

Structure Determination of Hybrid Films of Clay and Clay/Dendrimer Nanocomposite on Langmuir-Blodgett Film by X-Ray Reflectometry

Koji Mitamura* and Toyoko Imae***

*Graduate School of Science and **Research Center for Materials Science,
Nagoya University, Chikusa, Nagoya 464-8602, Japan
FAX: +81-52-789-5912, e-mail: imae@nano.chem.nagoya-u.ac.jp

Nanocomposite of positively charged clay hydrotalcite with carboxylate terminated 4.5th generation poly(amido amine) dendrimer has been prepared by intercalating the dendrimer into the clay sheets. The nanocomposite was adsorbed on arachidic acid Langmuir monolayer from water subphase and transferred on a substrate covered with arachidic acid Langmuir-Blodgett monolayer. The structure of the hybrid film was characterized by X-ray reflectometry and compared with that of a film consisting of only clay on arachidic acid bilayer. It was indicated that the hybrid film with nanocomposite was constituted with four layers of clay/dendrimer, while the hybrid film with only clay was composed of four layers of clay/counter anion or hydrated water. The detailed structure of these films was revealed by further analysis.

Key words: Clay, Hydrotalcite, Dendrimer, Poly(amido amine) Dendrimer, Dendrimer/Clay Nanocomposite, Nanocomposite, Arachidic Acid, Hybrid Film, Langmuir-Blodgett Film, Langmuir Monolayer, Bilayer, X-Ray Reflectometry, Reflectometry, Intercalation

1. INTRODUCTION

Clay compounds have been focused, since they have a unique structure of accumulated sheets [1]. By using this property, there was a study where a negatively charged clay was complexed with a positively charged polymer [2]. The polymer was not only adsorbed on the clay surface but also intercalated into the clay sheets. This nanocomposite consists of the alternate polymer/clay layers. As the application to drug delivery system, anticancer reagents were intercalated into the interlayer of the clay montmorillonite [3]. The complexation with organic compound changes the physical and chemical properties of the clay from those of original one [4,5]. Phthalocyanine was intercalated into the hydrophobic clay and the resulting composite showed the photo-decomposition reaction of *n*-nonylphenol [6]. In another study, conductive poly(aniline) intercalated into bentonite-vanadium(V) indicated conductivity and strong interaction with the clay [7].

In the present study, we prepared the nanocomposite of negatively charged dendrimer with positively charged hydrotalcite. The composite is expected as a material that has the characteristics of both dendrimer and clay. Especially, dendrimer can provide reaction matrix [8] and has ability to encapsulate some reagents in its internal void [9]. Thus, the dendrimer is expected to play a role on nanotechnology and drug delivery system etc. Here, we focused on the formation of a thin film of nanocomposite, since more advanced applications like sensor and electronics device are expected by the fixation of the nanocomposite film on a substrate. It is very important for building up the thin film with functional moieties that the array of the moieties is two- or three-dimensionally controlled. Then, its component and structure should be related to its physical property. In this point of view, reflectometric analysis by X-ray or

neutron provides the information about molecular orientation, as many researchers have reported [10-12]. We employed an X-ray reflectometry in order to reveal the internal structure of a nanocomposite film. By analyzing the obtained X-ray reflection (XR) data, we determined the composition and layer structure of the nanocomposite film and compared with those of clay film.

2. EXPERIMENTAL SECTION

2.1 Materials

Cationic clay, hydrotalcite ($[\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13}\text{Cl}_2]3.5\text{H}_2\text{O}$, anionic exchange capacity = 350 meq/100g, Kyowa Chemical Co. Ltd.), was donated by Prof. K. Takagi, Nagoya University. Carboxylate terminated 4.5th generation poly(amido amine) (PAMAM) dendrimer (Mw = 26,256, number of terminal groups = 128) in methanol was purchased from Aldrich Chemical Co. Arachidic acid (eicosanoic acid) and chloroform were purchased from Wako Pure Chemical Industries Co. Ltd. All chemicals were used without further purification. Silicon substrate was cleaned up by immersing into $\text{H}_2\text{SO}_4 / \text{H}_2\text{O}_2$ (= 3 : 1 volume ratio) for 10 min at 80 °C before use [13,14].

2.2 Preparation of Nanocomposite

Solvent in a methanol solution of PAMAM dendrimer was lyophilized by nitrogen gas-purge for 1h and afterwards in vacuo for 30 min. The residue was dissolved in water. Hydrotalcite was added into the aqueous PAMAM dendrimer solution at a charge ratio of 1 : 4 (hydrotalcite : PAMAM dendrimer). After shaken for 24 h at 70 °C, the mixture was filtered using a Millipore filter of 0.22 μm pore size and washed by water. The filtered residue was redispersed in water at a concentration of 20 mgcm^{-3} .

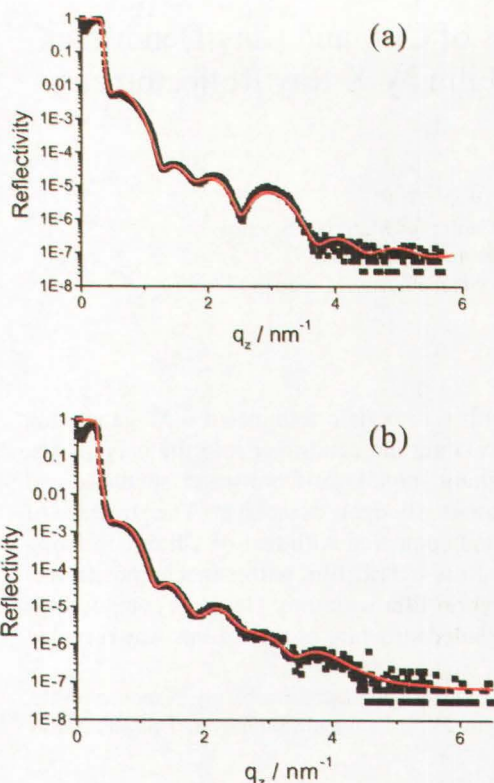


Fig.1 X ray reflection curves of the hydrotalcite (a) and hydrotalcite/dendrimer nanocomposite (b) on arachidic acid bilayer. The closed squares are experimental data and red lines are the calculated one.

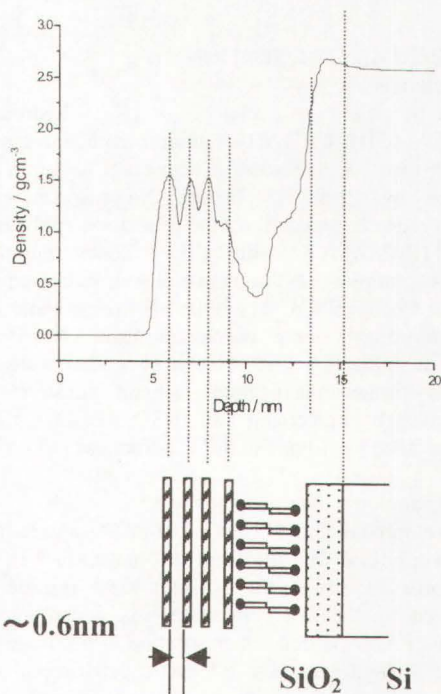


Fig.2 Depth profile and layer structure of hydrotalcite on ZX-type arachidic acid LB film.

2.3 Preparation of Thin films on Langmuir-Blodgett (LB) Film

A Langmuir monolayer of arachidic acid was prepared from a chloroform solution at room temperature ($\sim 25^\circ\text{C}$) using a LB film deposition apparatus (Nippon Laser & Electronics Laboratory), according to the procedure previously reported [15]. The monolayer was compressed up to 35 mNm^{-1} and transferred onto a silicon substrate, by a vertical dipping method with a transfer speed of 5 mmmin^{-1} , to obtain the Z-type film. After hydrotalcite or hydrotalcite/dendrimer nanocomposite was dispersed in the water subphase, a Langmuir monolayer of arachidic acid was prepared on it and transferred at 35 mNm^{-1} on the Z-type arachidic acid LB film after 2 h. Thus, the ZX-type LB film adsorbed hydrotalcite or its nanocomposite was obtained.

2.4 Measurement

XR measurement was carried out by a Rigaku X ray reflectometer (RINT2000) with X ray source from Cu/K α (200 mA / 40 kV). The X ray beam was monochromized by a multi-layered monochromator ($\lambda = 0.154\text{ nm}$). The divergence and receiving slits were 0.05 cm and 0.1 cm, respectively, in width. The adjustment of the sample stage was performed by a goniometer. The scan rate was $0.04^\circ\text{min}^{-1}$, and the angle step was 0.001° . The XR data were subtracted the background (the intensity at sufficiently large angle $2\theta = 8.0^\circ$) [16].

3. RESULTS AND DISCUSSION

Figure 1 shows X ray reflectivity as a function of a scattering vector component q_z at the direction ($=z$ axis) normal to the substrate surface. The curves were

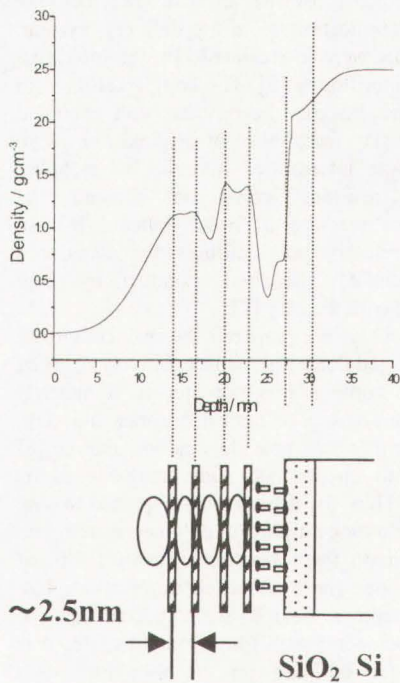


Fig.3 Depth profile and layer structure of nanocomposite on ZX-type arachidic acid LB film.

Table I Structure Parameters (Density, Thickness and Roughness) of Layers in Hybrid Film of Hydrotalcite on Arachidic Acid Bilayer.

Layer ^a	Density (g/cm ³)	Thickness (nm)	Roughness (nm)
Count	0.748	0.300	0.200
Hyd4	1.58	0.955	0.524
Count	0.745	0.300	0.200
Hyd3	1.59	0.716	0.600
Count	0.966	0.299	0.200
Hyd2	1.61	0.676	0.600
Count	0.798	0.299	0.200
Hyd1	1.53	0.664	0.606
Arach	0.352	2.03	1.19
Arach	1.10	200	0.357
SiO ₂	2.77	1.49	0.858
Si	2.58	∞	1.61

^a HydX, Xth hydrotalcite layer (X=1, 2, 3, 4); Count, layer of counter anion and/or hydrated water molecule; Arach, layer of arachidic acid monolayer.

measured for hybrid films of hydrotalcite and its nanocomposite with dendrimer on ZX-type arachidic acid LB film. In the both cases, several fringes that were produced by the reflection at the interface were observed with different profiles. This indicates that some finite layers exist in the films but the profiles are different between hydrotalcite and its nanocomposite hybrid films. The observed XR curves were analyzed by a following Equation (1) [17];

$$\frac{R(q_z)}{R_F(q_z)} = \left| \frac{1}{\rho_{sub}} \int_{-\infty}^{\infty} \frac{d\rho(z)}{dz} \exp(iq_z z) dz \right|^2 \quad (1)$$

where $R(q_z)$ and $R_F(q_z)$ are the reflectivity and the Fresnel reflectivity ($R_F \sim q_z^{-4}$), respectively, $\rho(z)$ is the averaged electron density of the layer at the distance z normal to the substrate surface, and ρ_{sub} means the electron density of the substrate.

It must be noticed that there is a silicon oxide layer on the surface of silicon substrate, the structure parameters (thickness and roughness) of which is changeable, since the surface structure of silicon oxide layer varies depending on the treatment of silicon substrate. In addition, clay consists of some sheets and there is a layer of counter anion or hydrating water molecule between clay sheets and on clay surface. Dendrimers are intercalated between the clay sheets and adsorbed on the clay surface by replacing counter anion or hydrated water. The initial structure parameters were appropriately selected for determining the film structure: Densities of dendrimer, clay, and arachidic acid were assumed to be ~ 1.22 [18], ~ 2.2 [19], and ~ 0.82 gcm⁻³ [20], respectively. In addition, the theoretical density (~ 2.33 gcm⁻³) of silicon substrate is already known. As further assumption, thickness of clay sheet is 0.5~1 nm [21] and that of intercalated dendrimer layer must be

Table II Structure Parameters (Density, Thickness and Roughness) of Layers in Hybrid Film of Hydrotalcite/Dendrimer Nanocomposite on Arachidic Acid Bilayer.

Layer ^a	Density (g/cm ³)	Thickness (nm)	Roughness (nm)
Den4	0.763	3.80	3.80
Hyd4	1.61	0.700	1.50
Den3	1.3	2.63	1.43
Hyd3	1.73	0.700	0.600
Den2	0.704	2.63	1.53
Hyd2	1.68	0.800	0.600
Den1	1.29	2.57	0.590
Hyd1	1.92	0.992	0.600
Arach	0.676	1.94	0.603
Arach	1.03	1.73	0.287
SiO ₂	2.18	3.00	0.153
Si	2.65	∞	2.00

^a DenX, Xth dendrimer layer (X=1, 2, 3, 4); HydX, Xth hydrotalcite layer (X=1, 2, 3, 4); Count, layer of counter anion and/or hydrated water molecule; Arach, layer of arachidic acid monolayer.

less than diameter (~ 5.9 nm) of spherical dendrimer in solution [22]. The molecular length of extended arachidic acid is evaluated to 2.8 nm [15].

The analytical simulation of the XR curves was performed on the basis of equation (1) with considering structural assumption and initial parameters: The XR curves were fitted by the least-square method from initial values. Then, optimum structure parameters, that is, density, thickness and error function of a series of layers were evaluated [23] and their numerical values were listed in Tables I and II, respectively, for two films of clay and its nanocomposite with dendrimer on ZX-type arachidic acid LB film. The error function is interpreted as roughness of interface or cosolubilization of different materials at the interface. The reflectivity vs. q_z curves calculated from the optimum parameters are shown in Figure 1. The calculation reproduced well the observed curves, indicating that the obtained parameters are physically reasonable. From the parameters in Tables I and II, the density profile was obtained as a function of depth and shown in Figures 2 and 3, respectively, where layer structures are also included.

Figure 2 indicates that the hybrid film with only clay without dendrimers consists of arachidic acid double layer and four clay sheets. Four layer structure was determined from the best fit to the observed XR curve among three to five layer structures. Furthermore, the density of the clay sheets (see Table I) was much lower than the theoretical value. This discrepancy can be explained by the following two possibilities; incomplete formation of clay film (loose packing of clay) and/or the roughness of arachidic acid bilayer or substrate. In the former case, the clay density averaged at the distance perpendicular to the substrate surface decreases. The latter possibility might also decrease the clay density due to the mixing effect [23], since it caused loose packing

of clay sheets. The distance from arachidic acid surface to top of the film was totally around 4.5 nm.

The structure of the nanocomposite film on arachidic acid LB film was comprised of arachidic acid double layer and four alternate clay/dendrimer layers, as seen in Figure 3, different from that of hybrid film without dendrimer. After the complexation with dendrimer, the distance between clay sheets was expanded from ~0.3 nm to ~2.6 nm. Accordingly, the distance between top and bottom (surface of film and surface of arachidic acid bilayer) was increased from 4.5 nm to 12.6 nm through the complexation. The short distance between clay, that is, thin layer thickness of intercalated dendrimer (~2.6 nm) indicates that the intercalated dendrimer is ellipsoid, since the diameter of spherical dendrimer is known to be ~5.9 nm in solution [22]. This fact suggests that the dendrimer is compressed between clay sheets in the film, which was also confirmed from the comparison of density of dendrimer between intercalated and neat conditions. The density (1.3 g cm^{-3}) of the first and third intercalated dendrimer layers was close to that (1.22 g cm^{-3}) of dendrimer in the neat condition where the dendrimer is supposed to be densely packed. For the case of the second intercalated dendrimer layer, the density was less because of less amount of the intercalation. The compression of dendrimer in the layer-by-layer system was observed even between lamellar bilayer of surfactant [22].

The most outer layer of the nanocomposite film, which is the adsorption layer of the dendrimer on the clay sheet, should be discriminated from the intercalated dendrimer layers, since the thickness (3.8 nm) of this adsorbed dendrimer layer is larger than that (~2.6 nm) of intercalated dendrimer layer. This implies that the adsorbed dendrimer is less compressed than the intercalated dendrimer. Further, relatively high error function σ of the most outer layer of the composite film as listed in Table II indicates the high roughness of this layer. It is assumed that the adsorbed dendrimer is loosely packed and made the surface roughened, since the density (0.76 g cm^{-3}) of the adsorbed dendrimer was less than that in neat condition (1.22 g cm^{-3}). On the other hand, the roughness of surface of clay film without dendrimer was low and in atomic scale (see Table I). This is reasonable, since the clay adsorbs small counter anions and/or hydrated water molecules on its surface.

From Figure 3, we can also notice the absence of dendrimer layer between the arachidic acid bilayer and the most inner clay sheet. Dendrimers adsorbed on the clay on the time course of the preparation of the hybrid film could be desorbed due to the electrostatic repulsion between COO^- terminal groups of the dendrimer and COO^- groups of the arachidic acid in LB film, which resulted in the formation of hybrid thin film as shown in Figure 3. Similar modification happened between clay and arachidic acid LB film as seen in Figure 2. Counter anion or hydrated water adsorbed on the clay surface removed after clay was adsorbed on arachidic acid Langmuir film.

4. CONCLUSIONS

In this study, we prepared the hybrid thin films consisting of clay and clay/dendrimer nanocomposite on arachidic acid LB film. The electrostatic interaction promoted the formation of these hybrids. The structural

characterization was performed by X-ray reflectometry, which is a powerful tool for analyzing the interfacial structure. It was revealed that the hybrid film of nanocomposite was constructed by the accumulated clay/dendrimer layers, which resulted from the replacement of counter anions or hydrated water molecules between clay sheets by dendrimers.

Acknowledgment

Authors are grateful to Mr. A. S. Costa for the preparation of samples.

References

- [1] Z. Liu, Z. Wang, X. Yang and K. Ooi, *Langmuir*, **18**, 4926-4932 (2002)
- [2] K. Glinel, A. Laschewsky and A. M. Jones, *J. Phys. Chem. B*, **106**, 11246-11252 (2002)
- [3] F. H. Lin, Y. H. Lee, C. H. Jian, J.-M. Wong, M.-J. Shieh and C.-Y. Wang, *Biomaterials*, **23**, 1981-1987 (2002)
- [4] J. W. Kim, F. Liu, H. J. Choi, S. H. Hong and J. Joo, *Polymer*, **44**, 289-293 (2003)
- [5] K. M. Lee and C. D. Han, *Polymer*, in press
- [6] R. Sasai, D. Sugiyama, S. Takahashi, Z. Tong, T. Shichi, H. Itoh and K. Takagi, *J. Photochemistry Photobiology A, Chemistry*, **155**, 223-229 (2003)
- [7] F. J. Anaissi, G. J. F. Demets, R. A. Timm and H. E. Toma, *Materials Science Engineering A*, **347**, 374-381 (2003)
- [8] F. Grohn, B. J. Bauer, Y. A. Akpalu, C. L. Jackson and E. J. Amis, *Macromolecules*, **33**, 6042-6050 (2000)
- [9] D. M. Watkins, Y. Sayed-Sweet, J. W. Klimash, N. J. Turro and D. A. Tomalia, *Langmuir*, **13**, 3136-3141 (1997)
- [10] X. Arys, A. M. Jonas, B. Laguitton, R. Legrasa, A. Laschewsky and E. Wischerhoff, *Progress in Organic Coatings*, **34**, 108-118 (1998)
- [11] S. Huebner, E. Politsch, U. Vierl and G. Cevc, *Biochim. Biophys. Acta*, **1421**, 1-4 (1999)
- [12] Z. Chen, Y. Ma and J. Yao, *Thin Solid Films*, **384**, 160-165 (2001)
- [13] Z. Zhang and T. Imae, *J. Colloid Interface Sci.*, **233**, 99-106 (2001)
- [14] K. M. Ashley, J. C. Meredith, E. Amis, D. Raghavan and A. Karim, *Polymer*, **44**, 769-772 (2003)
- [15] O. Mori and T. Imae, *Langmuir*, **11**, 4779-4784 (1995)
- [16] H. Yamaoka, H. Matsuoka, K. Kago, H. Endo, J. Eckelt and R. Yoshitome, *Chemical Physics Letters*, **295**, 245-248 (1998)
- [17] A. van der Lee, *Solid State Sciences*, **2**, 257-278 (2000)
- [18] S. Uppuluri, *Diss. Abstr. Int.*, **B**, **58**, 446 (1997)
- [19] Filler katsuyou-jiten edited by filler community, published by taiseisya
- [20] *The Merk Index 13th* Ed. by M. J. O'Neil et al., Merk & Co., Inc. press pp 769
- [21] V. Ambrogi, G. Fardella, G. Grandolini and L. Perioli, *Int. J. Pharmaceutics*, **220**, 23-32 (2001)
- [22] X. Li, T. Imae, D. Leisner and M. A. Lopez-Quintela, *J. Phys. Chem. B*, **106**, 12170-12177 (2002)
- [23] T. Salditt, Q. An, A. Plech, J. Peisl, C. Eschbaumer, C. H. Weidl and U. S. Schubert, *Thin Solid Films*, **354**, 208-214 (1999)