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A Method for Imaging Single Clay Platelets by Scanning Electron Microscopy

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Summary: A method for preparing and observing clay platelets for size and shape analysis using scanning electron microscopy (SEM) was developed. Samples of the clay platelets were prepared by polyelectrolyte-assisted adsorption onto a pyrolytic graphite surface. The use of graphite as a substrate was advantageous because of the low number of secondary electrons emitted from it during imaging by SEM. The resulting low background noise allowed the emission from the ~1 nm thick clay sheets to be clearly visualized. Images of centrifuged montmorillonite showed large exfoliated platelets with lateral dimensions between 200 and 600 nm. In contrast, uncentrifuged montmorillonite appeared to contain a large amount of unexfoliated clusters. Although it was not possible to obtain high-quality images of the smaller sheets of Laponite RD, the images of this material did contain size features comparable to the ~30 nm^2 size reported previously using light scattering, as well as transmission electron and atomic force microscopies.

Key words: clay, polyelectrolyte, scanning electron microscopy

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Introduction

The ability to determine the size and shape of clay platelets accurately is of fundamental importance in understanding the structure of polyelectrolyte/clay multilayer films (Kleinfeld and Ferguson 1994, Rouse *et al*. 2000), the behavior of clay suspensions (Avery and Ramsay 1986, Bonn *et al*. 1999, Kroon *et al.* 1998, Mourchid *et al.* 1998, Nicolai and Cocard 2000, Rosta and von Gunten 1990) and clay/polymer composites (Balazs *et al*. 1999, Gilman 1999, Kawasumi *et al*. 1997, Kornmann *et al*. 2001, Sonobe *et al*. 1999, Tyan *et al*. 1999, Vaia *et al*. 1996; 1999). Although scattering techniques (e.g., visible light, x-ray, neutron) have proven useful for characterizing clay suspensions, the ability to differentiate between scattering from single particles and aggregates has proven difficult (Nicolai and Cocard 2000, Rosta and von Guten 1990). Direct methods for determining particle size have relied mainly on electron microscopy, and, more recently, on atomic force microscopy (AFM) (Bickmore *et al*. 1999, Tamura *et al*. 1999, van Duffel *et al*. 2001). Transmission electron microscopy (TEM) has been used extensively to characterize platelet dimensions, interlayer spacing, degree of aggregation, and relative orientation of either the single sheets or larger aggregates (Alcover *et al.* 2000, Greene *et al.* 1974, Kawasumi *et al*. 1997, Kornmann *et al*. 2001, McAtee and Henslee 1969, Sonobe *et al*. 1999, Thompson and Butterworth 1992, Tyan *et al*. 1999, Vaia *et al.* 1996). Due to the relative transparency of a single clay sheet, however, the images reported usually give only a cross-sectional view of the platelets. These images provide detailed information such as sheet thickness and an estimate of the lateral dimensions, but not a clear picture of the overall size and shape of the individual platelets.

The use of scanning electron microscopy (SEM) to determine platelet size has been hampered by its lower magnification, relative to TEM and AFM, and the need to coat samples with conducting overlayers to reduce charging and increase signal intensity. To reduce these difficulties, clay particles have been imaged by allowing a clay suspension to evaporate on a metal-coated substrate (Smart and Tovey 1982). While this method did result in improved particle analysis, evaporation is not conducive to the deposition of individual clay platelets, which tend to aggregate and curl during drying. To determine the lateral dimensions of clay platelets by SEM, we have modified a technique developed for imaging clays by TEM (Greene *et al.* 1974, McAtee and Henslee 1969). That technique involved adsorption of single montmorillonite sheets and aggregates

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onto a carbon-coated microscope grid that had been treated with Cytochrome C, a positively charged biomolecule. Our adaptation of this technique for use in SEM has several attractive features: (1) the deposition of a monolayer of clay sheets, and not larger aggregates, onto the substrate; (2) the ability to detect the weak electron emission, produced by a single clay sheet over the background emission, without the use of coatings; and (3) little or no curling or bending of the larger platelets.

Clay platelets were imaged by polyelectrolyte-assisted adsorption onto a pyrolytic graphite surface. Use of graphite, a substrate with a low atomic number, is advantageous for SEM imaging because of the small number of secondary electrons produced upon electron beam exposure —low background noise (Goldstein *et al*. 1992). Instead of Cytochrome C, we first adsorbed a layer of the simpler commercially available polyelectrolyte, poly(diallyldimethylammonium chloride) (PDDA), from an aqueous solution to provide a positively charged substrate appropriate for adsorption of anionic clay platelets (Kleinfeld and Ferguson 1994). It was thus possible to adsorb predominately single clay sheets, with adsorption of additional platelets inhibited by Coulombic repulsion. With the clay particles tightly bound to the graphite surface by electrostatic interactions, rinsing the graphite surface with deionized water removed any unbound material, thus limiting deposition of aggregates. These strong electrostatic interactions also had the benefit of minimizing the tendency of the clay platelets to bend or curl. Graphite is uncharged, so adsorption of the polyelectrolyte onto its surface may be facilitated by oxidized defects within the individual graphite sheets, especially at their edges (McCreery 1991).

Materials and Methods

Both the sodium montmorillonite (2.71% [w/w] aqueous suspension) and Laponite RD (powder) were obtained as a gift from Southern Clay Products, Inc. (Gonzales, Tx, USA). To remove large aggregates from the as-received sodium montmorillonite, the suspension was diluted by a factor of 10 with Milli-Q water and centrifuged at 3300 rpm for 24 h using a Fisher safety centrifuge (Fisher Scientifc, International, Pittsburgh, Pa., USA) The resulting yellowish supernatant was used in these experiments and had a concentration of 0.25% (w/w), as determined by gravimetric analysis.

Samples for microscopy were prepared by attaching a thin layer of freshly peeled pyrolytic graphite "ZYH grade," (Advanced Ceramics, Cleveland, Ohio, USA) onto the surface of a silicon wafer using double-sided tape. The surface of the graphite was treated with 1% (w/w) aqueous PDDA (MW 200,000–350,000, Aldrich) (Sigma Aldrich Corp., St. Louis, Mo., USA) and after 5 min carefully rinsed with purified water (Milli-Q) and blown dry with N_2. Subsequently, the surface was treated with a 0.20% (w/w) aqueous suspension of the clay for 5 min, and then rinsed with water and dried. This technique produced a clay-covered surface of ~1 cm^2 in area.

Scanning electron micrographs were obtained using a Hitachi S-4700 field emission SEM with an upper secondary electron detector (through-the-lens) (Hitachi High Technologies, Tokyo, Japan). Images were acquired at accelerating voltages between 0.6 and 1.0 kV. Samples were uncoated and mounted on aluminum stubs.

Results and Discussion

Microscopy of Centrifuged Montmorillonite

Representative micrographs of centrifuged montmorillonite (supernatant) adsorbed onto polyelectrolyte-treated graphite are shown in Figure 1. At low magnification (Fig. 1a), a large number of clay platelets adsorbed on the surface are clearly visible. Most of the surface area is occupied by irregularly shaped particles ~200 to 600 nm in lateral dimensions, though a large number of smaller particles is also present. At higher magnification (Fig. 1b), the uniformity in intensity of the majority of the platelets is consistent with the adsorption of single, exfoliated sheets rather than of aggregates containing multiple sheets. In areas where it appears that two sheets are lying on top of

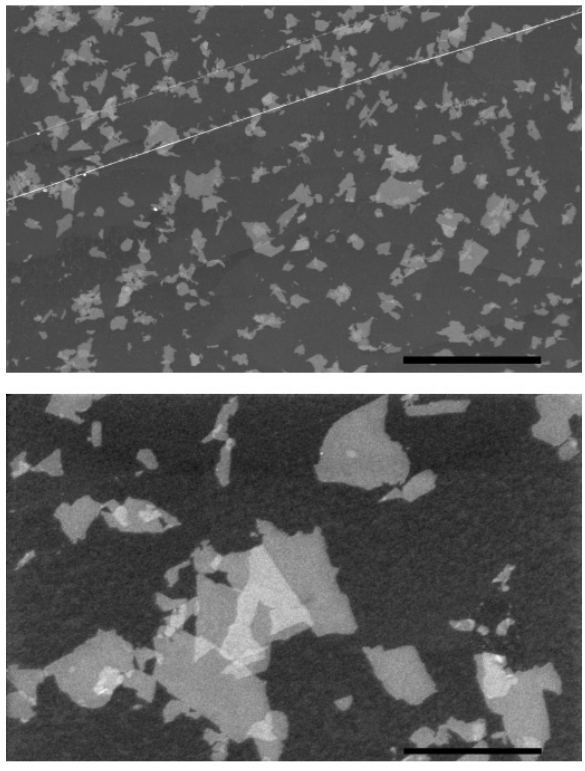

FIG. 1 Low-magnification (a, 10 k) and higher-magnification (b, 50 k) scanning electron micrographs of centrifuged montmorillonite adsorbed onto a polyelectrolyte-treated pyrolytic graphite surface. The images were acquired at an accelerating voltage of 1.0 kV and the scale bars are 3 μm (a) and 600 nm (b) in length.

one another, the intensity is again uniformly higher over that area, consistent with the presence of only one additional sheet. The adsorption of more than one clay layer could be due to the presence of excess polyelectrolyte on top of an adsorbed platelet, which could absorb a second layer or trap a folded platelet. From the uniformity of these various brighter regions, it is clear that they are not due to the presence of unexfoliated material in the clay suspension. Adsorption of unexfoliated material would be expected to give a range of brightnesses arising from a distribution of clusters with different numbers of platelets (vide infra). From the quality of these images, it appears that platelets at least as small as ~60-nm can be characterized by this imaging technique.

Microscopy of the Uncentrifuged Montmorillonite

Centrifugation of the as-received montmorillonite suspension resulted in about a 90% reduction in clay content, so images were also obtained of the montmorillonite prior to centrifugation for comparison. Even though the as-received (2.71% w/w) aqueous montmorillonite was diluted to 0.20% (w/w) with deionized water and stirred for 2 days, the resulting dispersion had a slightly cloudy appearance, compared with the yellow-tinted, but clear, centrifuged dispersion (0.20% w/w). In contrast to the low surface coverage of platelets seen in Figure 1, the surface treated with the uncentrifuged clay contained such a high coverage of material that individual platelets could not be identified (Fig. 2). At higher magnification (Fig. 2b), it was clear from the numerous contrast levels present in the image that the adsorbed material contained a significant fraction of unexfoliated clusters of platelets. Given that the same treatment conditions were used for both the centrifuged and uncentrifuged clay, the adsorption of single clay sheets versus unexfoliated clusters would explain the stark differences in the surface coverages. These images also demonstrate the importance of using centrifugation or other purification procedures, and not simple dilution, to prepare montmorillonite for use in applications requiring exfoliated clay (e.g., composite formation).

Microscopy of Laponite RD

Compared with the high-quality images obtained for centrifuged montmorillonite, imaging the much smaller platelets of Laponite RD proved difficult. At low magnification (Fig. 3a), micrographs revealed that the surface coverage was not as uniform as found for centrifuged montmorillonite (Fig. 1a). Instead, the Laponite RD appeared to

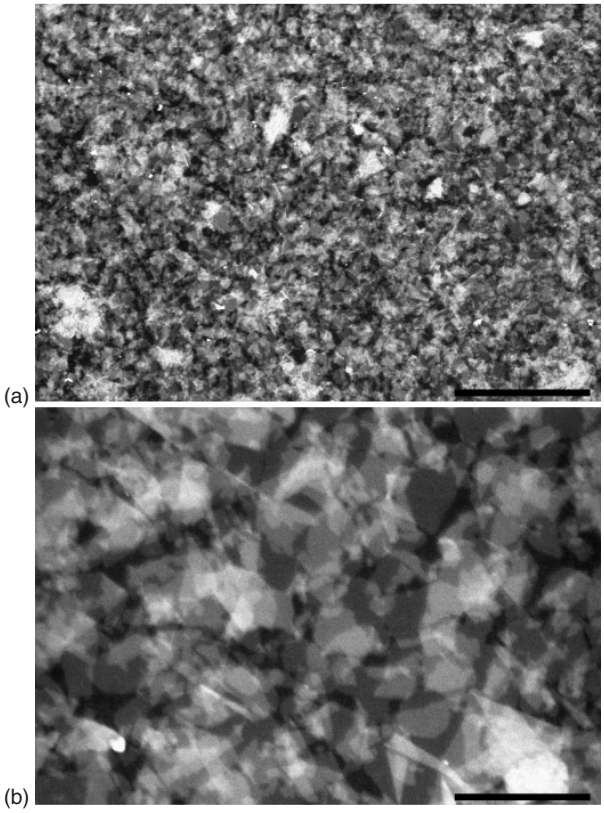

FIG. 2 Low-magnification (a, 10 k) and higher-magnification (b, 50 k) scanning electron micrographs of uncentrifuged montmorillonite adsorbed onto a polyelectrolyte-treated pyrolytic graphite surface. The images were acquired at an accelerating voltage of 0.8 kV and the scale bars are 3 μm (a) and 600 nm (b) in length.

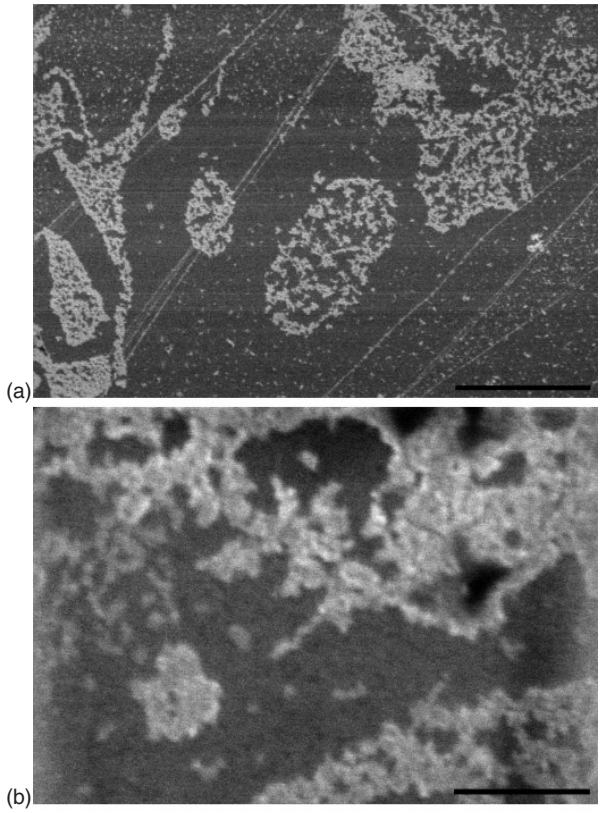

FIG. 3 Low-magnification (a) and higher-magnification (b) scanning electron micrographs of Laponite RD adsorbed onto a polyelectrolyte-treated pyrolytic graphite surface. The images were acquired at an accelerating voltage of 0.6 kV and the scale bars are 3 μm (a) and 300 nm (b) in length.

have aggregated into clusters upon adsorption onto the polyelectrolyte-treated surface. Although clustering prevented us from identifying single sheets, even at very high magnification (Fig. 3b), the average feature size did correspond to the ~30 nm^2 reported for Laponite RD (Alcover *et al*. 2000, Kleinfeld and Ferguson 1994, Nicolai and Cocard 2000, Rosta and von Gunten 1990, Thompson and Butterworth 1992).

Conclusions

A method for obtaining unambiguous images of clay particles by scanning electron microscopy (SEM) by adsorption of the particles onto a polyelectrolyte-treated graphite surface has been described. Images of centrifuged montmorillonite showed that the material contained predominately single, exfoliated sheets between 200 and 600 nm in lateral dimensions. Films adsorbed from an unexfoliated montmorillonite suspension, however, contained large unexfoliated clusters, indicating the importance of centrifugation in the purification of the montmorillonite for use in applications requiring exfoliation. Images obtained of the synthetic clay Laponite RD had size features consistent with those reported previously (Alcover *et al*. 2000, Kleinfeld and Ferguson 1994, Nicolai and Cocard 2000, Rosta and von Gunten 1990, Thompson and Butterworth 1992). The ability to determine the size and shape of clay platelets accurately using this technique should facilitate the interpretation of images of clay platelets adsorbed onto other substrates (e.g., silicon) or of clay platelets within other matrices (e.g., polymer composites).

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