Formation and Structure of Organized Molecular Films of Organo-modified Montmorillonite

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Molecular arrangement and morphology of Langmuir-Blodgett (LB) films for the several organo-modified montmorillonites were investigated by out-of plane and in-plane X-ray diffraction (XRD), and atomic force microscopy (AFM). These organo-modified montmorillonites are formed by cation exchange reaction with quaternary ammonium reagents containing octadecyl chain. The organo-modified montmorillonites formed extremely condensed monolayer on the water surface estimated by surface pressure-area (π -A) isotherms. From the results of out-of plane XRD, formation of highly ordered layer structure was confirmed in these clay LB film. Further, two-dimensional lattice of long alkyl chain of organo-modified parts packed hexagonally or orthorhombically in the films. Surface morphology of Z-type monolayers on solid of organo-modified montmorillonites indicates heterogeneous modification ratio in montmorillonite surface by tapping mode AFM observation.

Key words: Langmuir-Blodgett film, organo-modified montmorillonite, molecular arrangement, surface morphology

1. INTRODUCTION

Clay minerals have played important roles in the modern technology. For example, new materials of functional ceramics are made from mica.¹ Organo-clay composites have been extensively investigated in material science.² Thin films of clay minerals have been studied in application to modified electrodes, sensors, photochromic devices, nonlinear optical devices, and so on.³ The Langmuir-Blodgett (LB) method is one of the most useful techniques to prepare ultra-thin films.⁴ In this method, floating molecular monolayers formed at an air/water interface are deposited on a solid substrate in a layer-by-layer way. Ultra-thin films of clay minerals prepared by the LB method have been reported.⁵ Recently, the clay LB films have been hybridized with alkylammonium cations.⁶ Smectite clay is exfoliated into single clay sheets with the negative charge in an aqueous suspension at a low concentration.⁷ When a solution of an amphiphilic alkylammonium salt is spread onto the clay suspension, the negatively charged clay platelets in the suspension are adsorbed onto a floating monolayer of the alkylammonium cation at an air-clay suspension interface. The hybrid monolayers of the clay platelets and the ammonium cations formed at the interface can be transferred onto a solid surface to fabricate a hybrid multilayer. Interestingly, a floating monolayer of a water-soluble alkylammonium cation is stabilized at the air-suspension interface by the hybridization with the clay platelets.⁶ The surface pressure-area (π -A) isotherm of the hybrid monolayer is dependent on the clay

concentration in the suspension: as the concentration is higher, the isotherm shifts to the larger area side.⁶ This suggests that structure and properties of the hybrid mono- and

Figure 1 (a) Illustration of structure of montmorillonite before and after cation exchange reaction. (b) Chemical structure of quaternary ammonium reagents; (A) dimethyl methylbenzile octadecyl (DMPO), (B) dimethyl dioctadecyl (DMDO), (C) methyl hydroxy ethyl octadecyl (MHEO), and (D) trimethyl octadecyl (TMO) ammonium cations.

Figure 2 π -A isotherms of monolayers for organo-modified clays on the water surface (15 °C); (a) compression percentage vs. surface pressure (b) mean area per repeating units vs. surface pressure.

multi-layers would be varied depending on the clay concentration in the suspension. In this work, floating molecular monolayers and ultra-thin films on solid of pre-formed organo-modified montmorillonites (MMTs) were constructed by LB method. These LB multilayers of organo-modified MMTs were characterized by the out-of plane and in-plane X-ray diffraction (XRD) methods and atomic force microscopic (AFM) observation.

2. EXPERIMENTAL

2.1 Materials

Natural Na^+ -montmorillonite was kindly supplied by Kunimine Co. with the cation-exchange capacity of 108.6 meq/100 g. The organophilic clay was prepared by cation exchange reactions of natural clay (aqueous dispersion) with 20 % aqueous solution of dimethyl methylphenyl octadecyl (DMPO), dimethyl dioctadecyl (DMDO), trimethyl octadecyl (TMO), and methyl hydroxy ethyl octadecyl (MHEO) ammonium chloride (Fig. 1). Procedures of these organo-modifications of montmorillonites are described in reference.⁸

2.2 Formation of organized molecular films

The organo-modified clays were spread from

Figure 3 AFM images with the height information of Z-type monolayers of organo-modified clays; (a) DMPO-MMT, (b) DMDO-MMT, (c) MHEO-MMT, and (d) TMO-MMT (transferred at 15 mN/m², 1 × 1 μm² scales).

Figure 4 (a) X-ray powder diffraction profiles, and (b) Out-of plane XRD profiles of LB films (20 layers, 15 mN/m, 15 °C) for organo-modified clays: (A) DMPO-MMT, (B) DMDO-MMT, (C) MHEO-MMT, (D) TMO-MMT.

toluene solution (approximately 10^{-4} M) onto distilled water (approximately 18 MΩ·cm), respectively. The π -A isotherms were measured by a FACE film balance (Kyowa Kaimen Co.) at 15 °C. These monolayers were transferred onto

Figure 5 (a) SAXS pattern and profile of DMPO-MMT in bulk and (b) Out-of plane XRD profile of LB film for DMPO-MMT.

glass (XRD samples) or mica (AFM samples) substrates at 15 °C using the LB method.

2.3. Wide-angle X-ray diffraction (WAXD) of bulk powder and out-of plane X-ray diffraction of organized molecular films

The structures of the organo-modified MMTs in bulk and the layer structures of organized molecular films were characterized with a RAD-rA diffractometer (RIGAKU Co.; in the case of organized molecular films, the out-of plane X-ray diffraction method was used). Ni-filtered CuK α radiation (wavelength $\lambda = 0.154$ nm) was generated at 40 kV and 100 mA. The diffracted X-ray beam was monochromatized by a pyrographite monochromatic system and monitored by a scintillation counter.

2.4. Small-angle X-ray scattering (SAXS)

The crystalline morphology of the organo-modified clays was characterized with a SAXS instrument (M18XHF, MAC Science Co.) comprised of an 18 kW rotating-anode X-ray generator with a Cu target ($\lambda = 0.154$ nm) operated at 50 kV and 300 mA. This instrument was equipped with a pyrographite monochromator, pinhole collimation system ($\phi \sim 0.3, 0.3, 1.1$ mm), vacuum chamber for the scattered beam path, and two-dimensional imaging plate detector (DIP-220).

2.5 Atomic force microscopy (AFM)

The surface morphologies of the transferred monolayers were observed using a scanning probe

Table 1 Values of long spacings of organo-modified clays (a) in bulk and (b) in the LB films.

(a)

	2 θ (degree)	<i>d</i> -Spacing (Å)	<i>hkl</i>
DMPO-MMT	4.84	18.3	001
DMDO-MMT	3.98	22.2	001
MHEO-MMT	4.22	20.9	001
TMO-MMT	4.84	18.3	001

(b)

	2 θ (degree)	<i>d</i> -Spacing (Å)	<i>hkl</i>
DMPO-MMT	1.42	61.4	001
	2.78	31.8	002
	4.90	18.0	003
DMDO-MMT	1.44	62.2	001
	2.78	31.1	002
	4.90	18.0	003
	7.02	12.6	005
MHEO-MMT	1.53	57.9	001
	4.62	19.1	003
TMO-MMT	1.47	60.0	001
	4.40	20.0	003

microscope (Seiko Instrument, SPA300 with SPI-3800 probe station) using microfabricated rectangular Si cantilevers with integrated pyramidal tips with a constant force of 1.3 Nm⁻¹.

2.6 In-plane X-ray diffraction

The in-plane spacing of the two-dimensional lattice of the films was determined by analysis using an X-ray diffractometer for two-dimensional geometrical arrangements (Bruker AXS, MXP-BX, CuK α radiation, 40 kV, 40 mA, an instrument specially made to order) equipped with a parabolic graded multilayer mirror.

3. RESULTS AND DISCUSSION

Figure 2 shows the π -A isotherms of monolayer on the water surface of organo-modified MMTs. From these isotherms, we recognize formation of extremely stable monolayers. In this measurement, we represent two-type expression as “compression percentage vs. surface pressure” and “mean area per repeating units vs. surface pressure” plots because surface modification ratios are not always constant each other and 100 % coverage.

Figure 3 shows the AFM images of Z-type monolayer on solid transferred by LB method of organo-modified MMTs. From this measurement, it is found that surface morphology of these monolayers of organo-modified clays indicates heterogeneous modification ratio on montmorillonite surface.

Figure 4 shows comparison between wide-angle X-ray diffraction profiles in bulk and LB films of organo-modified MMTs. In the case of LB film, this measurement corresponds to out-of plane XRD along the layer axis of molecules (*c*-axis). In the bulk state (Fig. 4(a)), all four organo-modified MMTs indicate single diffraction peak around 20 Å on these profiles. Based on the results of SAXS measurement in bulk (Fig. 5(a)), it is found that all WAXD peaks

Figure 6 In-plane XRD profiles of LB films (20 layers, 15 mNm^{-1} , 15°C) for organo-modified montmorillonites; (a) DMPO-MMT, (b) DMDO-MMT, (c) MHEO-MMT and (d) TMO-MMT.

around $20 \text{ \AA}$ correspond to first order diffraction peaks along the c -axis (001).

From the results of out-of plane XRD at low angle region (Fig. 5(b)) to the LB film, it is found that organo-modified MMTs indicate long spacings around $60 \text{ \AA}$. Therefore, diffraction peaks confirmed at wide-angle region (Fig. 4(b)) correspond to higher order diffraction. These results are summarized in table 1. Comparison between regularity of layer structure in bulk and their LB films, organo-modified MMTs form the extremely developed layered organization in their LB multilayers.

Figure 6 shows in-plane XRD profiles of LB films of organo-modified MMTs. In order to estimate the packing mode of long alkyl chain in the organo-modified part, this measurement are carried out at the region related to sub-cell formation of hydrocarbons ($2\theta=10\sim30^\circ$). The organo-clay of only DMPO-MMT indicates single peak at $4.5 \text{ \AA}$ and other organo-modified clays show double peaks at 4.1 and $4.5 \text{ \AA}$ in the profiles of LB multilayers. Figure 7 shows schematic illustration of packing models for hydrocarbons in organo-modified parts on montmorillonite in the LB films. In the two-dimensional plane, alkyl-chains of DMPO-MMT packed hexagonally in their LB film. On the other hand, hydrocarbons of DMDO-MMT, MHEO-MMT, and TMO-MMT commonly form the two-dimensional orthorhombic lattice in the film plane. This structural change may show the influence on the existence of bulky phenyl groups in DMPO reagent

Figure 7 Two-dimensional lattice formed by long alkyl chain of organo-modified montorillonites in their LB films.

and its steric hindrance.

These experimental findings show the formation of highly order layered organization of organo-modified MMTs constructed by LB method. In this case, hydrocarbons in organo-modified part are closely packed as two-dimensional lattice although organo-modified ratio on montorillonite does not always indicate higher values.

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