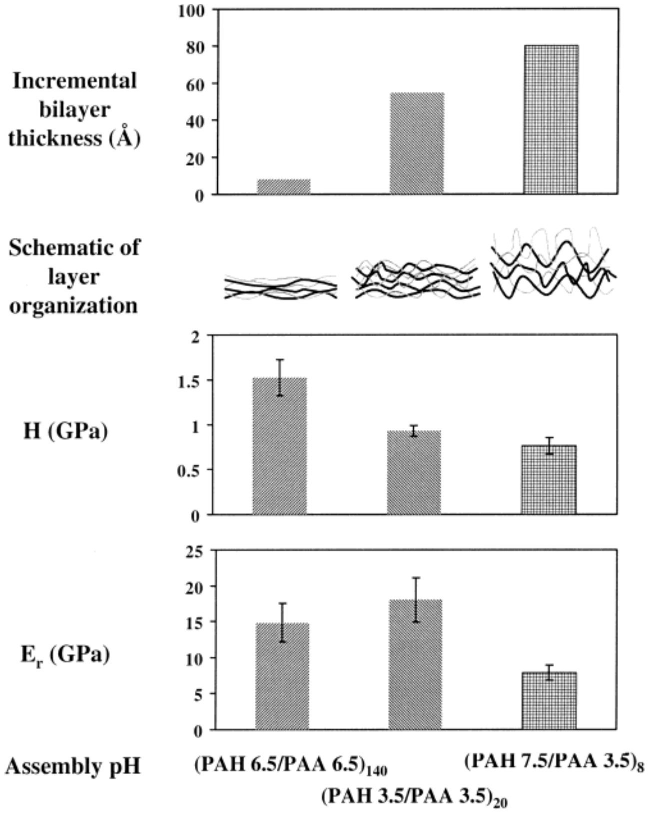

Figure 4. Incremental bilayer thicknesses,[29] schematic structures, and measured hardness and effective modulus values for three assembly pH combinations. A cube-corner indenter tip was used for this study. Film thicknesses were 80−100 nm.

The hardness of a sample is defined as its resistance to plastic deformation. From Figure 4, it is evident that the hardness is highest for the (PAH 6.5/PAA 6.5) architectures, with a value of 1.5 GPa. The (PAH 7.5/PAA 3.5) films exhibit the least resistance to plastic deformation with a hardness of 0.76 GPa (see Figure 2 for the detailed hardness profile of this film). The modulus values for (PAH 3.5/PAA 3.5) and (PAH 6.5/PAA 6.5) assemblies are comparable within error; the loopy coil configurations of the (PAH 7.5/PAA 3.5) films are associated with the lowest values of the modulus.

3.3. Comparison with Other Polymeric Systems. Table 2 compares the mechanical properties of the (PAH 7.5/PAA 3.5) PEM structures with those measured for thin spin-coated PMMA films. In addition, some literature values for elastic moduli and hardness of polystyrene (PS),[27] polycarbonate (PC),[27] and poly(tetrafluoroethylene) (PTFE)[25] spin-coated films are presented. The comparisons in Table 2 are made with respect to the (PAH 7.5/PAA 3.5) system, which is associated with the lowest modulus and hardness values among the PAH/PAA pH combinations studied (see Figure 4).

3.4. Mechanical Behavior in Water. It is well-known that the PEM structure swells in the presence

Table 2. Comparison of Mechanical Properties of PEMs (see Figures 1, 2, and 4) with Those Measured for Spin-Coated PMMA Films and Reported Values for Other Polymer Thin Films

	film	appr thickness (nm)	h_c (nm)	H (GPa)	E_r (GPa)	elastic modulus (GPa)
1	(PAH 7.5/PAA 3.5)$_{600}$[a]	6000	316.3 ± 9.9	0.389 ± 0.025	12.64 ± 0.47	10.08−11.85[c]
2	PMMA[b]	2700	104 ± 4.5	0.30 ± 0.04	5.91 ± 0.2	5.23[d]
3	PC[26]					2.2
4	PS[26]					2.6
5	PTFE[21]			0.058		2.3

[a] A trapezoidal 33s−2s−33s loading function and a Berkovich indenter were used. [b] A trapezoidal 5s−2s−5s loading function and a Berkovich indenter were used. [c] Calculated using a 0.25−0.45 range for Poisson's ratio. [d] Using a value of 0.34 for Poisson's ratio.

Table 3. Comparison of Mechanical Properties of Water-Swollen and Unswollen PEMs

	film[a]	surrounding medium	h_c (nm)	H (GPa)	E_r (GPa)
1	(PAH 7.5/PAA 3.5)	air[b]	312.2	0.363	10.87
2	(PAH 7.5/PAA 3.5) heated at 150 °C for 6 h	air	459.5 ± 2.8	0.432 ± 0.006	11.2 ± 0.37
3	(PAH 7.5/PAA 3.5)	pH 7 water	512.3 ± 69.2	0.014 ± 0.003	0.07 ± 0.02
4	(PAH 7.5/PAA 3.5) heated at 150 °C for 6 h	pH 7 water	445.7 ± 37.7	0.109 ± 0.016	0.41 ± 0.04

[a] All films were 6000 nm thick (600 bilayers) in the dry state. A cube-corner indenter tip with a 5s−2s−5s loading function was used in all cases. [b] Relative humidity 50%; temperature 20−25 °C.

of a hydrating or plasticizing medium. In the case of aqueous systems, the degree of swelling depends on pH and ionic strength. The amount of swelling for PAH/PAA films also depends strongly on the assembly pH conditions.[5,35,36] To investigate the mechanical behavior of PEM films swollen in a liquid medium, (PAH 7.5/PAA 3.5) architectures were subjected to indentation while immersed in pH neutral water. The results are presented in Table 3. Rubner and co-workers[5] have reported thickness increases of 130% for this PEM architecture upon exposure to phosphate-buffered saline at physiological pH. The hydrated structures exhibit modulus values that are about 2 orders of magnitude lower than those in the identical film in the dry state at ambient conditions (compare lines 1 and 3 of Table 3). This film architecture does not lose polyelectrolyte material (no soluble chains) at pH 7 so the observed reduction in modulus is not a result of network deterioration but instead reflects the expected reduction in modulus associated with plasticization by a low molecular weight diluent When covalent bonds replace some of the ionic cross-links between PAH and PAA, the swollen structure exhibits a modulus that is significantly larger than the ionically cross-linked precursor film in pH 7 water, as seen from lines 3 and 4 of Table 3.

4. Discussion

The PEM system that most closely resembles our PAH/PAA films, and that has also been studied in the context of mechanical properties, is the PAH/poly(styrenesulfonate) (PSS) polyelectrolyte pair. In those studies,[17−20] the PEM moduli were estimated from various observations on microcapsules. AFM deformation[17,18] of microcapsules produced estimates of modulus in the range 0.001−0.1 GPa, while osmotic swelling[19] of similar systems led to values between 0.20 and 0.24 GPa. Another osmotic pressure study[20] of PAH/PSS microcapsules led to modulus values between 0.50 and 0.75 GPa. These previous estimates of wet-state PAH/PSS moduli are consistent with the rubbery/leathery modulus values (0.07 and 0.41 GPa) measured directly in this study via flat-film nanoindentation of our PAH/PAA PEMs in pH 7 water. The wet-state, flat film AFM study[23] of a significantly different PEM system (PAH/azo-benzene-containing polyanion) showed lower modulus values, 0.007 GPa and below, while a 50-fold variation in modulus was observed, depending on the pH conditions used in the film assembly.

To our knowledge, the results reported here are among the first direct measurements of the mechanical properties of dry PAH/PAA PEMs through quasi-static nanoindentation. By carefully mapping E_r and H as a function of contact depth for these films (Figures 1 and 2), the mechanical properties have been determined without significant influence from the underlying glass substrate. Consistent with the previously mentioned AFM study,[23] we found that the mechanical properties of our PEMs, constructed from the weak polyelectrolyte pair PAH and PAA, can be tuned by varying the processing conditions. Manipulation of the assembly polyelectrolyte pH influences the chain conformation and the degree of interchain ionic cross-linking in the PEM structure; a 2-fold variation in the hardness and modulus results (Figure 4).

Both the (PAH 7.5/PAA 3.5) and (PAH 6.5/PAA 6.5) architectures are associated with interpenetrated structures and high degrees of ion pairing between the parent polyelectrolytes.[1,15] While the chains of the (PAH 6.5/PAA 6.5) constructs exist in highly stretched chain conformations leading to low incremental bilayer thicknesses of 5 Å (see Figure 4), the (PAH 7.5/PAA 3.5) structures are thicker and loop-rich. The latter configuration can deform to accommodate the moving indenter tip with greater ease than the (PAH 6.5/PAA 6.5) system; this is reflected in the lowest values of modulus and hardness for the (PAH 7.5/PAA 3.5) systems. The (PAH 6.5/PAA 6.5) film exhibits the most stretched-out chain conformation, and thus a great degree of resilience, leading to the highest hardness values, although not the highest modulus. For the latter parameter, chain orientation should lead to high values of the *in-plane* modulus, whereas the nanoindentation experiment measures a modulus that is transverse to the plane of chain extension. This may explain the relatively lower than expected value of modulus for the 6.5/6.5 films. The (PAH 3.5/PAA 3.5) architecture may be viewed as intermediate between the above two conformations; PAA is partially ionized and PAH is fully charged. This structure is associated with a hardness value between the two extremes, while the modulus is, within error, the same as the (PAH 6.5/PAA 6.5) films. Noting the remarkably high value of modulus for the PAA homopolymer (Table 1), we see that the higher than expected modulus for the 3.5/3.5 film might arise from PAA enrichment that results when partially charged PAA is incorporated into the PEM to compensate the fully charged PAH. Clearly the overall set of results demonstrates a complex interplay of ionic cross-link density, chain orientation, and PEM composition on the anisotropy and the mechanical behavior of the PEM films.

The ultrathin PAH/PAA PEM films exhibit mechanical properties that are superior to some commercial polymers in thin-film form (see Table 2). The spin-coated PMMA film had a hardness and modulus value of 0.3 and 5.2 GPa, respectively, compared to the corresponding values of 0.39 GPa and approximately 11 GPa for the (PAH 7.5/PAA 3.5) system. For PMMA, the hardness and modulus values obtained in this investigation for a 2700 nm thick film are higher than those obtained for bulk PMMA samples, studied via indentation. Pruitt and co-workers[30] reported a hardness value of 0.05 GPa and an elastic modulus of 3.8 GPa through nanoindentation of bulk PMMA. The molecular level structure of a spin-coated film may be significantly different from that of the bulk sample.[37] Stronger associations, due to hydrogen-bonding interactions, have also been reported for thin polymer films that might contain trace amounts of residual solvent.[38] For PMMA films, a decreasing glass transition temperature with increasing film thickness has been observed.[25]

It is interesting that the values of modulus and hardness for the multilayer structures can be higher than those of either parent polyelectrolyte. The mechanical response of the PEMs builds on the contribution of the dominant PAA component (See Table 1, lines 4, 7, and 8). The mechanical integrity of the PEM films is enhanced over that of the parent materials by the interpenetration and ionic stitching of the polyelectrolyte chains, leading to an entangled and cross-linked network that resists movement of the indenter tip through the structure. The detailed nature of the bonds that cross-link the PAH and PAA does not significantly affect the mechanical response of the films under ambient conditions; E_r and H values are comparable for the as-assembled film (ionic cross-links) and post thermal treatment (covalent bonds); see Table 1, lines 4 and 6. The properties are strongly influenced, however, by the conformations of the polyelectrolyte chains in the construct, an inherent function of the assembly PAH/PAA pH combination.

Thermally treating the films after assembly, however, significantly affects the mechanical response of the swollen structure in the presence of water (see Table 3). Covalent linkages limit swelling more than their ionic precursors. The reduced uptake of water and smaller degree of swelling results in larger values of E_r and H for the chemically cross-linked films compared to the ionically cross-linked counterparts (Table 3, lines 3 and 4). When swollen, however, both the as-assembled and thermally treated films have modulus and hardness values that are much lower than their counterparts in the dry state; the modulus values for the swollen, ionically cross-linked films are on the same order of magnitude as those for various rubberlike materials.[39]

PAH/PAA PEMs have been used as nanoreactors for the in situ synthesis of metallic and semiconducting nanoparticles.[40] Also it is known that surfaces of these PEMs can be modified through the use of block copolymer-capping agents[34] and that layer-by-layer assembly can be used to create nanocomposites containing clay particles, carbon nanotubes,[41] nanocrystalline materials, graphite oxide, and other nanocolloids.[42] Advincula and co-workers[26] have studied the mechanical properties of polyelectrolyte/clay multilayer films through nanoindentation, and they reported modulus and hardness values of 9.5 and 0.46 GPa, respectively, for their structures. Nanoindentation studies on block copolymer-modified PEM structures, on silver nanoparticle-containing PAH/PAA PEMs, and on PAH/carbon nanotube composites can be found in a previous publication from our group,[43] in which effective modulus values in the range of 1−20 GPa are reported.

5. Conclusions

The mechanical properties of layer-by-layer films composed of weak polyelectrolytes PAH and PAA were elucidated using quasi-static nanoindentation in a range of instrument operation and specimen thickness where the elastic modulus and hardness of the films were demonstrably free of the influence of the underlying supporting material. The mechanical properties of these ultrathin PEM films can be altered significantly by varying the pH of the PAH and PAA assembly solutions. All of the PEM films exhibited modulus values that were larger than those of spin-coated films of commercial polymers, including PMMA.

Some of the PEMs are mechanically superior to either parent polyelectrolyte. In the dry state, the PEM properties are virtually unaffected by whether the linkages between the functional groups of the parent polyelectrolytes are ionic or covalent in nature. The essence of mechanical strength of PEMs lies in the high density of linkages in the film. The modulus values of these interpenetrated polyelectrolyte structures in the swollen state (in water) are about 2 orders of magnitude lower than the corresponding values in dry conditions; in the swollen state, chemical cross-links do augment the modulus values owing to the smaller amount of water uptake in cross-linked films.

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