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Irreversible Compression of Polyelectrolyte Multilayers

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Control over surface and interface properties is very important in many existing and emerging technologies, especially those with electroactive or bioactive materials. Subtle changes in organization and composition at the molecular level often would result in dramatic performance enhancement of surfaces or interfaces, which can be fulfilled by the layer-by-layer (LbL) technique, a method to build multilayers of polyelectrolytes.[1] In this process, when a surface is exposed alternately to polyelectrolytes of opposite charge, a polymer composite film of uniform thickness is fabricated. Combinations of polyelectrolytes with other charged materials, including small organic molecules or inorganic compounds, biomacromolecules, macromolecules, and dendrimers, and colloids or latex particles,[2] have proven the flexibility and promise of the LbL technique. Furthermore, by expanding the LbL assembly to spherical surfaces, hollow microcapsules with sizes ranging from 60 nm to several tens of micrometers have been produced.[3] Applications of these films include conducting layers, light-emitting thin films, biosensors, selective membranes, nonlinear optics, patterned surfaces and templates, electrochromic films, and encapsulation technology.[4]

A consistent picture of polyelectrolyte multilayer (PEMU) growth and structure has been rather difficult to obtain. However, the integration of the observations of layer interpenetration, individual layer profiles, charge stoichiometry, surface charge, counterion content in a consistent way, permeability, and swell−shrink properties have conveyed a hint of the intrinsic structure of PEMUs.[5] Herein we present a novel standpoint to view the issue of the PEMU structure based on a recently discovered property of the films: the deformability of the multilayers. When a patterned poly(dimethylsiloxane) (PDMS) stamp was brought into contact with poly(styrenesulfonated) (PSS)/poly(diallyldimethylammonium chloride) (PDADMAC) PEMUs on mica, surprisingly, compression of the multilayers at the contacted regions was observed as shown in Figure 1. Further investigations demonstrated that this is a common rather than an occasional phenomenon for PSS/PDADMAC multilayers assembled under different conditions, provided that the multilayers were kept at appropriate conditions. The compression extent varied from several to hundreds of nanometers following a positive correlation with the multilayer thickness, which can be normally tuned by layer number or salt concentration as shown in Figure 2. Obtained by atomic force microscopy (AFM), the height of the patterns increased with the added salt concentrations of polymer solutions at a constant layer number or layer number at a constant salt concentration. Taking into account the film thickness deposited on the silicone wafer,[5] the remaining thickness of the compressed films was estimated as approximately 10%−30% of the uncompressed thickness, depending on the layer numbers and salt concentrations. These results reveal a surprising fact that PSS/PDADMAC multilayers could be compressed to a large extent that was not reported previously. The compression of the PEMUs, on one hand, may reflect their inherent microstructure that closely correlates with their properties and, on the other hand, may also contribute some novel functions to expand their applications.

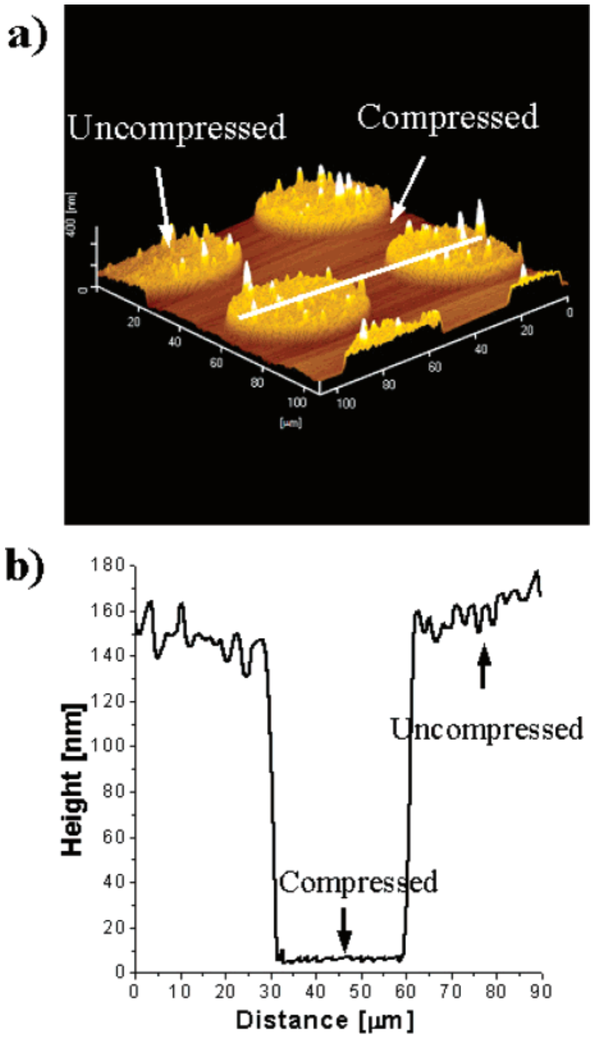

Figure 1. (a) AFM image of compressed (PDADMAC/PSS)$_7$PDADMAC multilayers deposited with 1 M NaCl solution on mica. Concave regions had been brought into contact with the stamp. (b) Line profile of surface topography shown in (a). For this condition of deposition, the height of the pattern could be up to 155 ± 10 nm. The pressure was 0.12 MPa, and the pressing time was 20 min if not otherwise indicated.

This deformability was dramatically affected by the desiccation process of the multilayers, which closely associates with their inner structure. Exposing the films to ambient atmosphere of approximate 40% and 70% relative humidity for 12 h at 10 °C, we have found that those exposed to 70% relative humidity could be com-

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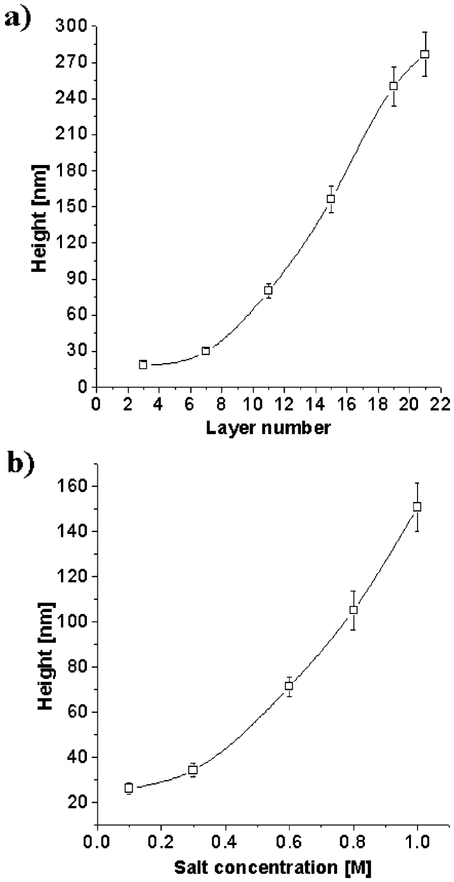

Figure 2. Pattern height as a function of (a) layer number and (b) salt concentration. To check the role of the layer number, different layer numbers of PSS/PDADMAC were fabricated with 1.0 M NaCl. Odd and even numbers represent PDADMAC and PSS, respectively. To examine the effect of salt concentration, (PDADMAC/PSS)$_7$PDADMAC multilayers were deposited in NaCl solution with concentrations ranging from 0.1 to 1.0 M.

pressed while those at 40% could not. Moreover, films dried in a soft nitrogen stream for 1 min to remove the apparent water on the surface could not be compressed either. All these results suggest that the deformability has a close relationship with the water content in PEMUs. It has been demonstrated that, usually, 6−8 water molecules are associated with one ion pair in polyanion/polycation complexes particular for PSS/PDADMAC and PSS/PAH at 100% relative humidity and that the number would increase toward the solid/liquid interface.[6] Furthermore, the outer layers (toward air) lose more water than the inner layers in the drying process. We believe that, for those films dried with a soft nitrogen stream, although the apparent water on the surface and a portion in the outer layers was removed, the water in the inner layers still existed. One possibility is that the water possibly functions as physical cross-linkages due to the hydrogen bonds and also might enhance the hydrophobic interaction of the polyelectrolyte complexes or merely physically support the porous films. Anyway, for these effects, the mechanical property of the films was so markedly strengthened that the compression could not take place. The other possibility is that the recovery of the compression is too rapid to be observed with out-line approaches. This accelerated recover perhaps can be attributed to the absence of the state transition with the effects of water. During the process of complete desiccation as in the case of drying at 40% relative humidity, the films collapse, and the conformation of the polymer chains has been "frozen", leading to the impossibility of compression. Only when a dynamic equilibrium was reached, for example, in the atmosphere of 70% relative humidity, would multilayers show deformability. In this condition, the appropriate amount of water molecules in the multilayers can support the multilayers to avoid collapse, which enables the reorientation of polyelectrolyte segments in response to stress. From this point of view, the compression should be a rather slow process so that the segments have enough time to adjust their conformation. We indeed found that compression at least for 15 min is required to create the physical patterns regardless of the pressure adopted. Pressure ranging from 0.105 to 0.200 MPa, above atmosphere pressure, was utilized to press the PSS/PDADMAC multilayers. In this range of pressure, there was no detectable change of multilayers' deformability. We believe that the range of effective pressure in a sense reflects the mechanical property of certain combinations of polyelectrolytes. Furthermore, supposing that the distribution of stress is homogeneous for the contact regions, this range of pressure does provide an effective approach to estimate the lower limit of the energy density required to compress PEMUs.

The deformability is not restricted to PSS/PDADMAC pairs. Other combinations such as poly(acrylic acid) (PAA)/PDADMAC could also be compressed. For example, for (PDADMAC/PAA)7PDADMAC, deposited at 1 M NaCl and pH = 11, the height of patterns was 45 ± 4 nm. Taking into account the film thickness reported by Schlenoff,[7] the deformability was estimated as 50%. We suppose that PAA is expected to form hydrogen bonds between the carboxylic groups, which compensate the electrostatic PAA−PDADMAC interactions. Additionally, the PAA is less soluble and exhibits secondary attractive interactions. This enhanced interaction acts as an obstacle against compression. However, compression of PSS/poly(allylamine hydrochloride) (PAH) multilayers had not been observed even at much higher pressure (up to 0.5 MPa) and for a prolonged period of time. The nondeformability of the PSS/PAH multilayers would mean that the interactions between the polymer chains are much stronger and the microstructure of the multilayers is more compact. This conclusion is persuasive considering our previous results that the modulus of PSS/PAH multilayers is higher than that of PSS/PDADMAC multilayers by a factor of 5.[8]

The deformation of the PSS/PDADMAC multilayers cannot be recovered even incubated in 2 M NaCl solution for 8 h after compression because of the passive and extensive alteration of the polymer chains that may result in strong interaction between the approached layers. However, the deformability of the multilayers can be regained iteratively following the treatment cycles of complete drying and reincubation in salt solution. For example, the completely dried PSS/PDADMAC multilayers were immersed in 2 M NaCl solution for 6 h and then were dried in an ambient atmosphere of 70% relative humidity for another 12 h. The films again could be compressed, although the pattern height was decreased to 50% of that directly dried in an ambient atmosphere of 70% relative humidity. This would mean that the salt could only induce partial recovery of the collapsed multilayers.[6] The situation could be discussed like a pressure-induced glass transi-

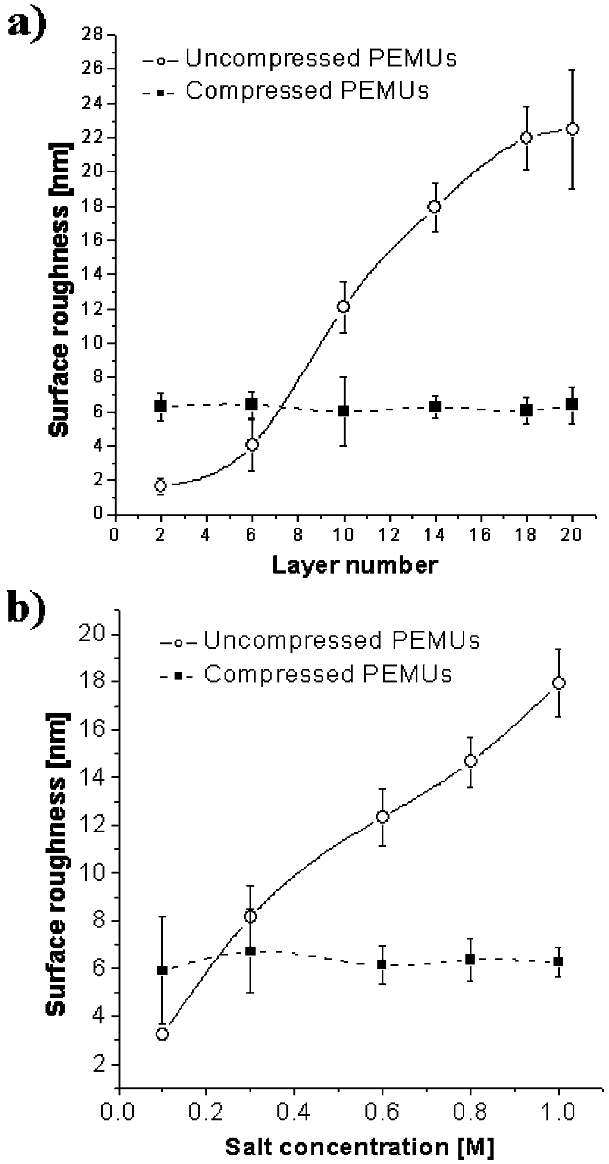

Figure 3. Root-mean-square roughness as a function of (a) layer number and (b) salt concentration. For detailed conditions, see Figure 2.

tion. In this case, the transition from melt to glass may be affected by squeezing out water. The relaxation time may have thus become so long that a relaxation is not observable. This, however, should be very specific for each system and requires more detailed studies.

Compression provides not only an insight view of the inner structure of the PEMUs but also a novel and useful approach to modify the surface properties without variation of chemical composition. For example, the surface roughness of the PSS/PDADMAC multilayers changed remarkably after compression (Figure 3). The surface roughness became around 6 nm after compression regardless of the deposition conditions which resulted in the variation of surface morphology.[5] It is worth noting that these values were also much smaller than the roughness of the stamp surface, which is quite reasonable considering the flexibility of PDMS. Accompanying with the roughness variation, the compression of the multilayers caused also permeability alteration. For those films compressed with a flat PDMS stamp, it seems that, at least, the dye molecules (fluorescein as representation) did not diffuse into the films with sufficient amount that can be detected. Apparently, this is due to the more compact packing. Spatially localized adsorption of dyes and other molecules on the patterned compressed PEMUs has also been achieved (data not shown here), which would provide a wide range of applications in sensing and of characterization techniques.

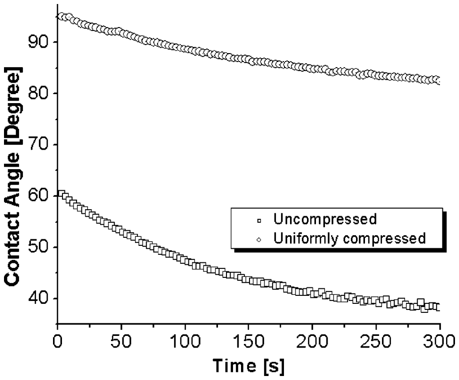

Figure 4. Dynamic contact angle measurements on uncompressed (open square) and uniformly compressed (open circle) (PDADMAC/PSS)$_7$PDADMAC multilayers.

Because the surface properties are largely manipulated by both the surface chemical structure and the morphology,[9] it is reasonable to anticipate that the compression may simultaneously induce a change of wettability. We carried out the dynamic contact angle measurements on both the multilayers before and after a uniform compression with a flat PDMS stamp. Figure 4 reveals that both the initial value and the declination slope were different. The variation could be explained by the fact that the polymer chains came much closer, with hydrophilic groups embedded in the multilayers.

In summary, irreversible deformability of PEMUs has been discovered and discussed in detail with respect to its mechanism and compression conditions. The novel finding provides an insightful view in the microstructure of PEMUs and contributes to a comprehensive understanding of the intrinsic properties of the multilayers. Compressed multilayers have shown some distinctive properties, such as permeability, wettability, and surface morphology from those uncompressed, which in turn may find wide applications in the design of electronic and photonic devices as well as biosensors.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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