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DOES WATER SWELL THE ORDERED DOMAINS IN POLYELECTROLYTE/CLAY MULTILAYERS?

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Abstract—X-ray diffraction has been used to study the sorption of water by multilayer films containing ordered stacks of alternating layers of an organic polyelectrolyte and individual platelets of a smectite. The position and shape of the 001 reflections due to the ordered polyelectrolyte/platelet stacks were essentially the same when in air at low relative humidity (23−25% RH) and under water. These data indicate that swelling occurs exclusively in X-ray amorphous regions within the film, and that the ordered polyelectrolyte/clay domains themselves are not 'swellable' by water.

Key Words—Laponite, Montmorillonite, Multilayer, Polyelectrolyte, Polymer-clay Composite, Stepwise Adsorption, Swelling.

INTRODUCTION

One of the most characteristic properties of smectites is their 'swellability' by water (Barrer and MacLeod, 1954; Mooney *et. al*., 1952a, 1952b; Hendricks *et al*., 1940; Bradley *et al*., 1937; Hofmann *et al*., 1933). Sorption of water by cations in the interlamellar spaces between the silicate sheets as relative humidity (RH) is increased typically leads to discrete increases in the basal spacing, associated with the layering of water molecules around the cations within these galleries. In the case of some smectites, the layers can be completely exfoliated (dispersed) in aqueous solution. Our research group has used individual layers of these smectites for the formation of ordered multilayer films by the alternate adsorption of cationic polyelectrolytes and the exfoliated anionic silicates (Kleinfeld and Ferguson, 1994, 1995; MacNeill *et al*., 1999; Rouse *et. al*., 2000; Kotov *et al*., 1997). The polyelectrolytes that we have used are hydrophilic and soluble in water, and in the multilayer films, they replace the Na cations originally associated with the clay. During formation of the films, the silicate layers are preferentially aligned parallel to the substrate surface, resulting in a structure of alternating layers of polyelectrolytes and silicate that are sufficiently ordered to diffract X-rays (Figure 1, ordered domains).

Not surprisingly, these multilayers swell (*i.e*. increase in volume) reversibly in humid air, though much more rapidly than the parent clays. This property has proven useful in building humidity sensors based on rapid, reversible changes in: optical properties associated with changes in thickness (Kleinfeld and Ferguson, 1995); mass, measured using a quartz-crystal microbalance (Kleinfeld and Ferguson, 1995); and infrared (IR) absorption in the H−OH stretching region (MacNeill *et al*., 1999). We also reported that these multilayers could be swollen by solutions of tetraethyl orthosilicate (TEOS) and that oligomerization of TEOS within the films led to rigid structures (Rouse *et. al*., 2000). X-ray diffractometry demonstrated that the multilayers were still ordered after this sol-gel processing, though it also showed no change in the d_{001} spacings of the ordered domains in the multilayer. This result indicates that swelling with TEOS occurred in the X-ray amorphous regions of the film rather than within the ordered polyelectrolyte/platelet stacks (Figure 1). It also led us to reconsider the mechanism of swelling by water itself − whether it swells the ordered domains, or rather, like TEOS, swells primarily the X-ray amorphous regions between them. These amorphous regions (structural defects) within the films are probably areas rich in polyelectrolyte, caused by the adsorption of polyelectrolyte loops and/or entanglements during the film-formation process.

METHODS

Laponite RD (powder, Southern Clay Products, Inc., Gonzales, Texas) was added to purified water (Milli-Q, $\geqslant$ 15 MΩ) and stirred overnight to form a clear 0.2% (by wt.) dispersion. Montmorillonite was obtained from Southern Clay Products as a 2.71% (by wt.) Cloisite-Na^+ slurry. Prior to use, the slurry was diluted with Milli-Q water by a factor of 10 and centrifuged in 13 × 100 mL cuvettes (~80% filled) at 3300 rpm for 24 h using a Fisher Safety Centrifuge. Following centrifugation, the concentration of the resulting yellowish suspension was determined to be 0.25% (by wt.) by drying two separate

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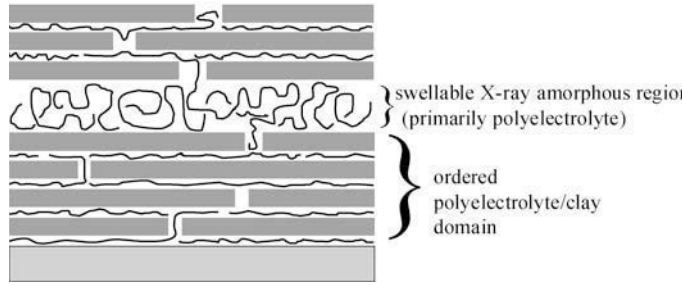


Figure 1. Idealized illustration of the proposed structure of a PDDA/clay multilayer film, comprising both ordered polyelectrolyte/platelet stacks and polyelectrolyte-rich X-ray amorphous regions.

aliquots of the suspension, one initially weighing ~14 g and the other ~18 g, in 20 mL glass vials for 2 days at 150ºC. After removal of the vials from the oven, they were immediately placed in a desiccator to cool to room temperature and then weighed. This analysis should be interpreted with caution and the concentration taken as an upper limit, given the propensity of clays to sorb water and the slow loss of that water once sorbed. The 0.25% suspension of montmorillonite was diluted to 0.20% with Milli-Q water prior to use.

Polyelectrolyte/clay multilayers were prepared on freshly cleaned silicon wafers as reported previously (Kleinfeld and Ferguson, 1995). A 5% (by wt.) solution of poly(diallyldimethylammonium chloride) (PDDA, Aldrich) was first dripped onto the wafer to cover its surface completely for 5 s. The wafer was then rinsed with Milli-Q water and blown dried with nitrogen. After an additional rinsing-and-drying step, the wafer was treated in the same way with the 0.2% (by wt.) clay dispersion. An adsorption of PDDA followed by an adsorption of clay constitutes one adsorption cycle.

The ellipsometric data were obtained using a Rudolph Auto-EL III nulling ellipsometer with a HeNe laser (λ = 632.8 nm) at angle of incidence of 70º. To obtain data at variable relative humidities (RH), the sample stage was enclosed in a plastic bag into which a plastic tube carrying humid nitrogen was inserted. Nitrogen was humidified by passing it through water bubblers, and the RH in the chamber was measured using a Vaisala HMC 20 RH calibrator. Ellipsometric measurements were obtained 5 and 10 min after the RH in the chamber had equilibrated. The apparatus and this procedure have been described in more detail previously (Kleinfeld and Ferguson, 1995).

X-ray diffraction (XRD) patterns were obtained using a Philips APD 3720 powder diffractometer, in $\theta/2\theta$ mode, with monochromatized CuKα radiation (λ = 0.154 nm), and operating at 45 kV and 30 mA. Data were obtained using 0.05º steps and a 3 s/step collection time. The relative humidity of the X-ray chamber was determined using a RH calibrator (Vaisala HMC 20). The XRD pattern of the film under water was obtained by first covering the sample surface with Milli-Q water and then placing a thin film of Mylar (Chemplex) over it, ensuring that the sample remained wet for the duration of the experiment.

RESULTS AND DISCUSSION

Does the swelling behavior of polyelectrolyte/clay multilayers mirror that of the parent clay mineral, or does the organic polymer in the composite structure impart properties different from those of the parent clay? To answer this question, we examined the 'swellability' of two types of multilayer comprising a polyelectrolyte, poly(diallyldimethylammonium chloride) (PDDA), and either Laponite RD (a synthetic hectorite) or natural montmorillonite. The thickness of both films was ~100 nm, measured ellipsometrically at 4% RH, and corresponded to 39 adsorption cycles for the Laponite film and 35 cycles for the montmorillonite film. Ellipsometry can be used to determine both the thickness and refractive index of a thin film prepared on a reflective substrate (*e.g.* silicon) by measuring the change in the polarization and intensity of polarized light as it reflects from the film/air and film/substrate interfaces (Tompkins, 1993).

As the relative humidity was increased, the thickness of the films increased monotonically. Figure 2 shows this behavior for the polyelectrolyte/montmorillonite film, as well as the corresponding change in the refractive index of the film. Between ~4 and 20% RH, the refractive index increased abruptly, accompanied by only a modest increase in film thickness, indicating that some of the sorbed water displaced air from void spaces within the film. Above ~20% RH, the thickness of the film increased substantially with only a marginal increase in refractive index. These data are similar to analogous measurements reported previously for polyelectrolyte/Laponite films (Kleinfeld and Ferguson, 1995; Rouse *et al*., 2000); experiments with polyelectrolyte/Laponite films were repeated for this study and are shown for comparison as dotted lines in Figure 2. For the Laponite system, however, the magnitude of swelling was greater and showed a small hysteresis, and the refractive index of the Laponite film actually decreased slightly at high humidity. The difference in swellability of these films is not the result of the slower

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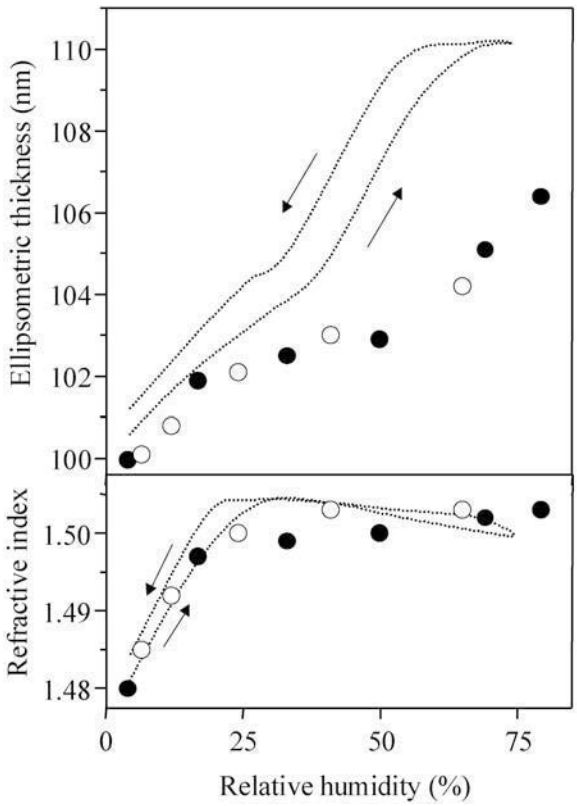


Figure 2. Ellipsometric thickness (upper) of ~100 nm thick multilayer films prepared with 5% (w/w) poly(diallyldimethylammonium chloride) and either 0.2% (w/w) montmorillonite (circles) or 0.2% (w/w) Laponite RD (dotted line) as a function of relative humidity (RH). Refractive index (lower) of the same films as a function of RH. The filled circles correspond to data obtained with increasing RH, and the open circles to those obtained with decreasing RH.

kinetics of water sorption in the montmorillonite films (MacNeill and Ferguson, unpublished results). Ellipsometric data obtained 5 and 10 min after allowing the RH to equilibrate were nearly identical (to within ~1 Å) for both types of film. The largest of the differences between the Laponite and montmorillonite films – the magnitude of swelling – will be discussed below.

To identify the location of swelling by water, XRD patterns of both types of film were recorded in air at low relative humidity and then again under water (Figure 3). In air at 23±2% RH, the 001 reflection for the PDDA/Laponite film occurred at 6.1º2θ, corresponding to a *d* spacing of 1.45±0.02 nm. Under similar conditions (25±2% RH), the 001 reflection for the montmorillonite film occurred at 5.9º (1.50±0.02 nm). This basal spacing is significantly larger than that reported for Na-montmorillonite at such low humidity (Bérend *et al*., 1995; Cases *et al*., 1992), consistent with the systematic presence of intercalated polyelectrolyte within our multilayers. In addition, the 001 reflection of both samples appears symmetric on the high-angle side,

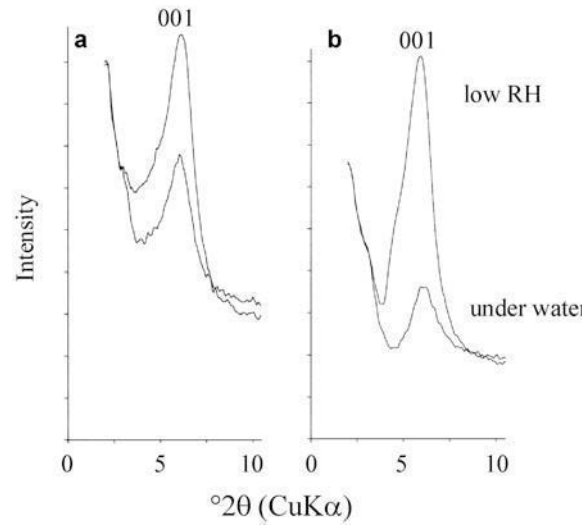


Figure 3. XRD patterns of ~100 nm thick PDDA/Laponite RD (a) and PDDA/montmorillonite (b) multilayer films under different environmental conditions: upper scans were taken at 23% RH (Laponite) and 25% RH (montmorillonite), and the lower scans were taken with the films under a film of water. The vertical axes in (a) and (b) both show the square root of intensity, but are plotted on different scales.

consistent with homogeneous PDDA/clay crystals not interstratified with Na-montmorillonite.

When the films were under a thin layer of water, the 001 reflection occurred at 6.1º2θ for both films, corresponding to a *d* spacing of 1.45±0.02 nm. We attribute the reduced intensities of the 001 reflections for the films under water to attenuation of the X-ray beam by the water covering the sample, and not to a loss of coherent scattering domains within the film. Swelling by water could, in principle, reduce the reflection intensity of such a sample by either reducing the average size of the scattering domains (the ordered polyelectrolyte/platelet stacks) or by destroying some of them altogether. A reduction in the size of the ordered domains, however, should cause a broadening in the shape of the reflection as well as a shift to lower 2θ angles (Drits and Tchoubar, 1990), not the case here. In a control experiment, a similar reduction in the intensity of the 001 reflection was observed for a sample of mica (muscovite, a non-swelling clay) treated in the same way (Grim, 1968). The small decrease in the *d* spacing for the montmorillonite-only film may result from a difference in alignment or positioning of the sample between measurements.

The nearly identical position of the 001 reflections at low humidity and under water indicates that swelling by water occurs primarily in 'swellable' X-ray amorphous regions within the films, and not in the ordered domains. If swelling had occurred either only within the ordered domains or equally between these domains and amorphous regions, then a minimum of an 8% increase in *d* spacing would have been expected for the Laponite film,

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given the increase in thickness observed ellipsometrically between 23 and 75% RH. Such a change would have placed the 001 reflection at 5.7º2θ or 1.55±0.02 nm. In the montmorillonite case, the increase would be 4%, also placing the reflection at 5.7º2θ. These values correspond to minimum increases because swelling in liquid water should be at least as great as it is in air at 75 or 79% RH. Given that the polyelectrolyte is a flexible, water-soluble polymer, the data are consistent with the presence of 'swellable' X-ray amorphous regions rich in polyelectrolyte.

The XRD studies also provide insight into the reason for the greater 'swellability' of polyelectrolyte/Laponite films relative to the polyelectrolyte/montmorillonite films. Because swelling by water occurs primarily within X-ray amorphous regions, the Laponite-containing films must contain a greater proportion of 'swellable' X-ray amorphous material, relative to the montmorillonite-containing films. The differences between XRD patterns of films having the same overall thickness and run under the same conditions are consistent with this conclusion (Figure 4). The intensities of the basal reflections for the polyelectrolyte/montmorillonite film are greater than those for the Laponite film. We attribute the difference in the fraction of the films comprising ordered polymer/clay domains (relative to the amorphous material) to the larger platelet sizes contained in the naturally occurring montmorillonite (Rouse *et al*., 2004). Analysis of the positions of the basal reflections in Figure 4 reveals that they are either rational (Laponite) or almost rational (montmorillonite), consistent with regular interstratification in the polymer/clay crystallites. The standard deviation and coefficient of variation (Bailey, 1982) of the $l{\cdot}d_{00l}$ values for the Laponite film were 0.093 and 0.65, respectively. The corresponding values for the montmorillonite film were 0.26 and 1.8, respectively. Using only the higher-order reflections for the montmorillonite film, these values fell to 0.11 and 0.77.

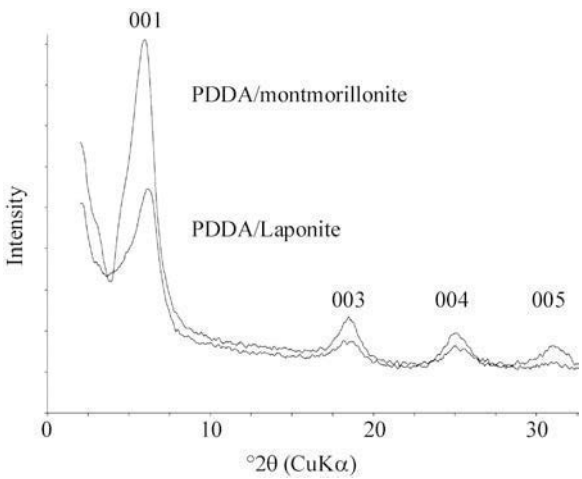


Figure 4. XRD patterns comparing the intensities of reflections in ~100 nm thick films of PDDA/montmorillonite (upper) and PDDA/Laponite RD (lower) at low RH (25% for PDDA/montmorillonite and 23% for PDDA/Laponite RD). The vertical axis shows the square root of intensity.

CONCLUSIONS

We have analyzed the effect of water sorption on the 001 spacing of ordered domains contained within polyelectrolyte/clay multilayers. X-ray diffraction indicates that unlike the parent clays themselves, the ordered polyelectrolyte/clay domains in our multilayers are held tightly together and are not swellable by water. We attribute this rigidity to the replacement of monovalent cations in the parent clay with a polyelectrolyte 'glue' that serves as a multivalent cation. The absence of Na from the clay platelets after formation of the film has been communicated previously (Kleinfeld and Ferguson, 1994). The multiple (electrostatic) points of attachment between the polyelectrolyte and the clay platelets within these domains probably restrict the swellability of these portions of the film. The similarity in the shape of the 001 reflections in air at low RH and under water suggests that sorption of water in the films did not cause a loss of ordered domains via swelling.

Of practical importance, this study suggests that film rigidity can be increased by increasing the fraction of the film made up of ordered polymer/clay domains (as opposed to X-ray amorphous material) through the use of larger clay platelets, thus improving their usefulness as stable coatings. The stark difference between the swelling behavior of these ordered domains and the parent clays provides additional evidence that our proposed structure (polyelectrolyte/clay/polyelectrolyte/clay···) is correct, and that the XRD in these films is not due to included particles of unexfoliated clay. Finally, we note that these results do not imply that water is rigorously excluded from the interlayer galleries, only that any such intercalation does not change the 001 spacing, *i.e*. swell the ordered domains.

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