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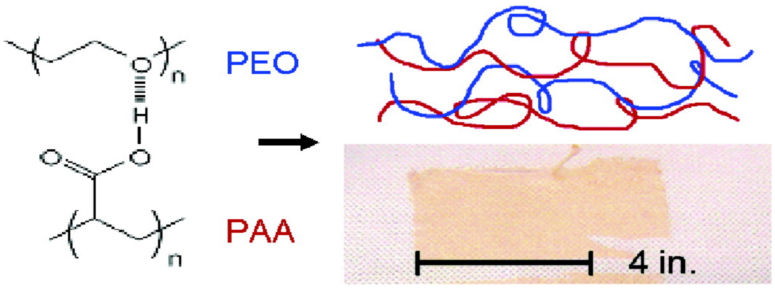

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Elastomeric Flexible Free-Standing Hydrogen-Bonded Nanoscale Assemblies

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Abstract: Poly(ethylene oxide) (PEO) is a key material in solid polymer electrolytes, biomaterials, drug delivery devices, and sensors. Through the use of hydrogen bonds, layer-by-layer (LBL) assemblies allow for the incorporation of PEO in a controllable tunable thin film, but little is known about the bulk properties of LBL thin films because they are often tightly bound to the substrate of assembly. The construction technique involves alternately exposing a substrate to a hydrogen-bond-donating polymer (poly(acrylic acid)) and a hydrogen-bond-accepting polymer (PEO) in solution, producing mechanically stable interdigitated layers of PEO and poly(acrylic acid) (PAA). Here, we introduce a new method of LBL film isolation using low-energy surfaces that facilitate the removal of substantial mass and area of the film, allowing, for the first time, the thermal and mechanical characterization that was previously difficult or impossible to perform. To further understand the morphology of the nanoscale blend, the glass transition is measured as a function of assembly pH via differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The resulting trends give clues as to how the morphology and composition of a hydrogen-bonded composite film evolve as a function of pH. We also demonstrate that LBL films of PEO and PAA behave as flexible elastomeric blends at ambient conditions and allow for nanoscale control of thickness and film composition. Furthermore, we show that the crystallization of PEO is fully suppressed in these composite assemblies, a fact that proves advantageous for applications such as ultrathin hydrogels, membranes, and solid-state polymer electrolytes.

Introduction

Poly(ethylene oxide) (PEO) is one of the most versatile synthetic polymers available because of its promise for drug delivery,[1] biomaterial applications, pH-sensitive sensors, and solid polymer electrolytes.[2] Unfortunately, the common form of PEO is a semicrystalline solid which is fully water soluble; for this reason, PEO is often more useful in its cross-linked, hydrated form as a gel. This can present limitations for the creation of thin-film systems requiring reasonable mechanical integrity, including certain functional biomaterials and solid electrolytes. Stable complexes can readily form between PEO and polyacids such as poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMAA),[3−6] and these complexes have been studied for decades because of the interest in their use for a number of the above-named applications. Unfortunately, the precipitation of these hydrogen-bonded complexes from solution results in films with poorly controlled geometries and morphologies. Attempts to process the complexes into usable forms generally result in either dissolution or degradation; for these reasons, these interesting complex structures have remained elusive in terms of real applications.

The layer-by-layer (LBL) assembly technique takes advantage of the same attractive forces that form complexes, but in a controlled manner that produces thin, conformal films that can coat a variety of surfaces (Figure 1). Since their first demonstration by Decher et al.[7,8] in the early 1990s using oppositely charged polyions, layer-by-layer thin films have been investigated for biomaterials, drug delivery, photovoltaics, electrochromics, fuel cell membranes, and dry battery electrolytes.[9−18] These assemblies are formed by alternately exposing a substrate to positively and negatively charged polymers or polymers with

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(1) Park, T. G.; Cohen, S.; Langer, R. *Macromolecules* **1992**, *25* (1), 116−122.

(2) Gray, F. M.; Royal Society of Chemistry (Great Britain) *Polymer electrolytes*; Royal Society of Chemistry: Cambridge, 1997.

(3) Ikawa, T.; Abe, K.; Honda, K.; Tsuchida, E. *J. Polym. Sci.* **1975**, *13* (7), 1505−1514.

(4) Khutoryanskiy, V. V.; Dubolazov, A. V.; Nurkeeva, Z. S.; Mun, G. A. *Langmuir* **2004**, *20* (9), 3785−3790.

(5) Bailey, F. E.; Lundberg, R. D.; Callard, R. W. *J. Polym. Sci., Part A* **1964**, *2* (2), 845−851.

(6) Jeon, S. H.; Ree, T. *J. Polym. Sci., Part A* **1988**, *26* (5), 1419−1428.

(7) Decher, G.; Hong, J. *Thin Solid Films* **1992**, *210* (1−2), 831.

(8) Decher, G. *Science* **1997**, *277*, 1232.

(9) Sukhishvili, S.; Granick, S. *J. Am. Chem. Soc.* **2000**, *122* (39), 9550−9551.

(10) Hammond, P. T. *Colloid Interface Sci.* **2000**, *4*, 430−442.

(11) Delongchamp, D. M.; Hammond, P. T. *Chem. Mater.* **2003**, *15* (5), 1165.

(12) Wood, K.; Boedicker, J.; Lynn, D. M.; Hammond, P. T. *Langmuir* **2005**, *21* (4), 1603−1609.

(13) Berg, M.; Yang, S. Y.; Hammond, P. T.; Rubner, M. F. *Langmuir* **2004**, *20* (4), 1362−1368.

(14) Zhai, L.; Cebeci, F.; Cohen, R.; Rubner, M. F. *Nano Lett.* **2004**, *4* (7), 1349−1353.

(15) Lowman, G.; Tokuhisa, H.; Lutkenhaus, J. L.; Hammond, P. T. *Langmuir* **2004**, *20*, 9791.

(16) Delongchamp, D. M.; Hammond, P. T. *Langmuir* **2004**, *20* (13), 5403−5411.

(17) Delongchamp, D. M.; Kastantin, M.; Hammond, P. T. *Chem. Mater.* **2003**, *15* (8), 1575.

(18) Hammond, P. T. *Adv. Mater.* **2004**, *16* (15), 1271−1293.

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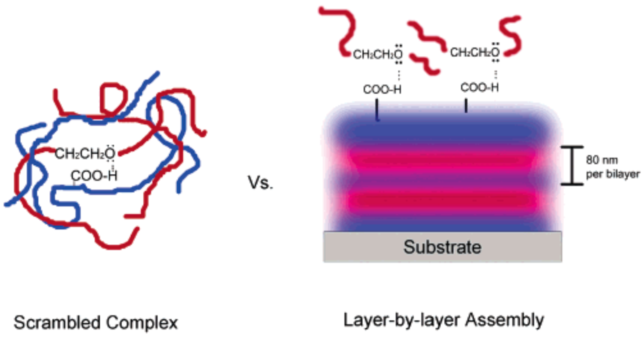

Figure 1. Although both solution-based polymer complexes (left) and LBL films (right) may be held together with hydrogen bonds (or electrostatic bonds), the LBL film exhibits nanoscale control while conformally coating the assembly substrate. The fuzzy layers are meant to illustrate the interdigitated nature of the two polymers, which can be extensive enough to create effective blends.

complementary hydrogen-bond donors and acceptors. The wide range of applications and the large parameter space available to multilayer fabrication, including polymer composition, pH, and ionic strength, result in a broad variety of polymer nanocomposites.[16,19,20] Additionally, this process is not exclusive to polyelectrolytes but may include any multiply charged species. Clay particles,[21] DNA, proteins, gold nanoparticles,[22] and carbon nanotubes[23] have all been incorporated in thin films using the LBL method.

Whereas Coulombic forces drive electrostatic LBL formation, hydrogen bonding can foster multilayer formation when a hydrogen-bond donor and acceptor are used. Here, we examine the characteristics and morphology of poly(ethylene oxide) (PEO) and poly(acrylic acid) (PAA) LBL assemblies. Hydrogen-bonded LBL films were first demonstrated by Rubner et al.[24,25] and later investigated by Sukhishvili et al.,[9,26] who showed that hydrogen-bonded assemblies can undergo a pH-induced deconstruction. Delongchamp also investigated the PEO/PAA multilayer couple as a solid polymer electrolyte.[16]

The LBL film is usually tightly bound to its substrate (glass, ITO, or silicon) so that the substrate either plays an active role or remains as a passive support in the end application. Previous methods to isolate the multilayer composite from the substrate have involved dissolving substrates,[27] sacrificial layers,[28] and even HF;[21] however, all these techniques expose the film to further treatment post-assembly that could potentially alter the original, pristine state of the assembly; furthermore, the resulting area and mass of the film is often too small to perform bulk-scale characterization. Without fully understanding the thermal and mechanical properties of an LBL film, it is not possible to establish fundamental concepts around their materials design, and the assembly cannot be fine-tuned for real-world applications.

Here, we demonstrate a novel approach to the solid-state isolation of multilayered polymer nanocomposites containing PEO and PAA as elastomeric thin films. The ability to isolate large uniform sheets of this material while maintaining mechanical integrity enables the use of characterization tools previously inaccessible to thin films confined to their substrate, including the direct measurement of bulk properties using Fourier transform infrared spectroscopy (FTIR), mechanical tensile testing, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermal gravimetric analysis (TGA), and impedance spectroscopy. We demonstrate the first direct measurement of a glass transition by DSC and DMA for these unique assemblies, as well as the first direct tensile test of a hydrogen-bonded multilayer assembly. The nonaqueous removal and isolation of multilayer films allows for their direct incorporation in electrochemical devices, free-standing thin-film drug delivery systems, and even electrochemical sensors. Remarkably, we have found that these H-bonded films act as physically cross-linked, fully miscible amorphous polymer blends, suppressing PEO crystallization, with substantive mechanical cohesion in the solid state without the need for a chemical cross-link step.

Results

The key difference in obtaining free-standing films in the dry solid state as opposed to film removal with an aqueous method lies in the choice of substrate. Whereas previously mentioned methods use glass or silicon platforms, we employ neutral, hydrophobic surfaces such as Teflon and polypropylene with water contact angles of 108° and 94°, respectively. First, aqueous poly(ethylene oxide) (molecular weight (MW) = 4 000 000 g/mol) is uniformly adsorbed onto the Teflon surface by van der Waals interactions. Subsequent exposure to poly(acrylic acid) (MW = 90 000 g/mol), a hydrogen-bond donor, results in a layer of PAA hydrogen bonded to the PEO. As these steps are repeated, the two polymers are deposited as highly interdigitated layers joined by hydrogen bonds. The growth of the polymer layers was shown to be exponential, and the average thickness per polymer bilayer was found to be 80 nm for a 100 layer pair film. A 100 bilayer film can be peeled away from the substrate with tweezers, resulting in a pinhole-free, continuous film of approximately 8 μm thickness and a root-mean-square (RMS) roughness of 0.4 μm, as determined by profilometry. Electrostatically assembled layers of the weak polyelectrolytes, poly(ethylene imine) and poly(acrylic acid), were also isolated in this manner; the structure and properties of these electrostatic films will be reported in a future work.

Because van der Waals forces were the only interactions between the film and the neutral substrate, isolation of the free-standing film was easily and quickly performed[28a] without the aid of water, salt, or acids. The isolated hydrogen-bonded layers were transparent, smooth to the touch, and exhibited elastomeric properties during handling (Figure 2). At this time, the thinnest continuous cohesive structure obtained by this method is a 20 bilayer assembly of PEO and PAA approximately 2 μm thick with a surface area of 4 cm^2, the total area of the substrate on which it was assembled. Thinner films can be lifted off but tear into smaller fragments during isolation.

FTIR of the free-standing film indicated the presence of both poly(ethylene oxide)[29] and poly(acrylic acid)[26] (Supporting

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(19) Dubas, S.; Schlenoff, J. *Macromolecules* **1999**, *32* (24), 8153−8160.
(20) Shiratori, S.; Rubner, M. F. *Macromolecules* **2000**, *33* (11), 4213.
(21) Tang, Z.; Kotov, N. A.; Magonov, S.; Ozturk, B. *Nat. Mater.* **2003**, *2*, 413.
(22) Jiang, C.; Markutsya, S.; Pikus, Y.; Tsukruk, V. V. *Nat. Mater.* **2004**, *3*, 721−728.
(23) Mamedov, A. A.; Kotov, N. A.; Prato, M.; Guldi, D. M.; Wicksted, J. P.; Hirsch, A. *Nat. Mater.* **2002**, *1*, 190−194.
(24) Stockton, W.; Rubner, M. F. *Macromolecules* **1997**, *30*, 2717.
(25) Yang, S. Y.; Rubner, M. F. *J. Am. Chem. Soc.* **2002**, *124* (10), 2100−2101.
(26) Sukhishvili, S.; Granick, S. *Macromolecules* **2002**, *35* (1), 301.
(27) Mamedov, A. A.; Kotov, N. A. *Langmuir* **2000**, *16*, 5530.
(28) Dubas, S. T.; Farhat, T. R.; Schlenoff, J. B. *J. Am. Chem. Soc.* **2001**, *123* (22), 5368. (a) See the video in the Supporting Information.

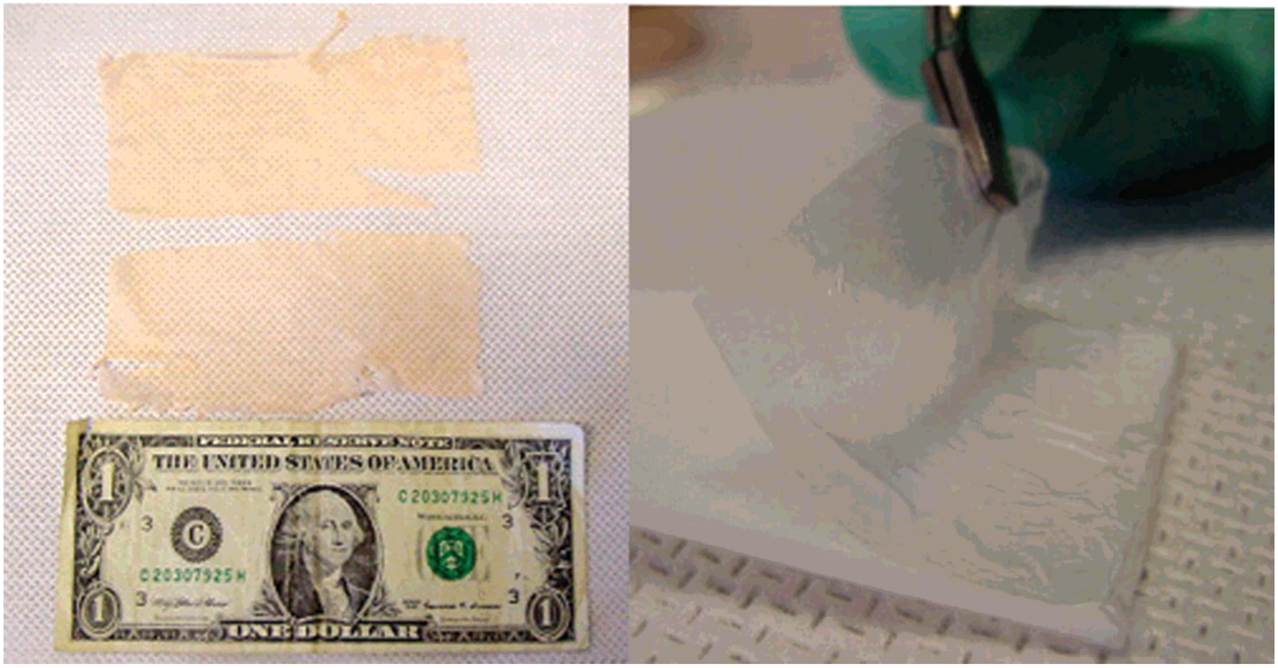

Figure 2. Isolated layer-by-layer PEO/PAA assembled at pH 2.5. Both films shown, isolated from a Teflon substrate, were clear and flexible.

Information Figure 1). The carboxylic acid was in its protonated state (1708 cm^{-1}), and the acid ionization peak (1570 cm^{-1}) was absent. Exposure to the dry nitrogen purge in the FTIR dehydrated a small fraction of the PAA to form anhydride linkages (1804 cm^{-1}).[25]

Thermal and Mechanical Characteristics. Differential scanning calorimetry of a PEO/PAA multilayer assembly in nitrogen, shown in Figure 3a,b, illustrates that the melting peak of PEO at 65 °C is completely suppressed. The lack of a melting endotherm in both the multilayer film and its analogous complex indicates that when hydrogen bonding is introduced with PAA *crystallization of PEO can be fully prevented*, even when the polymer has a high molecular weight. Additionally, a single glass transition (52 °C) was detected between those of pure PEO (−56 °C) and PAA (99 °C). The thermal properties and the transparency of the multilayer assemblies indicate that the hydrogen-bonded multilayer films are, in fact, a true, fully miscible nanoassembled polymer blend. The Fox equation,[30] a mixing rule for polymer blends, was used to estimate film composition. This equation is most accurate for LBL films that are fully dried because trace water lowers the observed glass transition. The DSC conditions were maintained under constant nitrogen air flow, and the first and second cycles were measured; this process resulted in relatively dry conditions. A glass transition temperature of 52 °C gave a composition of 20 wt % PEO and 80 wt % PAA. Complexes of PEO and PAA formed directly from solution via precipitation were used as a control for the determination of thermal properties. The properties were similar to those for multilayer assemblies made under analogous experimental conditions, further evidence of the ability of the layer-by-layer technique to create nanoscale blends of two polymers. First scans of both complexes and LBL assemblies exhibited an endothermic peak at the boiling point of water for the release of bound water, suggesting the PEO/PAA film's hygroscopic nature; this peak was not present in additional cycles which were preformed under nitrogen. This DSC study demonstrates, to the best of the our knowledge, the first thermal analysis evaluation of an LBL film; ultimately, estimating the glass transition and composition by DSC of an LBL film is a new, but familiar, method now available to the LBL community with the introduction of a simple lift-off approach to isolating free-standing films.

Weight loss detected by thermal gravimetric analysis (TGA) confirmed the composition of the layered assembly determined by the Fox equation. To minimize moisture and oxygen exposure, the samples were rigorously dried in a vacuum overnight and stored in <1 ppm argon for days before testing, and the analysis was conducted under nitrogen. For hydrogen-bonded multilayers assembled at pH 2.25, two distinct weight-loss regions were measured (Supporting Information Figure 2). Upon heating from room temperature, the sample first exhibited small losses (2 wt %) attributed to water. The first significant decomposition region, from 175 to 300 °C, was attributed to PAA, which normally degrades in three steps in its pure form. The remainder of the sample degraded above 375 °C, a temperature at which both PEO and PAA rapidly decompose.[31] Comparison of the TGA responses of both the PEO/PAA assembly and its pure constituents aided in analysis of the LBL composite. Data from TGA showed that the multilayer assembly composition was 22 wt % PEO and 78 wt % PAA from analysis of the curve's first derivative. These values closely match the results stated above from thermal analysis, where a measured T_g of 52 °C gave compositions of 20 wt % PEO and 80 wt % PAA (or 30 mol % PEO and 70 mol % PAA by monomer unit). Although previous investigations[3,5] indicated that precipitated H-bonded complexes form in equimolar ratios, we found the PAA content was double that of PEO in both precipitated complexes and multilayer assemblies. This discrepancy is

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(29) Kimura, N.; Umemura, J.; Hayashi, S. *J. Colloid Interface Sci.* **1996**, *182* (2), 356−364.

(30) Painter, P. C.; Coleman, M. M. *Fundamentals of polymer science: an introductory text*, 2nd ed.; Technomic Publishing Co.: Lancaster, PA, 1997.

(31) *Polymers: A Property Database*; CRC Press: Boca Raton, FL, 2004.

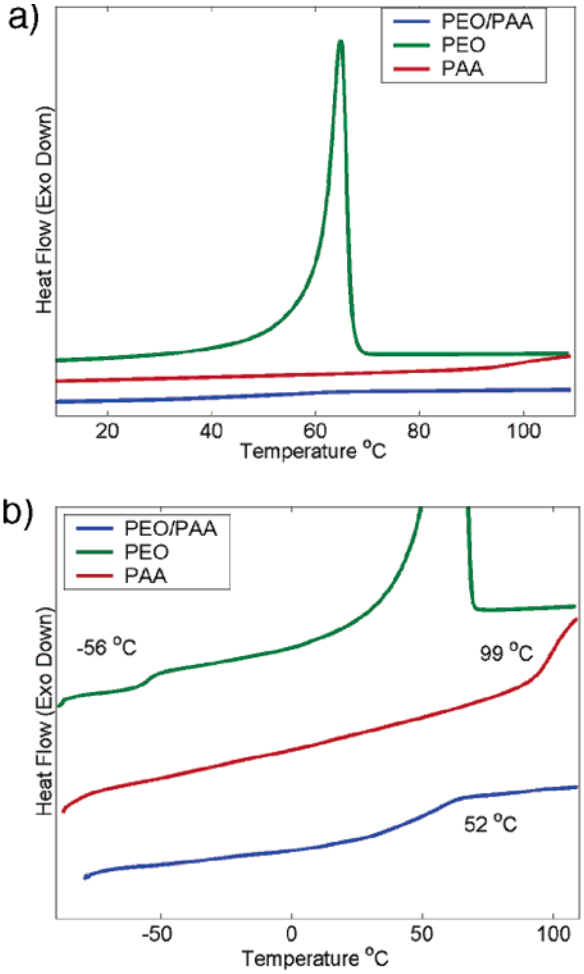

Figure 3. (a) Differential scanning calorimetry of PEO/PAA assemblies compared to that of pure PEO and PAA (second scan retained). (b) A closeup of the glass transition regions. The LBL film assembled at pH 2.25 exhibits a single T_g between that of its pure components.

explained by the internal hydrogen bonding of poly(acrylic acid) in the form of acid dimerization[32] This mechanism, whether occurring by intrachain or interchain means, may have prevented a significant quantity of carboxylic acid groups from participating in hydrogen bonding with PEO. The carboxylic acid structure is also confirmed by FTIR where the C═O peak at 1708 cm^{-1} is indicative of intramolecular or intermolecular dimers.[33,34]

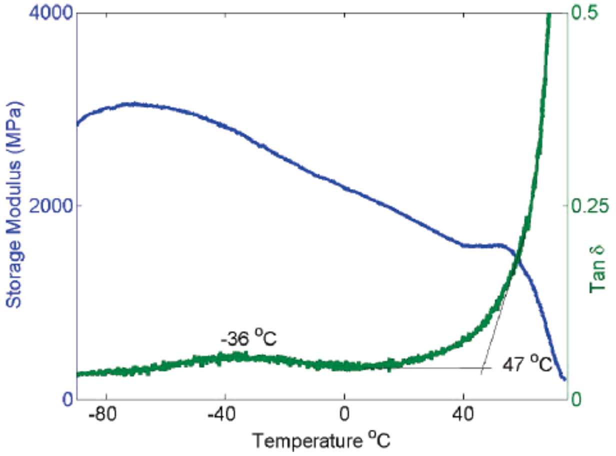

Figure 4. DMA of PEO/PAA assembled at pH 2.25. The leftmost peak corresponds to a secondary transition, and failure at 47 °C occurs near the glass transition of the film.

Besides thermally characterizing PEO/PAA LBL films with DSC and TGA, the isolation of these thin films allows us to conduct dynamic mechanical analysis. A thin, dry film of PEO/PAA was subjected to an oscillating tensile force in a nitrogen purge. Tan δ, the ratio of out-of-phase response to in-phase response, indicates thermal relaxations such as glass transitions or second-order relaxations such as the rotation or vibrations of sidegroups. Figure 4 illustrates a typical PEO/PAA DMA curve. At low temperatures, the glassy storage modulus plateaus at 3 GPa and drops to 2 GPa with increasing temperature before failure via necking around 70 °C. The tan δ curve shows a peak at −37 °C and the onset of failure at 47 °C in the form of a much greater peak (off-scale of the plot). The former peak is attributed to the β relaxation of side chain movements of PAA in its hydrogen-bonded state, and the latter event relates to the glass transition of the LBL nanoblend. Under dry conditions, when the assembly is unplasticized, the glass transition is much higher at approximately 50 °C and approaches the temperature at which the hydrogen-bonded complex begins to weaken and break up, leading to necking and permanent flow, as observed during these experiments.

Because multilayer thin films have been generally inseparable from their assembly substrate, past measurements of mechanical properties were performed using indirect methods, such as nanoindentation[22,35−37] and microcapsule swelling,[38,39] which probe structures on a nanometer−micron scale, often when immersed in aqueous solutions. With sheets of multilayers now isolated in the solid state, mechanical properties can be tested in the bulk state via standard tensile testing without exposing the samples to an aqueous environment. The behavior of the multilayer under typical ambient conditions is of particular interest for a number of applications. The rubbery nature of the hydrogen-bonded multilayers when plasticized under ambient humidity was confirmed by tensile testing. Ambient experimental conditions of 50% relative humidity led to films containing sufficient water from the environment to lower the glass transition temperature, enhance the rubbery character of the film, and lower the observed modulus via plasticization. Thin sheets of multilayer film (8 μm) were isolated from a polypropylene substrate, trimmed with scissors (8 mm × 6 mm), and submitted to uniaxial tension in ambient conditions. A stress−strain curve typical for these films at ambient conditions is shown in Figure 5; the curve is similar to that of a standard rubbery material. The calculated tensile modulus, ultimate strain, and ultimate stress were 6.7 MPa, 360%, and 2 MPa, respectively. At small strains (0−4%), the initial modulus is directly impacted by the hydrogen bonds that act as physical cross-links

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(32) Ege, S. *Organic Chemistry*, 3rd ed.; D. C. Heath and Company: Lexington, MA, 1994.

(33) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21* (2), 346−354.

(34) Lu, X.; Weiss, R. A. *Macromolecules* **1995**, *28* (9), 3022−3029.

(35) Mermut, O.; Lefebvre, J.; Gray, D. G.; Barret, C. J. *Macromolecules* **2003**.

(36) Pavoor, P.; Bellare, A.; Strom, A.; Yang, D.; Cohen, R. *Macromolecules* **2004**, *37* (13), 4865−4871.

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

(38) Vinogradova, O. I.; Andrienko, D.; Lulevich, V. V.; Nordschild, S.; Sukhorukov, G. B. *Macromolecules* **2003**, *37* (3), 1113.

(39) Gao, C.; Leporatti, S.; Moya, S.; Donath, E.; Mohwald, H. *Langmuir* **2001**, *17* (11), 3491−3495.

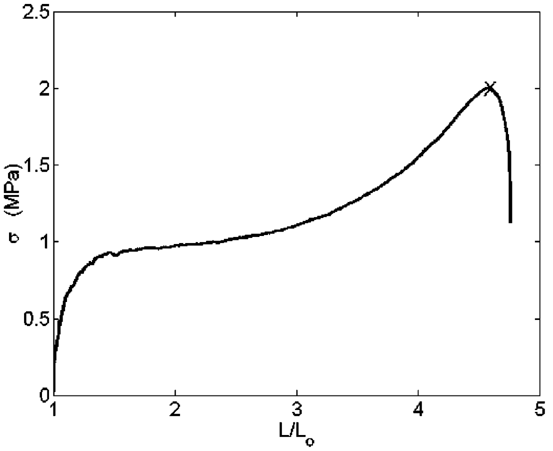

Figure 5. Tensile testing of PEO/PAA at pH 2.5 in ambient conditions. The shape of the curve mimics that of an elastomer.

and as molecular entanglements. A rubbery plateau exists as the loops between cross-links unwind and stretch, from 4% strain until about 300%. Finally, strain hardening was observed at higher strains until break, which may indicate the formation of ordered domains at large extensions (i.e., strain-induced crystallization) or the onset of the ultimate extensibility of the polymer chains. At break, the sample fractured, and the individual pieces retracted to their original dimensions in seconds. Differential scanning calorimetry and optical microscopy of the fractured sample confirmed the absence of any crystallites after tensile testing, similar to Flory's treatment of natural rubber.[40] The observed elastic, or rubbery, modulus fluctuated from 4 to 9 MPa depending on the humidity of the testing environment. It should be noted that this modulus is the rubbery modulus, corresponding to the rubbery plateau region that exists in the plasticized PEO/PAA matrix between the glass transition and the effective hydrogen-bond deconstruction or "melting point"; as expected, this modulus is orders of magnitude lower than the modulus measured under dry conditions, which corresponds to the polymer in its glassy state.

Water's influence can be observed both in DMA and in tensile testing. For example, DMA on a dried film gave a T_g of 47 °C and a glassy modulus of 2 GPa at room temperature, whereas DMA of a film at ambient humidity gave a T_g of 17 °C and a rubbery tensile modulus of 74 MPa at 20 °C. DMA of the humid film would exhibit a rubbery plateau at slightly higher temperatures, most likely at 4−9 MPa as reflected in tensile testing, but beyond 20 °C, the material was too soft for accurate measurement. Similarly, the observed modulus from tensile testing is a direct result of water plasticization. Once water exists in the film, the T_g is lowered and the mechanical properties reflect those found in the rubbery regime as opposed to the glassy response observed in dry DMA.[40b]

Previous studies of the Young's modulus in multilayer films focused upon electrostatically bound layers, giving modulus values ranging from 1 MPa to 10 GPa, depending on the component materials and the measurement method,[21,22,35−39] with fully hydrated materials often exhibiting a lower modulus. Our studies indicate that hydrogen-bonded multilayer assemblies are generally less stiff than their electrostatically assembled multilayer counterparts, especially when both are compared under hydrated conditions. This difference in modulus is explained in part by the comparative energies of hydrogen and electrostatic bonding and the differences in the effective cross-link density in these films. The density of ionic bonds found in the polyion-complexed films is generally greater than the density of hydrogen-bond-complexed groups in PEO/PAA because of much lower driving forces between hydrogen-bond functional groups. A third important difference is the relatively low glass transition temperature of PEO, which is expected to yield rubbery behavior in a chemical or physical network. A final, but significant, factor for the mechanical properties of the PEO/PAA assembly is the hygroscopic nature of PEO. Absorbed water, which acts as a plasticizer, enhances mobility in the thin film by lowering the glass transition, resulting in a higher extensibility and lower modulus at room temperature. Consequently, the mechanical property of the PEO/PAA thin film as a function of humidity is a subject of future work. Conversely, in a dry argon glovebox with <1 ppm water, the PEO/PAA films still bend and flex, but they tear at much lower strains under uniaxial tension than their humid counterparts. Schlenoff et al. have extensively studied the effect of water content in electrostatic multilayers, finding that water comprises 10−20% of the film's mass, all of which can be removed with heat.[41]

Table 1. Comparison of the Glass Transition Temperatures Measured under Dry Nitrogen Conditions (in °C) of PEO/PAA Films from DMA and DSC at Varying Assembly pH

pH	DMA T_g	DSC T_g
2.25	49	52
2.5	45	38
2.75	34	34
3.0	28	25

To understand the role of assembly solution pH as a control parameter, hydrogen-bonded LBL assemblies of pH 2.25, 2.5, 2.75, and 3.0 were investigated with DSC and DMA. Above pH 3.0, the films' construction competes with the ionization of PAA and results in thinner films. DSC indicated that increasing assembly pH results in a lower T_g. Consequently, a lower glass transition indicates the enrichment of these thin films with PEO. The trend was confirmed with TGA and DMA, as summarized in Table 1. In DMA, the onset of the glass transition clearly decreases with increasing assembly pH, but the β relaxation near −36 °C remains invariant under different pH values because β relaxations are much less sensitive to free-volume effects than the glass transition.

Examining pH as a control parameter allows us to elucidate the underlying factors that determine composition and morphology. In more acidic conditions, such as pH 2.25, PAA hydrogen bonds with itself as stated previously. As the solution pH increases, PAA is less likely to hydrogen bond with itself owing to small amounts of charge repulsion, so the polymer adsorbs in thinner layers with less relative amounts of PAA to PEO. As a limiting case, the film could approach a stoichiometric composition with a glass transition of 20.4 °C at higher pH values. However, to achieve this limiting composition, the pH approaches a "modulation window" where the LBL construction is electrostatically hindered by the ionization of PAA and the

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(40) (a) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953. (b) See Humidity and Modulus in the Supporting Information.

(41) Farhat, T.; Yassin, G.; Dubas, S.; Schlenoff, J. *Langmuir* **1999**, *15* (20), 6621.

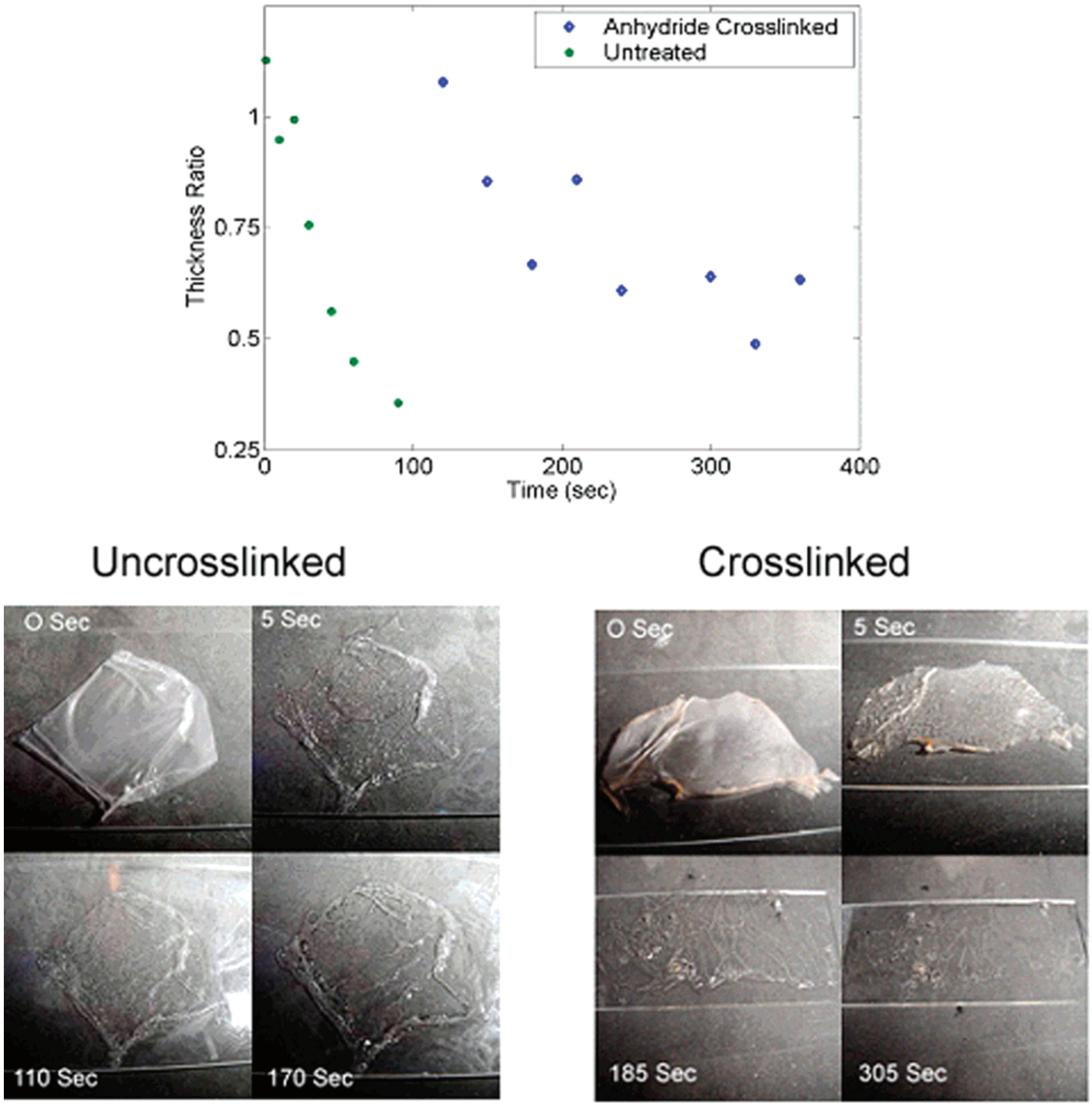

Figure 6. Representative un-cross-linked and anhydride cross-linked (105 °C overnight) PEO/PAA films assembled at pH 2.5 deconstructing with time as they are exposed to phosphate-buffer solution. (Top) In PBS, the anhydride cross-linked PEO/PAA assembly deconstructs slower than the untreated analogue. (Bottom) Although the un-cross-linked film (left) eventually dissolves away, the cross-linked film (right) persists in a swollen gellike state.

resulting electrostatic repulsion; ultimately, at pH 3.6 and above, the LBL film is unable to assemble.[16,26] At assembly pH 3.0, we approach the limiting case for which DSC demonstrates a glass transition of 25.3 °C, giving a composition of 47 mol % PEO while maintaining mechanically robust films.

Knowledge of the rubber tensile modulus (∼4−9 MPa at 25 °C and 50% relative humidity (RH)) and the overall composition allows the crude estimation of the average effective molecular weight between cross-links, M_c, and the cross-link density of this hydrogen-bonded network. Assuming constant volume, uniaxial tension, and Gaussian distribution, the hydrogen-bonded multilayer was treated as an elastomer as discussed in Flory, with $\sigma_n = \rho RT/M_c(\alpha - (1/\alpha^2))$, where σ_n and α represent the stress and strain, respectively.[40] At small extensions, the tensile modulus was modeled as the coefficient, $\rho RT/M_c$. Stress−strain measurements indicated an average molecular weight between cross-links ranging from 300 to 600 g/mol. If each PAA loop had twice as many monomers as a PEO loop, as indicated from TGA-based compositional estimates, we could roughly project that 16−31% of PEO monomers and 8−16% of PAA monomers participate in hydrogen bonding between the ether and carboxylic acid groups. Because of fluctuations from water content, humidity, and a breakdown of the Gaussian approximation, the cross-link density and molecular weight between cross-links are presented only as rough sketches of the true system.

Hydrogen-bonded layer-by-layer films are of interest for drug delivery systems, biomaterials, fuel cell membranes, dry battery electrolytes, and sensors; unfortunately, the difficult means of thin-film isolation presented a major obstacle for indepth characterization of the nature of these films. Peel-away, readily removed films present a strong argument for roll-to-roll processing because the area and mass of film only depends on substrate dimensions and bilayer number.

Sukhishvili et al. demonstrated the release of dye from multilayer capsules via the pH-induced deconstruction of PEO/PAA LBL films.[26] Above a critical pH, poly(acrylic acid) will ionize, thus eliminating its hydrogen bond with PEO and undergoing strong intermolecular repulsion. Depending on the pH, the deconstruction can take place in a matter of seconds–days. To mimic the deconstruction of PEO/PAA nanocomposites in the body, thin strips of PEO/PAA nanocomposites on Si were exposed to a phosphate-buffered saline (PBS) solution to observe the kinetics of deconstruction. A degradable film is desirable for applications such as therapeutic patches, coatings, and drug delivery. Controlling the rate of deconstruction, which may be altered by inducing anhydride linkages via heat treatment, is key for tailoring this hydrogen-bonded system. Although exposed to pH 7.4 buffer solution, the anhydride cross-linked film persisted for nearly four times as long as an untreated PEO/PAA assembly before delamination from the silicon substrate (Figure 6). Under these conditions, the cross-linked film swells and then persists for hours in its swollen state as opposed to the un-cross-linked film which deconstructs in a matter of minutes. Potentially, films cross-linked under higher temperatures for longer durations might deconstruct over even longer periods of time.

In addition to drug delivery, the isolation of LBL films allows for the design of asymmetric functionalized surfaces. One side of the assembly might promote wound healing, and the other side protects the wound from the external environment. To demonstrate the asymmetric properties of an LBL assembly, the water contact angle of each side was measured. The initial bilayer surface of PEO and the final surface of PAA showed receding water contact angles of 97° and 75°, respectively.[40b] In combination, we envision future hydrogen-bonded layer-by-layer assemblies to comprise asymmetrically functionalized free-standing films that controllably deconstruct while delivering therapy or molecules of interest to the surface of contact.

Hydrogen-bonded LBL assemblies have also been shown to conduct ions including protons and lithium ions, but in past and ongoing work, the multilayer films are usually constructed on active substrates such as ITO or porous membranes. For applications such as fuel cells or batteries, LBL films can now be peeled, lifted off, and trimmed for specific dimensions without requiring an active substrate. The untreated PEO/PAA assembly performs exceedingly well in its hydrated form as a fuel cell membrane, showing proton conductivities reaching 10^{-4} S cm^{-1}.[16] Another factor to note is that PEO crystallization, a significant obstacle to ion mobility, was completely suppressed as shown in DSC. Future work will entail tailoring the PEO composition through construction pH and measuring the subsequent ionic conductivity.

Conclusions

Novel solid-state hydrogen-bonded assemblies were created using a layer-by-layer method which allowed the incorporation of PAA and PEO on the nanometer length scale. Remarkably, these fully hydrogen-bonded nanoassemblies could be isolated as substantive, tough elastomeric thin films using a simple peel-off procedure from a low-energy surface. The new technique is applicable to not only hydrogen-bonded LBL assemblies but also electrostatic assemblies and those containing smaller molecules such as clay or dendrimers as well. By isolating these thin films as continuous sheets on the surface, it was possible to study the bulk structure and properties in PEO/PAA multilayer assemblies and directly observe their properties as an elastomeric blend. The structures were transparent, exhibited no melting peaks, and revealed one glass transition temperature rather than two. Importantly, the result of assembling these semicrystalline polymers was a fully amorphous, true polymer blend. The amorphous nature induced by the nanoscale blending of PEO with PAA in an LBL assembly mimics the scrambled complex first proposed by Michaels[42] and Decher,[8] behaving similarly to that of its analogous hydrogen-bonded complex.

The low glass transition of these nanoassembly networks led to rubbery behavior at room temperature; these systems exhibited thermal stability up to the point of degradation of the polymer components at high temperature. In basic aqueous solutions, the rate of film deconstruction can be controlled with anhydride cross-linking. In ongoing work, the tunable qualities of layer-by-layer assembly will lead us to tailor new PEO/PAA films for improved ion conduction, biomaterials, pH-sensitive sensors, and drug delivery by controlling the degree of inter- and intramolecular hydrogen bonding while maintaining the amorphous, elastomeric quality of the structure. Additionally, the influence of humidity and water content on the thermal and mechanical properties of LBL films will be investigated in future work. In the more general sense, the solid-state isolation of these films from hydrophobic surfaces opens a new door for the direct incorporation and characterization of multilayer assemblies for fuel cells, micropower devices, gas separation membranes, biomaterials substrates, drug delivery devices, and pH-sensitive sensors.

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Supporting Information Available: Video of PEO/PAA isolation from polypropylene, general experimental, FTIR spectrum of PEO/PAA LBL file, TGA of PEO/PAA, DSC of PEO/PAA, and DMA of PEO/PAA. This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) Michaels, A. S. *Ind. Eng. Chem.* **1965**, *57* (10), 32.