Hydrophobic Intercalation of Layered Silicate Clays and Hierarchical Self-Assemblies via Platelet-Shape Directing

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Summary: Most clay research in recent years has centered on the development of polymer/layered-silicate nanocomposites besides the conventional applications such as catalyst and adsorbents for organics. Recently, we have reported the hydrophobic modification of the naturally-occurring sodium montmorillonite clay (*d* spacing = 12 Å) by exchanging with hydrophobic poly(oxypropylene)-diamine salts (POP-salt) to afford the space-enlarged silicates (*d* spacing up to 50–60 Å). Owing to the geometrically plate-like shape and surface ionic charges, the organoclays enabled to self-assemble into rod-shape morphologies. For example, unique formation of lengthy rod (*ca.* 0.3 μm in diameter and up to 40 μm in length) was observed by using scanning electron microscopy (SEM). The self-assembling mechanism may involve the piling of the primary stack units by face-to-face and edge-to-edge alignments. The clay primary stacks intercalated by POP-salt and the hydrophilic analog of poly(oxyethylene)-diamine salts were observed by AFM.

Keywords: clay; hydrophobic; piling mechanism; self-assembly; silicate platelet

Introduction

Self-assembling phenomena are well-reported for the naturally occurring materials, including biomaterials,[1] inorganic clays[2] and biominerals[3–5] Recent development of bottom-up nanotechnology for fabricating the devices in nanometer scale have changed the face of material applications in the areas of electronic,[6] magnetic,[7] photonic materials,[8] and quantum dots.[9] The bottom-up syntheses mainly involves the principles of non-covalent bonding forces such as electrostatic charge attraction, hydrogen bonding, van der Waals forces, and hydrophobic effect, in a cooperative manner.

For the natural clays, the high-aspect-ratio plates in forming ordered orientation and exhibiting a liquid crystal behavior[10] had been reported, however, their self-assembling into microarrays is yet widely recognized. In our previous studies, it is realized that the montmorillonite clay has an average 8–10 plate stacks as the primary units with a widely dispersed plate dimension ranging from 80–100 nm wide and 1 nm thickness for individual plates. By using various molecular weight of hydrophobic poly(oxypropylene) (POP) amine salts, the originally hydrophilic clays were converted into hydrophobic property.[11] The ability of self-assembling to microarrays was reported.[12] Furthermore, both of montmorillonite (MMT) and synthetic fluorinated mica (mica) with different platelet sizes were compared for their self-assembling phenomenon. Based on the detailed analyses of the rod-like morphology, a mechanism to account for the observation was proposed. And the direct observation (by AFM) of the primary clay units with hydrophobic poly(oxypropylene)- and hydrophilic poly(oxyethylene)-amine salts was used to support the mechanism.

Materials and Methods

The synthetic fluorinated mica (mica; SOMASIF^{TM} ME-100) with a cation exchange capacity (CEC) = 1.20 mequiv./g

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was obtained from CO-OP Chemical Co. (Japan). Sodium montmorillonite (Na^+-MMT), Na^+ form of layered smectite clay with cation-exchange-capacity (CEC) of 1.20 mequiv./g was supplied from Nanocor Co. Poly(oxyalkylene)-backboned polyamines include hydrophilic poly(oxyethylene) (POE)-amine and poly(oxyproplylene) (POP)-amines which are commercially available under the trade name of Jeffamine® amines and purchased from Huntsman Chemical Co. or Aldrich Chemical Co. The POE2000 diamine is a α,ω-diamine of poly(oxypropylene)-*b*-poly(oxyethylene)-*b*-poly(oxyproplylene) of 2000 M_w (i.e. Jeffamine® ED-2003, amine content 0.93 mequiv./g and averaged 38.7 oxyethylene units and 6 oxypropylene units in the backbone), and water-soluble amine. The POP2000 diamine is a polyoxypropylene-bis-(2-propylamine) of 2000 M_w (i.e. Jeffamine® D-2000, amine content 0.97 mequiv./g and averaged 33 oxypropylene units in the backbone).

Preparation of Self-Assembled POP-mica and MMT

The preparation of POP-amine salt intercalation to MMT and mica has been reported previously. For the self-assemblies of these organoclays, the samples were obtained by using the following procedures. The air-dried POP-mica and MMT (0.2 CEC) and dispersing it in water at 1 wt% concentration by using an ultrasonic vibrator as the homogenizer until homogeneous. The water-dispersed sample was coated onto a glass plate surface for which was subsequently dried under a control evaporation to obtain the self-assemblies.

Results and Discussion

Hydrophobically Intercalated Layered Silicates by Poly(oxyalkylene)-amine Salts as the Intercalating Agents

Both of the natural montmorillonite (MMT) and the synthetic fluorinated mica (mica) have a similar layered structure with sodium counter metal ions in the primary stack. The mica clay has a dimensional range of 300–1000 nm, a 1 nm in thickness for each layer and an average of 4–6 platelets in one stack, compared to the smaller size for MMT (100 nm $\times$ 1 nm). The uses of poly(oxyalkylene)-amines of 2000 g/mol M_w for the intercalation of Na^+-MMT led to the preparation of orgnaoclays with hydrophobic property and enlarged *d* spacing. Poly(oxyalkylene)-diamines (POA-amine) are commercially available polyether amines, with polyethylene glycols or

Table 1.
Self-assemblies of hydrophobically-modified clays to orderly micro-arrays.

Polyether-amine-salt intercalated to clay CEC[a)]	*d* spacing (nm) and organic fraction (wt % in parenthesis)		Dispersion (MMT and mica)		Observation of self-assemblies by SEM (dispersed in water, then 80 °C drying)
	MMT	Mica	Water	Toluene	
Pristine	1.2	1.2	dispersible	aggregate	amorphous
POP-intercalated[b)]					
0.2	1.9 (22)	1.5 (24)	dispersible	aggregate	rods from MMT: 0.1–0.8 μm in width and ~10 μm in length rods from mica: 0.3–2.0 μm in width and ~30 μm in length
0.5	2.0 (34)	4.0 (48)	partially aggregate	partially aggregate	rods
1.0	5.7 (63)	4.1 (53)	aggregate	dispersible	amorphous
POE-intercalated[b)]					
1.0	1.9 (43)	1.8 (52)	dispersible	aggregate	Polymer-like amorphous

[a)] cation exchange capacity (CEC): MMT (montmorillonite) and Mica (Synthetic fluorinated mica) = 120 meqiv./100 g.
[b)] POP: Poly(oxypropylene) amine salt (2000 g/mol Mw); POE: Poly(oxyethylene) amine salt (2000 g/mol Mw).

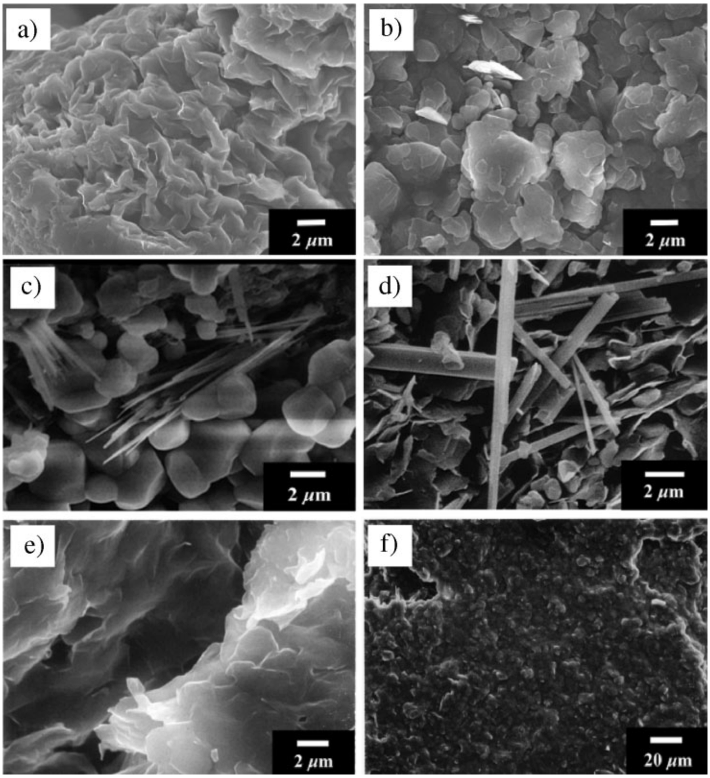

Figure 1.
SEM micrographs of self-assembling morphology from polyether-amine-salt intercalated clays (a) pristine Na^+-MMT, (b) pristine Mica, (c) POP-MMT (0.2 CEC),[12] (d) POP-Mica (0.2 CEC),[14] (e) POP-Mica (1.0 CEC), (f) POE-Mica (1.0 CEC).

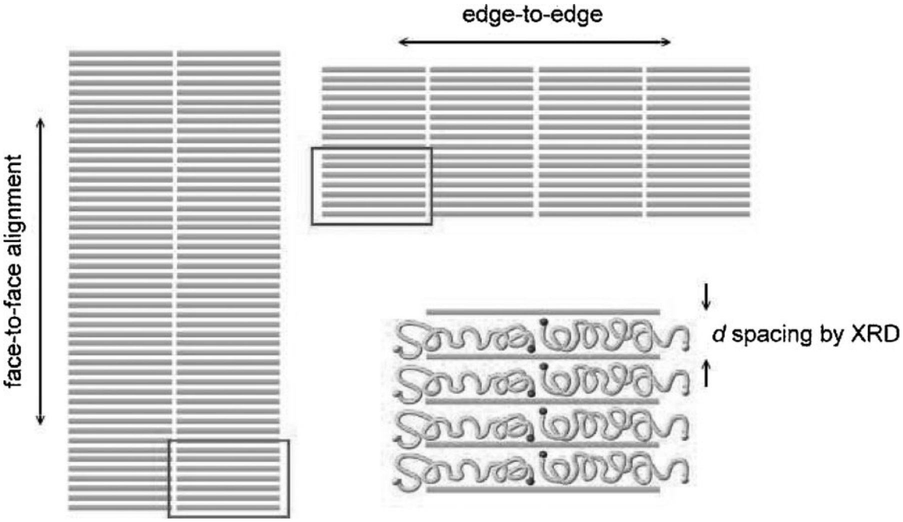

Figure 2.
Proposed mechanism for the self-assembling to rod-morphologies from the primary units of organoclays.

polypropylene glycols as the backbone. For example, there are hydrophobic and hydrophilic types of POA-amines, that is poly(oxypropylene)- amines (POP-amines) and poly(oxyethylene)- amines (POE-amines), respectively. By using the POP-salts of 230, 400, 2000, and 4000 g/mol for the Na^+-MMT intercalation, varied XRD basal spacing (15.0, 19.4, 58.0, and 92.0 Å, respectively were obtained.[13] On the other hand, the hydrophilic POE-salt of 2000 g/mol molecular weight gave the silicates of 19 Å spacing. For the POP intercalation, different hydrophobic properties of organoclays could be obtained by using the varied CEC ionic exchange equivalent ratio of POP/CEC clay. By using these clays with different hydrophobic character or POP amounts, the self-assembling behavior was investigated.

Morphologies of the Self-Assemblies from Organoclays

As summarized in Table 1, the hydrophobic POP may be intercalated into the layered structure of MMT and mica at various CEC equivalent ratios, for example, 0.2, 0.5 and 1.0. It was found that the particular organoclays at the 0.2 CEC equivalent ratio could self-assemble to form lengthy rods. Average dimension of 0.1–0.8 μm in width, 10 μm in length for MMT and a similar diameter but longer rods for mica were

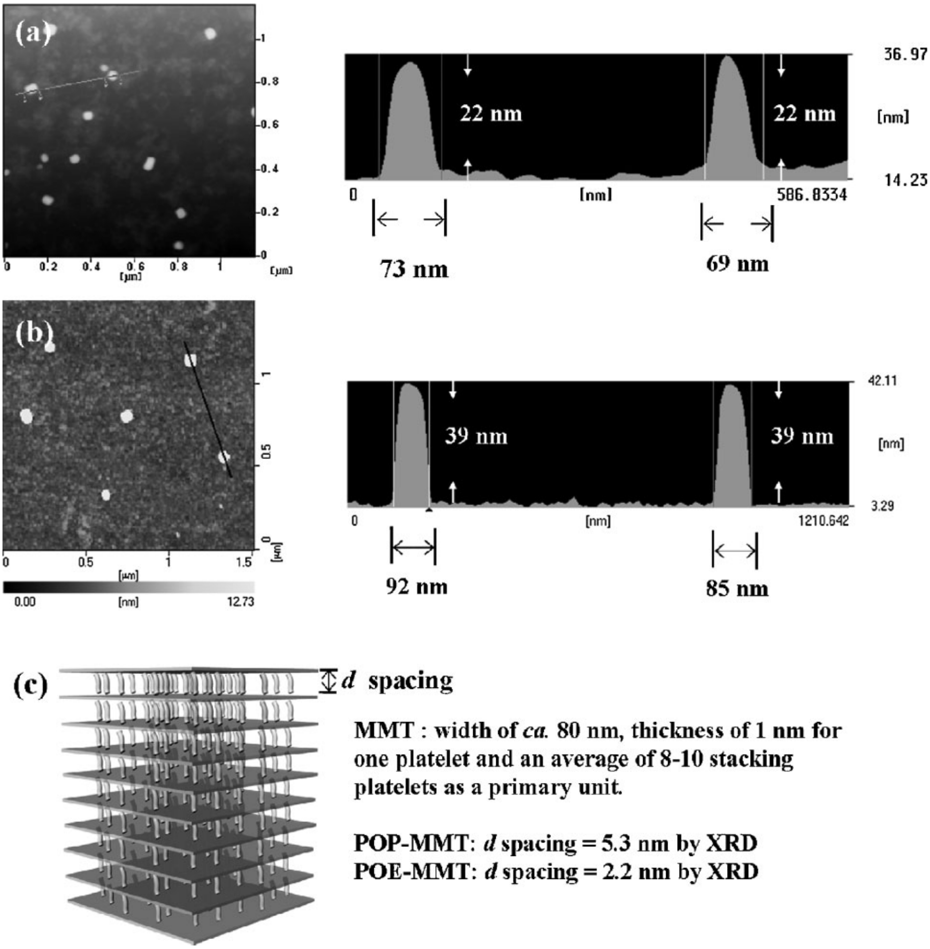

Figure 3.
AFM direct observation of the primary unit for the self-assembly (a) Primary structure of POE-MMT, (b) Primary structure of POP-MMT, (c) conceptual explanation for the primary unit of POP- and POE-MMT.

observed by SEM (Figure 1c, d). For the pristine clays and other organoclays such as the POP at 1.0 CEC intercalation, the hydrophobic nature is out of the balance in amphiphilicity and fails to afford an orderly morphology of self-assembling under the same self-assembling conditions (Figure 1a, b, e and f).

Mechanism of the Self-Assembly

The self-assembled morphologies may be explained by the primary unit piling through both of plate face-to-face and POP edge-to-edge arrangements to grow the rod diameter and length, respectively, as illustrated in Figure 2. It seems that the face-to-face piling was predominant for both types of organoclays, particularly for the mica organoclays.

Observation of Organoclay Units Enabling the Self-Assembly by AFM

In Figure 3, the fundamental organoclay units are examined by AFM. For example, the clay unit of POP-MMT (5.3 nm from the XRD *d* spacing) has an average height of 40 nm from the topographical image of AFM analysis. The approximate calculation amounts to 40 nm is amount to 7$\sim$8 layers for the primary unit. In the case of the organoclay with POE intercalation, the primary unit was also observed by AFM. The well defined structure with MMT is approximately 69, 73, 85 and 92 nm in width and 1 nm thickness for each layer and 8$\sim$10 platelets in a stack. X-ray diffraction analyses showed d spacing $= 2.2$ nm for the POE/MMT (one layer platelet and one interlayer). By using a AFM topographical analysis, the clay dimension of POE/MMT (2.2 nm XRD *d* spacing) exhibits an average height of 21 nm in height and 69–73 nm in width. These calculations was consistent with the number of 8$\sim$10 platelets in a stack.

For observation from POP/MMT, the organoclay was dispersed in water and thinly coated on glass substrate before the procedure of controlled evaporation. It is noted that all of these organoclays from POP- and POE-MMT had the units faced onto the glass substrate in the same direction. The vertical arrangement between the units and glass surface implies the self-assembling in favoring the face-to-face vertical growth of the rod-like structure. Hence, the formation of rod-morphologies is believed to be dominated by the factor of high aspect-ratio geometric shape.

Conclusions

The hydrophobic POP-amine-salt intercalated clays with an appropriated amount of POP embedment was capable of self-assembling into lengthy rod morphology. By comparison, the pristine MMT and mica clays and their organoclays with over 0.5 CEC intercalation could only lead to amorphous morphology. The requirement for the self-assemblies is relied on the balance of two directions of face-to-face platelet piling and edge-to-edge POP alignment. The observation of the fundamental unit of POP-MMT organoclays by AFM on glass substrate clearly illustrates the detailed structure of multiple lamella, platelet dimension and POP-silicate alternation. The unique self-assembling process opens up the possibility of fabricating a new class of clay crystals, in the current example, rod-like microstructures with a high regularity in space between the silicate and organics in an alternating manner.

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