

Synthesis of clay-amino acid layered nanocomposites by intercalation and their structural stability

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Layered nanocomposites of expandable clay (montmorillonite, M) and amino acids were prepared by an intercalation reaction in an aqueous solution. L-valine(V), L-threonine(T), L-glutamic acid(G), L-lysine(L), L-histidine(H) and L-arginine(A) were used as amino acid molecules. In the intercalation reaction, the solution pH played an important role in preparing the intercalation compounds; a pH of the solution below 4 was favorable to obtain intercalative layered nanocomposites due to the zwitterionic nature of amino acid molecules. Moreover, the basic side chain of amino acids had a crucial role in determining the structural stability of the layered nanocomposites; the basic amino acid such as L-arginine, L-lysine and L-histidine with basic side chain formed stable intercalated structures, while the other α -amino acids formed only transitory intercalative complexes, which were easily decomposed during the washing process.

Key words: intercalation, nanocomposite, clay, amino acid.

Introduction

In general, layered materials such as clays are used as host matrices in the preparation of nanocomposite materials. Na-montmorillonite has Na⁺-ions in interlayers to compensate for negative charges which come from the isomorphous substitution of Mg²⁺ for part of the Al³⁺ in the dioctahedral sheet. These interlayer Na⁺-ions are easily exchanged with other organic cations in solution by an ion-exchange reaction to form organo-clay nanocomposites [1-3].

Among many functional organic molecules, amino acids are of great interest as guest species in the intercalation compounds using clays. Amino acid molecules have a zwitterionic structure when they are in the solid state or in solution; the two cases allow hydrogen bonds to be formed, stabilizing the ionic conformation R-CH(COO⁻)NH₃⁺.

In previous studies, the intercalations of various types of amino acids into clays by a simple ion exchange reaction in aqueous solution have been reported [4-7]. Even though the formations of intercalation complexes between clays and amino acid molecules have been described, detailed synthetic conditions including the solution pH, types of amino acid, and washing effect have not been reported so far. In particular, the stability of clay-amino acid intercalation complexes has not been discussed yet. In the present study, therefore, our

primary attention has been paid to the determination of optimum formation conditions for montmorillonite and amino acids complexes. In particular, the influence of the solution pH on the amino acid intercalation complexes is described in detail. Furthermore, the stability of the intercalation complexes is discussed on the basis of the types of amino acid molecules.

Experimentals

Sample preparation

Na-montmorillonite (M), a dioctahedral layered silicate, is used as the host material in the preparation of amino acid molecules and composites. A commercial product of Kunipia-G (Kunimine Industry, Japan) with a cation exchange capacity (CEC) of 100 meq/100 g was used.

Six types of amino acids including L-valine (C₅H₁₁NO₂, 117.15, 99%, Junsei Chemical, Japan), L-threonine (C₄H₉NO₃, 119.12, 99%, Junsei Chemical, Japan), L-glutamic acid (C₅H₇NO₄, 147.13, 99%, Junsei Chemical, Japan), L-(+)-lysine monohydrochloride (C₆H₁₄N₂O₂·HCl, 182.65, 99%, Acros Organics, USA), L-histidine (C₆H₉N₃O₂, 155.16, 98%, Acros Organics, USA) and L-arginine (C₆H₁₄N₄O₂, 174.20, 99%, Alfa Aesar) were used as guest molecules.

The preparation of clay-amino acids composites was carried out by a typical ion exchange reaction. At first, Na-montmorillonite was preswelled in distilled water for 24 hr (1 wt%), and the pH of the clay suspension was controlled by adding 1 mol/dm³ HCl solution. The aqueous solutions of the amino acid were prepared separately by dissolving amino acids (3 times the CEC

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of montmorillonite) in distilled water and the pH of the solutions were also controlled by titrating 1 mol/dm³ HCl solution. Then the two solutions were mixed and reacted at 60 °C for 4 h under continuous stirring. The reaction products were separated by centrifugation and washed thoroughly with distilled water. During the ion exchange reaction, the solution pH was varied in the range of 1.5–12.0 to investigate the pH effect on the intercalation reaction.

Characterization

X-ray diffraction (XRD) patterns were taken on the samples spread on a slid glass using an MXP3 (MAC Science Co. Ltd., Japan) diffractometer with Ni-filtered Cu-K α radiation ($\lambda=1.54056$ Å) at 40 kV and 30 mA. Prior to the XRD analysis, all samples were dried at 100 °C for 24 hours. FT-IR spectra were also recorded with a IR Prestige-21 (Shimadzu Co. Ltd., Japan) in the range of 4000–650 cm⁻¹ using the KBr disk method. TG (Thermogravimetry) analysis of the intercalation compounds was performed with a STA409C/3/F (Netzsch Co. Ltd., Germany) in the temperature range of 110–1000 °C with a heating rate of 10 °C/min under an ambient atmosphere.

Results and Discussions

Structural Analysis

The powder X-ray diffraction patterns of clay-amino acid composites as a function of reaction pH are represented in Fig. 1. All the samples were washed thoroughly with distilled water and dried at 100 °C for 24 h before analysis. In the case of clay complexes of valine (A, MV), threonine (B, MT) and glutamic acid (C, MG), the (001) reflections are observed at around 9.7–10.2 Å, irrespective of the solution pH. The observed low basal spacings reveal that no amino acid molecules are intercalated into the silicate layers. On the other hand, the clay-histidine (E, MH), lysine (D, ML), and arginine (F, MA) composites exhibit expanded basal spacings. In particular, the composites prepared in an acidic pH domain show distinct diffraction peaks centered at ~13.3 Å, suggesting the intercalation of amino acid molecules between the clay layers. Judging from the observed interlayer separation (~4 Å) and the molecular geometry of amino acids, the interlayered amino acid molecules have a monolayer arrangement. In the montmorillonite-histidine composite (D), the intercalation phase begins to collapse at neutral pH (7), and no intercalation occurs in the basic pH domain. With the montmorillonite-lysine composite (E), the intercalation phase is obtained at least up to pH=7 beyond which the intercalation of amino acids is not effective as in the acid pH region. Furthermore, the montmorillonite-arginine composite (F) is effectively obtained even at quite basic pH region, a well defined intercalation phase is obtained at least up to pH=10. It

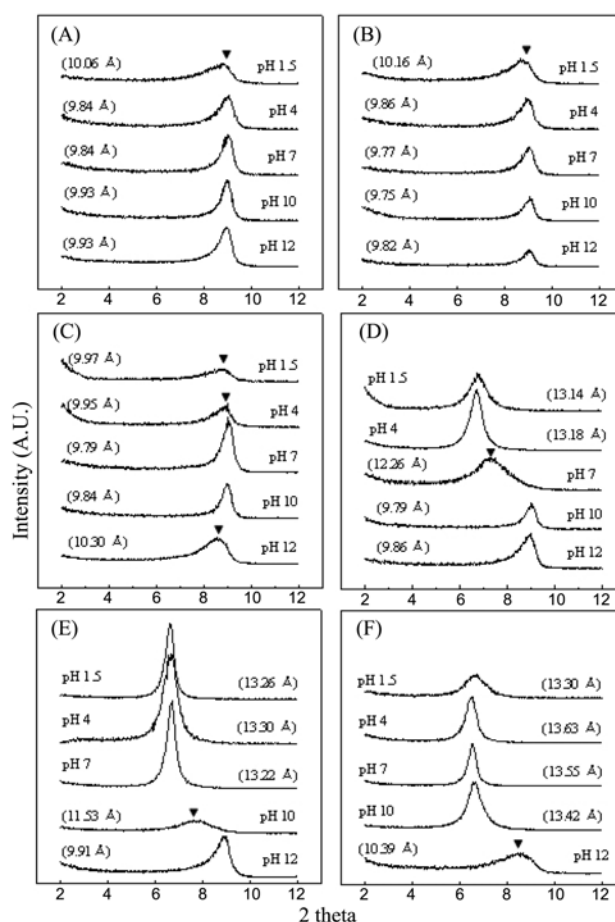


Fig. 1. XRD patterns of clay-amino acid Nanocomposites as a function of pH; (A) MV, (B) MT, (C) MG, (D) MH, (E) ML and (F) MA, respectively.

Table 1. The properties of amino acids used in the present study

Amino acid	DEC (°C)	pK1 (COOH)	pK2 (NH ₂)	pK R	Ionization form on R group
L-Arginine	244	1.8	9.0	12.5	NH ₃ ⁺
L-Lysine	225	2.2	9.2	10.8	NH ₃ ⁺
L-Histidine	287	1.8	9.2	6.0	NH ₃ ⁺
L-Valine	295	2.2	9.7	—	—
L-Threonine	255	2.2	9.2	~13	COO ⁻
L-Glutamic acid	225	2.1	9.5	4.1	COO ⁻

is worthy to note here that the pH domain for the formation of stable intercalation complexes corresponds to the order of the pK R (Table 1). That is, the higher pK R exhibit a broader formation pH domain for the formation of stable intercalation complexes.

Figure 2 represents the evolution of X-ray diffraction patterns of the four selected clay-amino acid composites depending upon the washing cycle. All the samples were prepared at the reaction pH of 1.5. As can be seen from Fig. 2, the ‘as-prepared’ samples obtained just after centrifugation of reaction products exhibit distinct diffraction profiles due to the intercalation of amino acid molecules between the silicate layers. According

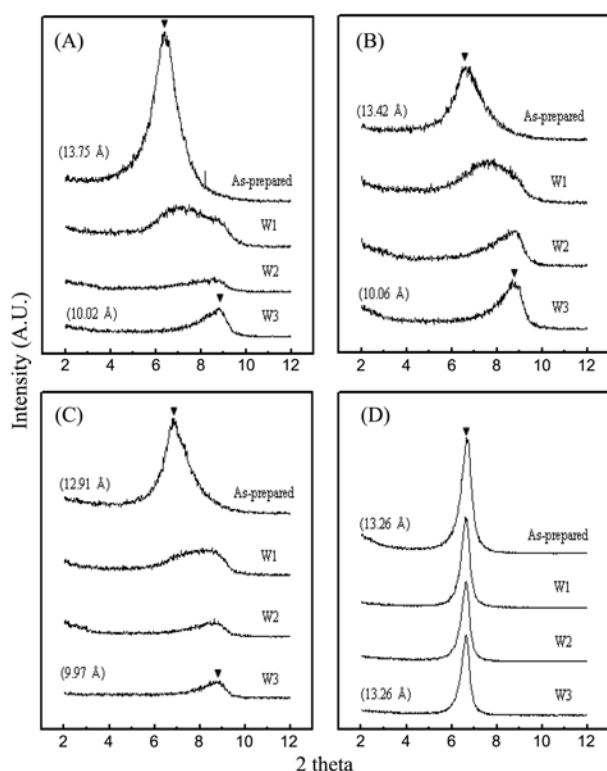
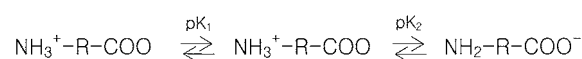


Fig. 2. Evolution of the XRD of clay-amino acid composites during washing; (A) MV, (B) MT, (C) MG and (D) ML, respectively. W_n (n : number of washing cycle)

to the observed basal spacings of 12.9–13.8 Å, the amino acid molecules adopt monolayer stacking between the silicate layers. Upon washing with distilled water, however, the well-defined diffraction peaks are drastically

disappeared except for the lysine-montmorillonite composite (D, ML). Instead diffraction patterns with lower basal spacings are observed, strongly suggesting that a deintercalation of interlayered amino acid molecules occurs during the washing step. As discussed before (Fig. 1), the lysine molecules with a basic side chain remain almost constant between the silicate layers irrespective of the washing cycle. This is the same for the other amino acid molecules with a basic side R-chain like histidine, and arginine. Since amino acids are dipolar molecules with a zwitterionic nature, they have different chemical states according to the solution pH; [8].



In the acidic pH domain ($\text{pH} < \text{pK}_1$), most amino acid molecules have a positive charge with a protonating of the basic amine moiety. While in the basic pH domain ($\text{pH} > \text{pK}_2$) they have negative charge with a deprotonating of acidic carboxylic group. During the intercalation in the reaction at acidic pH range the positively charged amino acid molecules are easily intercalated into the silicate layers to form clay- amino acid layer nanocomposites. Washing with distilled water, however, increased the solution which pH induces the deprotonation of carboxylic acids, subsequently forming anionic carboxylates. The formed anionic charge exerts repulsive interaction with the anionic silicate layer, destabilizing the amino acid-silicate layer complex. In addition, the deprotonation of the carboxylic group also facilitates the formation of an intermolecular complex. That is,

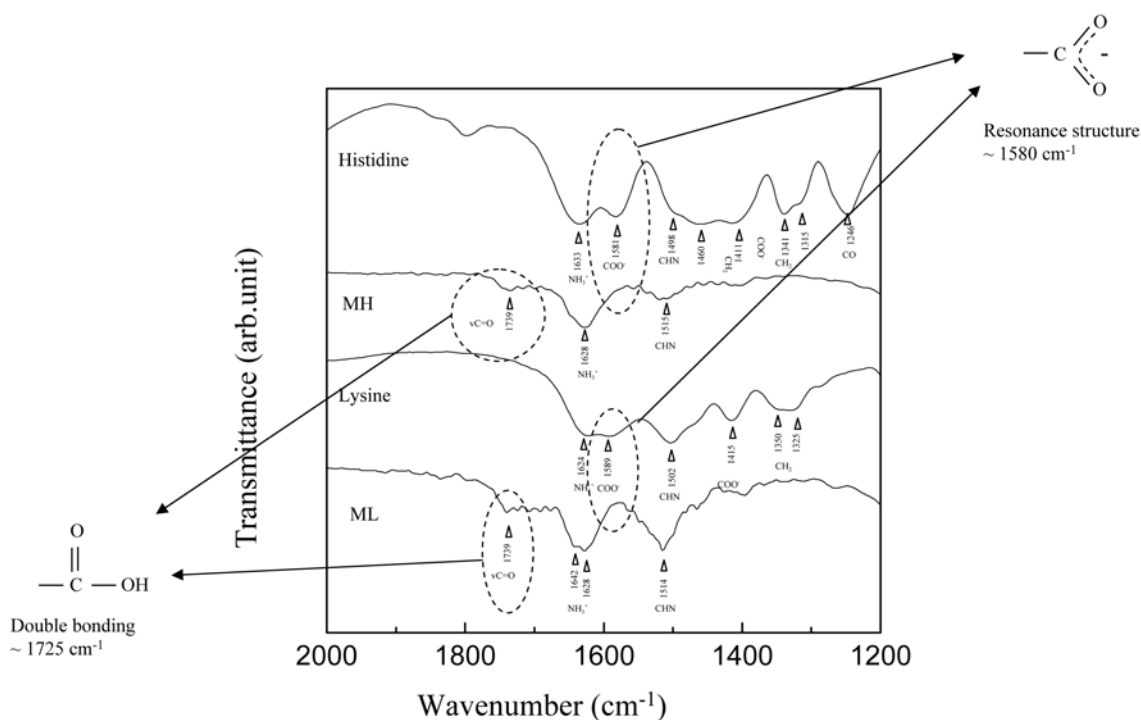


Fig. 3. The FT-IR spectra of clay-amino acid composites and amino acids.

the hydrogen bonds between COO^- and NH_3^+ stabilize the intermolecular complex rather than the electrostatic interaction between the NH_3^+ and anionic silicate layers. Therefore, the zwitterionic character and the intermolecular hydrogen bonding of amino acid molecules might be responsible for the poor stability of clay- amino acid complexes.

FT-IR spectroscopy

FT-IR spectra of the selected clay- amino acid composites are compared in Fig. 3 with the corresponding pure amino acids. Upon intercalation of amino acids into layer silicates, the absorption peaks origins from amino acid molecules are broadened. This line broadening is mainly attributed to the weakening of the hyperfine interaction between amino acid molecules. The spatial confinement of amino acid molecules in the interlayer space may reduce the hyperfine interaction between molecules. Since the interlayered amino acid molecules strongly interact with the anionic charge center of the clay layers, they are distributed homogeneously with a certain intermolecular distance in the interlayer space according to the charge distribution of the clay. This molecular level distribution in the composite reduces the intermolecular interaction, causing the weakening of hyperfine interaction.

In order to distinguish the bonding state of the carboxylic acid group between free amino acids and intercalated ones selected parts are magnified in this figure. The typical absorption peak of $\nu_{\text{C=O}}$ of carboxylic acid ($\begin{smallmatrix} \text{O} \\ || \\ -\text{C}-\text{OH} \end{smallmatrix}$) is generally observed at 1725 cm^{-1} , while the absorption frequency is shifted to $\sim 1580\text{ cm}^{-1}$ (ν_{as}) and $1420\text{ cm}^{-1}\sim 1400\text{ cm}^{-1}$ (ν_{s}) when it has a resonance form ($\begin{smallmatrix} \text{O} \\ // \\ -\text{C}=\text{O}^- \end{smallmatrix}$) as in the free amino acids [8, 9]. In a free amino acid the carboxylic group has resonance structure forming hydrogen bond with amino group ($\begin{smallmatrix} \text{O} \\ // \\ -\text{C}=\text{O} \end{smallmatrix} \text{H}-\text{NH}_2$).

Figure 3(a) and (c) show the unique absorption peaks at 1580 cm^{-1} and 1410 cm^{-1} due to the ν_{as} and ν_{s} of carboxylate group of free amino acid molecules which are in good agreement with previously reported data. In the intercalation compounds, (b and d), however, the two absorption peaks due to the stretching vibration modes of the carboxylate group are drastically reduced. Instead new absorption bonds at $\sim 1740\text{ cm}^{-1}$ due to the $\nu_{\text{C=O}}$ in carboxylic acid group are appeared to be dominant. As mentioned before, the presence of the carboxylic acid group in the intercalation compounds of basic amino acids might be due to the hydrogen bond formation between the carboxylic acid and the amine group in the side chain. This finding also supports the stability of intercalation compounds of basic

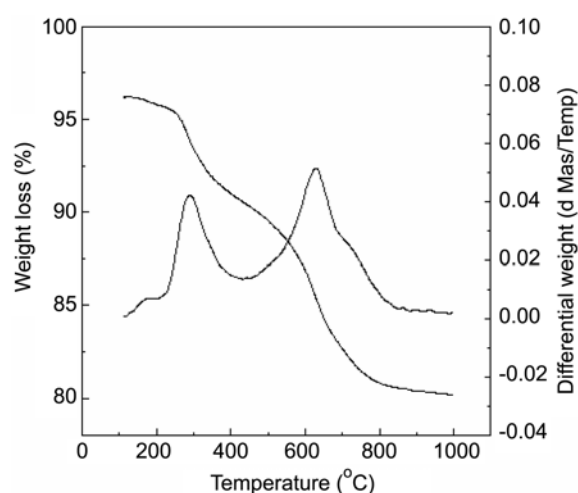


Fig. 4. The TG-DTG curves of Montmorillonite-Lysine (ML).

amino acids through the masking of anionic charge of carboxylates *via* an intermolecular hydrogen bonding.

TG analysis

A typical thermogram of a lysine-montmorillonite composite obtained at pH=4 is presented in Fig. 4. The amino acid contents estimated from TG analysis are summarized in Table 2 depending upon the reaction pH. In the thermogram (Fig. 4), as generally observed in the organoclays [7], the weight loss occurs in three steps. The first step weight loss below 150°C is mainly attributable to the dehydration of surface adsorbed water. Secondly, the loss observed in the temperature range of $150\text{--}500^\circ\text{C}$ can be assigned to the oxidative decomposition of amino acids. The contents of amino acids determined from this step weight loss are summarized in Table 2. An additional weight loss at around

Table 2. The content of amino acid estimated from TG analysis

Sample	pH	Content of amino acid (wt%)
MH (Montmorillonite + L-histidine)	1.5	6.84
	4	10.51
	7	8.21
	10	4.10
	12	1.63
ML (Montmorillonite + L-lysine)	1.5	7.58
	4	11.26
	7	5.48
	10	1.06
	12	0.21
MA (Montmorillonite + L-arginine)	1.5	8.01
	4	11.24
	7	11.64
	10	8.12
	12	2.11

~650°C is a characteristic loss of montmorillonite due to the dehydration of a structural hydroxyl group.

The variation of intercalated amino acid content depending upon the reaction pH shows a similar tendency to that of XRD result (Fig. 1(D), (E), (F)). All the samples reach a maximum loading level at pH =4, beyond which the loading level is decreased as the reaction pH is increased. As expected from the XRD analysis MH shows a drastic content change at pH=7, while MA shows a considerable amount of amino acid up to pH=10. This observation also supports again the suggestion that the reaction pH plays an important role in the formation of clay-amino acid composites.

Conclusions

Intercalation compounds of montmorillonite and amino acid were prepared as a function of reaction pH by a typical ion exchange reaction. In the intercalation reaction, the solution pH and basic side chain of amino acid molecules were founded to be crucial in determining the formation of amino acid-montmorillonite intercalation compounds and their stability. The basic amino acids such as histidine, lysine, and arginine form stable intercalation compounds, while the other amino acids form only transitory ones. The zwitterionic nature and intermolecular hydrogen bond have a determining effect on the intercalation reaction of amino acids and the stability of amino acids.

Acknowledgments

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