



Research paper

Reflections on the material science of clay minerals



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ABSTRACT

Possible new applications of clay minerals are explored continuously. Three such areas are clay–polymer nanocomposites, clay mineral films and clay mineral catalysts. Advances in these areas must come from the increase of fundamental knowledge of the clay minerals, especially the expanding clay minerals or smectites. Examples of fundamental research areas are: the mechanical properties of single clay layers and the change of these mechanical properties with the number of layers in a clay mineral particle; control of the organization of clay mineral layers and of molecules in the interlayer space for the production of functional films; and the distribution of pillars and of metal nanoparticles in the interlayer space for application as catalysts. Natural clay minerals suffer from several disadvantages, such as the presence of impurities and inhomogeneities in sizes and shapes of particles and in charge distribution. Synthesis of clay minerals with well-defined sizes and shapes of the particles and with homogeneous charge distribution is imperative to obtain significant advancement of knowledge.

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1. Introduction

“The production of clay minerals for industrial and environmental uses continues to grow annually and new applications of clays are an exciting area of research and development. Sorbent clays, pillared clays, swelling clays and surface modified clays all have applications in the expanding environmental markets such as landfills, fluid barrier applications, selective ion sorption and others. The major industrial applications of clays are still expanding including uses in paper, paint, plastics, ceramics, drilling fluids, foundry bondants, catalysts, agriculture, construction materials, pet litters, sorbents for oil and water spills and many others. The outlook for the future of applied clay science is indeed bright and hopefully we, the members of AIPEA, can cooperate to make AIPEA the focus of international research and development of clays and clay minerals for clay science” (Murray, 1994).

These words were written by H. Murray in 1993 as incoming president of AIPEA. They are prophetic indeed and still valid today. At that time the emphasis was clearly on the role of clays and clay minerals in environmental science and technology. Now, 22 years later, the environmental scope of clays and clay minerals is supplemented by increased interest in research and development in at least 3 areas: (1) clay–polymer nanocomposites (CPN), including clay–biopolymer nanocomposites; (2) hybrid clay mineral films with special optical and electrochemical properties; and (3) heterogeneous catalysis, including bioreactive clay minerals.

2. Clay–polymer nanocomposites

CPN's have been studied intensively for more than 20 years. The earlier work has been reviewed extensively by Ray and Okamoto (2003). More recently, several chapters in the handbook of Clay Science (Bergaya et al., 2013; Detellier and Letaief, 2013; Lambert et al., 2013; Ruiz-Hitzky et al., 2013) and a CMS workshop have also been devoted to CPN's (Carrado and Bergaya, 2007).

CPN's are expected to have improved mechanical properties, improved heat stability and improved gas barrier properties with respect to those of the neat polymer. In many applications the transparency of the CPN's is also an issue and one has to control the optical properties of the CPN's too. In particular, the light scattering has to be minimized. These improvements depend on (1) the dispersion of the clay mineral layers and particles in the polymer matrix; (2) the nature and strength of the clay mineral–polymer interactions; and (3) the properties of the clay mineral itself such as the shape of the layers and particles, the amount and location of the isomorphous substitution, and the number and type of edge sites.

In the successful preparation of CPN's the hydrophobic/hydrophilic properties of polymer and clay minerals have to be matched. This is most easily done by exchange of the clay mineral with alkylammonium, alkyl phosphonium and alkylpyridinium cations. Smectites are then the preferred clay minerals. The d_{001} spacing increases upon exchange of these alkylcations. This has two advantages: (1) polymer chains can more easily diffuse in the interlayer space; and (2) as a consequence the d_{001} spacing might increase to such an extent that exfoliation occurs. The CPN's contain then individual smectite layers and clay mineral particles of various sizes i.e. composed of 2, 3 or more layers.

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One might intuitively think that complete dispersion or complete exfoliation i.e. up to individual layers is the ideal to be achieved. It maximizes the number of clay mineral layers in the polymer matrix and it maximizes the contact and interaction between the clay mineral surfaces and the polymer molecules. However, the mechanical properties of individual clay mineral layers, 0.96 nm thick, are unknown. Sato et al. (2001) have performed a molecular dynamics (MD) simulation on a single layer of beidellite with composition $[\text{Si}_{31/3} \text{Al}_{2/3}]\text{IV}[\text{Al}_2]\text{O}_{10}(\text{OH})_2\text{Na}_{2/3}$. They found that a compression in the A direction by 3–40% leads to a curved layer, which breaks up once the compression exceeds 40% (Fig. 1). This curving is mainly due to a change in Si–O–Si bond angles and not to a change of bond lengths. This indicates that under external forces in a polymer matrix single layers might easily bend or curl. Measurement of the mechanical properties of single layers of natural smectites to confirm these predictions are extremely difficult to perform. The reasons are multifold: (1) presence of impurity particles on the clay mineral layers; (2) ill-defined edges of the layers and particles; (3) heterogeneity of the charge distribution in the layers; (4) non-uniform hydration of the layers in the clay mineral particles; (5) irregular stacking of the layers in the particles.

Kunz et al. (2009) measured the deformation of particles of a synthetic Fluor-hectorite (F-hectorite) by atomic force microscopy (AFM). F-hectorite is obtained by melt synthesis and consists of up to 10 μm crystals. The individual layers are aligned perfectly parallel in the particles and have a uniform charge density. The particles have sharp edges and a smooth well-defined morphology. The bending elasticity along the c^* -direction is measured to be $C_{33} = 21 \pm 9$ GPa, assuming that the particle is clamped on both sides and 48 ± 20 GPa under the assumption that the particle is free i.e. not clamped on both sides. These numbers have to be compared with those of rectorite, 18.3 ± 4.6 GPa and micas, 54.9–70.5 GPa. The differences in the numbers can be attributed to hydration, charge density and nature of the charge-compensating cation. F-hectorite is a one layer hydrate with $d_{001} = 1.23$ nm. In rectorite half of the interlayers are one layer hydrates. In micas there is no interlayer water. The charge compensating cation is K^+ in micas,

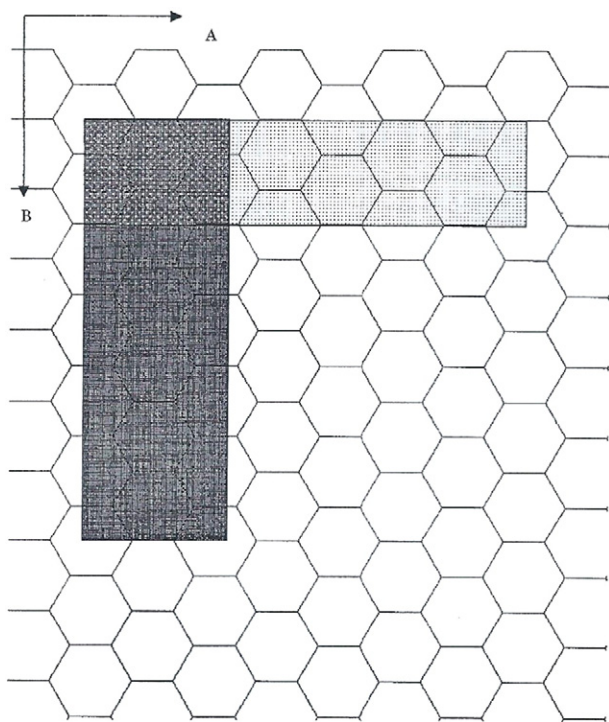


Fig. 1. Schematic drawing of the basic cell structure of beidellite: the A-type cell includes a $18 \times 3 \times 1$ A-bending layer; the B-type cell includes a $6 \times 12 \times 1$ B-bending layer. Adapted from Sato et al. (2001) with permission of ACS.

while it is Na^+ for F-hectorite and the charge density of mica is twice that of F-hectorite.

Particles with a thickness of less than 20 nm cannot yet be measured with this AFM technique. Such thin particles tend to be sucked into the gaps of the substrate (Fig. 2) and to be huddled against the wall of the substrate. This is an indirect proof of the easy bending and curling of single layers and of particles less than 20 nm thick or consisting of 2–15 layers.

The search for optimum dispersion of the clay mineral layers and particles is a research topic of primary importance. This optimum dispersion will depend on the size, shape, charge density and hydration of the clay mineral layers. It will be different for Laponite than for montmorillonite, saponite or hectorite. Recent studies on 1:1 clay minerals such as kaolinite might also be inspirational.

Several strategies can be followed to prepare CPN's from kaolinite, but they all start with a pre-intercalate (Detellier and Letaief, 2013; Detellier and Schoonheydt, 2014). Exfoliation can be achieved, producing single layers of kaolinite in the form of nanorolls or nanotubes. This is a very interesting observation. It shows that single layers of 1:1 clay minerals curl into nanotubes. At the basis is the difference in bond lengths between Si–O bonds in the tetrahedral sheet, typically 0.162 nm, and Al–O bonds in the octahedral sheets, typically 0.187 nm. Imogolite and halloysite are 1:1 nanotubes which exist in nature. Single layers of 2:1 clay minerals such as smectites do not curl into nanotubes. The same differences in bond lengths of Si–O bonds on one hand and Al–O or Mg–O bonds on the other hand exist, but the octahedral sheet is sandwiched between two tetrahedral sheets, preventing curling up of single layers into nanotubes. The expectation is that the single 2:1 layers do not spontaneously curl into nanotubes, but that they are easily bent. When deposited on a surface they will adapt their shape to the shape (roughness) of that surface. In a polymer matrix the shape of the single layers of 2:1 clay minerals such as smectites is determined by the interaction with the polymer chains. If the interaction of the single layer–polymer chain is weak, the polymer acts as a solvent. If the interaction of the single layer–polymer is strong, a smectite–polymer complex is present in the CPN and the mechanical properties of the CPN are expected to be different from those of the neat polymer and the neat clay mineral.

Nacre is an extremely hard natural material composed of inorganic nanoparticles cemented together by polymeric molecules. One would like to prepare artificial nacre, which could eventually be used as a bone implant. Clay minerals, in particular smectites, could be used and have been used to construct such artificial nacre-like implants. The composite has a “brick-and-mortar” structure (Fig. 3), the bricks being the smectite particles and the polymeric chains act as mortar. Such a brick-and-mortar structure can be obtained by layer-by-layer (LbL) assemblage in which layers and particles of Na-montmorillonite and of a cationic polymer such as PDDA (PDDA = poly(diallyldimethylammonium)) are alternately deposited and held together by electrostatic and van de Waals forces (Podsiadlo et al., 2005). Such structures can absorb quite a lot of energy. Upon deformation the layers of montmorillonite might

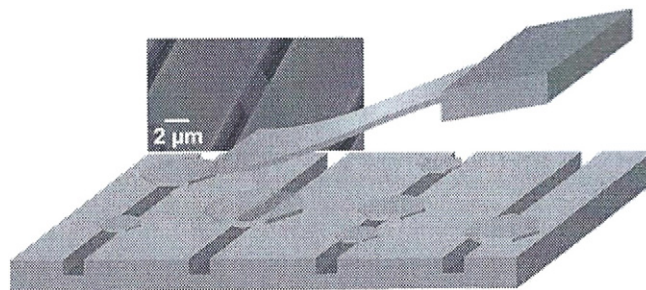


Fig. 2. AFM set-up to measure the mechanical properties of F-hectorite: The F-hectorite particles are shown as hexagons lying over the 2 μm wide channels of the substrate. Adapted from Kunz et al. (2009) with permission Of ACS.

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