Material Innovation of Organo-aluminosilicate —Development of Heat-resistant Powder with High Coverage, and Organized Film with High Regularity—

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We have attempted to fabricate heat-resistant ultrathin organized molecular films of several organo-modified montmorillonite (MMT) by applying the Langmuir-Blodgett (LB) method. Thermal degradation temperature of long-chain-phosphonium-modified MMT (C₁₆-P-MMT) in bulk has been found to exceed 300 °C. The out-of-plane X-ray diffraction patterns observed for multilayer of C₁₆-P-MMT with varying the sample temperature have indicated annealing effects on the film regularity, i.e., remarkable improvement of the long range order at the initial stage (up to 100 °C) and, in contrast, at the subsequent stage gradual collapse of the layered structure.

Key words: Organo-modified aluminosilicate, Two-dimensional organic/inorganic nano-hybrid, Modification at oil/water interface, Long-chain quaternary phosphonium salt, Langmuir-Blodgett method

1. INTRODUCTION

Currently, developing alternatives for endangered resources and materials to detect environmental contamination is at the forefront of material science research. In recent years, the exhaustion of deposits and rising market prices of rare metals and rare earth elements have become topics of public concern all over the world. Scientists are urgently looking for ways to substitute petroleum-derived resources and reduce greenhouse gas emissions. To address this problem, we investigated the use of aluminosilicate¹ as an alternative material. Aluminosilicate is comprised of ubiquitous elements, such as atoms with higher ranked Clarke numbers, such as O (ranked first), Si (ranked second), and Al (ranked third). Furthermore, aluminosilicate materials do not emit greenhouse CO₂ gas by combustion, whereas general polymer products burn with the emission of CO₂. In addition, because aluminosilicate clays, such as natural montmorillonite, are post-petroleum mineral resources, next generation eco-materials could potentially be developed. Aluminosilicate clays are unique in the sense that they consist of negatively charged aluminosilicate layers that are held together by exchangeable interlayer cations. These interlayer cations enable the clay to undergo ion exchange, enabling the modification of their surfaces by cationic surfactants that intercalate the interlayer spaces. Thus, many alkylammonium-modified layered silicates (organo-modified clays) have been developed and are now widely used to form various nanocomposite materials with enhanced properties.²

Over the past four decades, over 70,000 papers have been published in the academic field of clay materials.³

From 1987, almost all highly cited papers have been related to polymer/clay nanocomposites.⁴ Organo-modified clay composites have been extensively investigated in material science.⁵ For example, modified clays have been recently shown to be powerful compatibilization agents of polymer blends⁶ that behave in a synergistic manner with standard flame retardant formulations, rendering a large class of self-extinguishing polymers.⁷ In order to achieve enhanced mechanical and thermal properties, clays have been exfoliated in polymer matrices.⁸

Thin films of clay minerals have been studied for the development of modified electrodes, sensors, photochromic devices, and nonlinear optical devices. The Langmuir-Blodgett (LB) method⁹ is one of the most useful techniques used to prepare ultrathin films. Over the past four decades, approximately 140 papers have been reported in the field of clay LB films.¹⁰ Ultrathin films of clay minerals prepared using the LB method have been reported, and clay LB films have recently been hybridized with alkylammonium cations. Smectite clay is exfoliated into single negatively charged clay sheets containing low concentrations of aqueous suspension. 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 alkylammonium cations at the air/clay suspension interface. The surface pressure area (π -A) isotherm of the hybrid monolayer is dependent on the clay concentration in the suspension. As the concentration increases, the isotherm shifts to the side of the layer with the largest area, suggesting that the structure and

properties of hybrid monolayers and multilayers vary based upon the clay concentration in the suspension. In addition, because organo-modified montmorillonites are post-petroleum resources, these materials could potentially be used to form next generation eco-materials (e.g., biochips). The patterning surface used to construct the biological high density memory device is formed by a phase separation between a biodegradable polymer and natural mineral. In previous studies, dimethyl dioctadecyl ammonium-modified MMT ($2C_{18}$ -N-MMT) and trimethyl octadecyl ammonium-modified MMT (C_{18} -N-MMT) were synthesized by using modification methods to form organo-modified MMTs with extremely high surface coverage and localized negative charges on the bottom layer at oil/water interfaces.¹¹⁻¹⁵

On the other hand, it is found that clay has an effective anti-allergenic property in recent years. Further, request of formation of polymer/clay nanocomposite using polymers with high melting temperature are also increasing. Thus, attention of the use of clay in a high temperature environment and evaluation of the heat-resistance of the two-dimensional film is focused as recent trend of studies. In this work, newly C_{16} -P-MMT was synthesised. In addition, heat-resistance of organo-modified aluminosilicate and two-dimensional clay film of organo-modified aluminosilicate were investigated. The molecular arrangement and surface morphology of the films were estimated by π -A isotherm, out-of-plane X-ray diffraction (XRD), and atomic force microscopy (AFM).
2. EXPERIMENTAL

Natural Na^+ -montmorillonite (Fig. 1(a)) was supplied by Kunimine Co., Ltd. with a cation exchange capacity of 108.6 meq/100 g. The organophilic clay was prepared using cation exchange reactions of natural clay (aqueous dispersion) with 0.1% aqueous solution of dimethyl dioctadecyl ammonium cation ($2C_{18}$ -N), trimethyl octadecyl ammonium cation (C_{18} -N), tributyl hexadecyl phosphonium bromide (C_{16} -P) (Fig. 1(b), (c), and (d), respectively). Organo-

Fig. 1 Chemical structure of (a) montmorillonite and (b) dimethyl dioctadecyl ammonium cation ($2C_{18}$ -N) (c) trimethyl octadecyl ammonium cation (C_{18} -N) (d) tributyl hexadecyl phosphonium bromide (C_{16} -P) serving as organo-modification agent.

Fig. 2 Schematic illustrations of the organo-modification procedure of montmorillonite surface (a) in hot water and (b) at oil / water interface.

modified clays with low surface coverage (commercial grade) were formed in clay suspensions at 50 °C by the addition of four types of quaternary ammonium cations with stirring¹³, whereas those with high surface coverage were formed at the oil/water interface (chloroform solutions of quaternary ammonium chlorides/clay suspensions)¹². These procedures are illustrated in Fig. 2.

Thermo gravimetry (TG) of different organo-modified clay was obtained using Seiko Instrument, TG/DTA6200, EXSTRA6000, taking approximately 10 mg of sample heated in a platinum crucible. The samples were scanned by high-resolution TG instrument operating at ramp of 10 °C/min from ambient to 500 °C in a high purity flowing nitrogen atmosphere. The π -A isotherms were measured by using a USI-3-22 film balance (USI Co., Ltd.) at 15 °C.

The monolayers were transferred onto mica (AFM samples) substrates at 15 °C using the LB method. The surface morphologies of the transferred monolayers were observed in the air with a scanning probe microscope (Seiko Instrument, SPA300 with SPI-3800 probe station)

Fig. 3 TG thermograms of (a) C_{18} -N-MMT and (b) $2C_{18}$ -N-MMT and (c) C_{16} -P-MMT

Fig. 4 π -A isotherms of monolayers for organo-modified montmorillonite on the potassium buffer surface

in tapping mode, using microfabricated rectangular Si single-crystal cantilevers with integrated pyramidal tips at a constant force of 1.7 Nm^{-1} .

Multilayers of each organo-modified clays were fabricated by the horizontal lifting method (HLM). The layered structures of the multilayers of organo-modified clay were characterized with *in situ* temperature controlled out-of-plane XRD (Bruker AXS, MXP-18VA). Ni-filtered Cu-K α radiation (wavelength $\lambda = 0.154 \text{ nm}$) was generated at 40 kV and 80 mA.

3. RESULTS AND DISCUSSION

Figure 3 shows TG curves of organo-modified montmorillonite. Figs.3(a) and 3(b) are a TG curves of ammonium-modified montmorillonite having one and two long alkyl-chain, respectively. These samples have high surface coverage and thermal degradation temperature corresponds 220 °C. On the other hand, thermal degradation temperature was significantly improved over 300 °C in the case of phosphonium-modified montmorillonite. From these results, it is considered that surface modification of phosphonium salt is effective in suppressing desorption at the high temperature. However, the thermal degradation temperature of phosphonium-modified clay with low surface

coverage is not improved (Fig. 3(c)). In other words, it can be considered that thermal degradation temperature depends on influence of the van der Waals interaction between alkyl chains (high surface coverage of orano-modification agent is effective to suppress the thermal degradation), rather than relying on cationic species. Therefore, it was attempted that the production of two-dimensional organized films of various organo-clay with high surface coverage.

Figure 4 shows the π -A isotherms of organo-modified montmorillonite (2C₁₈-N-MMT and C₁₆-P-MMT) with high surface coverage. pH 7, 1.0 mM potassium buffer solution (potassium bicarbonate and potassium chloride) was used as the subphase. Potassium ions were introduced to make it possible to transfer organo-modified clay monolayers from the water surface to solid substrates by reducing the interaction between oxonium ions and anionic clay platelets. Otherwise, transferring of the film is prevented by that interaction because the negative charges in the clay platelets are localized at their unmodified surfaces.

Figure 5 shows the results of *in situ* temperature controlled out-of-plane XRD profiles of multilayers of 2C₁₈-N-MMT and C₁₆-P-MMT. The presence of a first and secondary reflection is confirmed with both multilayers at 25 °C. In this case, interlayer spacing indicates 38 Å. The diffraction intensity is increased with the temperature rising to 100 °C. In addition, the values of long period are shortened at 200 °C,

Fig. 5 *In situ* temperature controlled out-of-plane XRD profiles for multilayers of (a) 2C₁₈-N-MMT and (b) C₁₆-P-MMT (HLM, 20 layers).

Fig. 6 Schematic illustrations of thermal degradation of multilayers of (a) 2C₁₈-N-MMT and (b) C₁₆-P-MMT.

Fig. 7 (a) Schematic illustration of repeating compression-expansion process. AFM images of Z-type monolayer of (b) $2C_{18}$ -N-MMT and (c) C_{16} -P-MMT [left; compression speed: $4.8 \text{ cm}^2/\text{min}$, compression times: 1 time, right; $0.6 \text{ cm}^2/\text{min}$, 6 times]

and this trend is more remarkable at 300°C .

Figure 6 shows schematic illustration of thermal decomposition of multilayers of (a) $2C_{18}$ -N-MMT and (b) C_{16} -P-MMT. In room temperature, both materials have same layered periods at about $38 \text{ \AA}$. In the case of ammonium salts, multilayer has a long-range order. Also it was re-arranged by an annealing effect. This tendency is almost the same as the case of phosphonium salt (Fig. 6(b)). After further heating, some organo-modification agents were desorbed and interlayer spacing was shortened by the tilting of remaining part in the both materials. This tendency was remarkable by further heating. In the case of fabrication of two-dimensional film, it is found that films of both phosphonium and ammonium-modified clay indicate heat resistance property until $200\sim 300^\circ\text{C}$. Since there are almost no differences in thermal degradation temperature of organo-modification agent in two-dimensional films, it is supported that interaction between alkyl chain is effective in suppressing desorption.

However, in this point of view, there are many defects in organo-modified clay monolayer at mesoscopic scale. It is concerned that these defects causes a decrease in heat resistance. Formation of similar two-dimensional low defect film of inorganic particle have been reported.¹⁶ Then, fabrication of low defect organo-modified clay monolayer was attempted using a "repeating compression-expansion process" (Fig. 7(a)). It is considered that this process is effective in case that the inorganic particulates are relatively large and an interaction between the particulates are relatively weak. From the results of AFM observation, low defect monolayer was confirmed with decreasing of compression speed and increasing compression times (Fig. 7(b), (c)).

From these result, improvement of thermal decomposition temperature of organo-clay two-dimensional film is expected. Our next plan is evaluation of heat-resistance of these films.

4. CONCLUSION

Heat-resistance of organo-modified aluminosilicate and two-dimensional clay film of organo-modified aluminosilicate were investigated. From the results of TG-DTA of organo-modified clays, it is considered that surface modification of phosphonium salt is effective in suppressing desorption at the high temperature. However, the thermal degradation temperature of phosphonium-modified clay with low surface coverage is not improved. In other words, it can be considered that thermal degradation temperature depends on influence of the van der Waals interaction between alkyl chains, rather than relying on cationic species. From the results of in situ temperature controlled out-of-plane XRD profiles of multilayers of $2C_{18}$ -N-MMT and C_{16} -P-MMT, it is supported that interaction between alkyl chain is effective in suppressing desorption.

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