Preparation of a Kaolinite–Nylon 6 Intercalation Compound

Asako Matsumura, Yoshihiko Komori, Tetsuro Itagaki, Yoshiyuki Sugahara, and Kazuyuki Kuroda*

Department of Applied Chemistry and Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Shinjuku-ku, Tokyo 169-8555

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A kaolinite–nylon 6 intercalation compound was prepared by the polymerization of 6-aminohexanoic acid (AHA) in the interlayer space of kaolinite. The intercalation of AHA was achieved by a guest displacement reaction using a kaolinite–methanol intercalation compound as an intermediate. After AHA dissolved in a mixed solvent of methanol and water (1 : 3) was added to a kaolinite–methanol intercalation compound, the mixture was stirred for 3 h. The basal spacing of the product increased to 1.23 nm, indicating the intercalation of AHA molecules with a monolayer arrangement between the layers of kaolinite. AHA was polymerized by a heat treatment at 250 °C for 1 h under a nitrogen flow. Although the basal spacing of the heat-treated product slightly decreased to 1.16 nm, the spacing was larger than those of kaolinite and the kaolinite–methanol intermediate. The formation of a kaolinite-nylon 6 intercalation compound was confirmed by the appearance of IR bands due to amide I (1637 $\mathrm{cm^{-1}}$) and amide II (1550 $\mathrm{cm^{-1}}$).

Interactions between inorganic layered materials and organic substances have attracted increasing interest from both scientific and industrial perspectives.[1–4] The intercalation of polymers into inorganic layered materials, such as clay minerals, with a retention of the layered nature is an excellent way to construct novel inorganic–polymer nanoassemblies.[5] A smectite group of clay minerals, such as montmorillonite, has mainly been used because of their excellent intercalation abilities.[6–8] Other types of layered silicates have been used for preparing polymer intercalation compounds to a much lesser degree because of their lower reactivities for the intercalation of polymers. However, an extension of this kind of host material will lead to various layered silicate-based nanocomposites with compositional and structural variations, which can be directed toward new applications.[9]

Kaolinite, a 1 : 1 type clay mineral, is a unique layered material because the interlayer space is sandwiched by OH groups of octahedral aluminum hydroxide sheets and oxygen atoms of tetrahedral silicate sheets. Because of the inherent hydrogen bonds between the layers, a limited number of small polar guest molecules, such as dimethyl sulfoxide (DMSO) and *N*-methylformamide (NMF), are directly intercalated.[10] Guest molecules are intercalated by forming new hydrogen bonds. A guest displacement method has enabled the formation of various kinds of intercalation compounds of kaolinite. So far, intercalation compounds with NMF,[10] ammonium acetate,[11] and methanol[12] have mainly been used as intermediates for guest displacement reactions. In particular, a kaolinite–methanol intercalation compound has been found to be an excellent intermediate that can be used for the intercalation of relatively large molecules, such as alkylamines,[13] *p*-nitroaniline,[14] ε-caprolactam,[15] and poly(vinylpyrrolidone).[16]

Kaolinite–polymer intercalation compounds have been prepared by two methods. Some polymers are directly intercalated,[16–18] and the others are intercalated by the in situ polymerization of preintercalated monomers between the layers of kaolinite.[11,19–21] The number of polymers, which are intercalated directly, is so limited that the route utilizing preintercalated monomers is important. In addition to vinyl polymerization,[11,19,20] we have reported a polycondensation reaction of β-alanine [$\mathrm{H_2N{-}(CH_2)_2COOH}$].[21] Therefore, the formation of a kaolinite–nylon 6 intercalation compound is expected by an in situ polymerization reaction of 6-aminohexanoic acid (AHA) [$\mathrm{H_2N{-}(CH_2)_5COOH}$]. The nanocomposites of nylon 6 with kaolinite may possess better properties over nylon–smectite hybrids[22–24] because of the high crystallinity, high aspect ratio, and confined interlayer environment of kaolinite.

In this study, as a first step toward nylon–kaolinite hybrids, the intercalation of AHA and its polymerization reaction were investigated. The intercalation of several kinds of ω-amino acid with shorter carbon chains has been reported.[21,25] However, the formation of a kaolinite–AHA intercalation compound has not been successful because of its large size and low ability to form an intercalation compound with kaolinite, though AHA molecules are intercalated into vermiculite and montmorillonite.[26,27] To overcome this difficulty, we employed a guest displacement reaction using a kaolinite–methanol intercalation compound as an intermediate. Furthermore, we carried out an in situ polymerization reaction by a heat treatment under a nitrogen flow. By comparing with a kaolinite–β-alanine intercalation compound,[21] the interactions between kaolinite and AHA and its polymerization behavior are discussed.

Experimental

Materials. Kaolinite used in the present study was KGa-1, well-crystallized Georgia kaolinite obtained from the Source Clays Repository of Clay Minerals Society (U.S.A.).[28] The sample was used after grinding to pass a 100-mesh sieve. AHA was obtained from Junsei Chemical Co., Ltd.

Preparation of a Kaolinite–AHA Intercalation Compound and in situ Polymerization. The intercalation of AHA was performed by a fine guest displacement method using a kaolinite–methanol intercalation compound as the intermediate, because no intercalation reactions of AHA took place by utilizing kaolinite, a kaolinite–NMF intercalation compound, or a kaolinite–ammonium acetate intercalation compound. Because the basal spacing of a dried kaolinite–methanol intercalation compound decreased to 0.86 nm, a wet kaolinite–methanol intercalation compound with a larger spacing (1.11 nm, Fig. 1b) was prepared according to a method reported previously.[12,29] At first, a kaolinite–NMF intercalation compound (basal spacing, 1.08 nm) was prepared, and then a guest displacement reaction between NMF and methanol was conducted. The wet kaolinite-methanol intercalation compound was added into a saturated AHA solution (solvent (methanol : water = 1 : 3), AHA (740 g L^{-1})) and the mixture was stirred at 30 °C for 3 h. A slight excess of AHA was found in the medium. The product was centrifuged and dried in a dessicator. In situ polymerization of the kaolinite–AHA intercalation compound was performed by a heat treatment in a tube furnace at 250 °C for 1 h under a nitrogen flow. For a comparison, bulk AHA without kaolinite was also heated under the same conditions.

Characterization. XRD patterns were obtained by using a Mac Science MXP[3] diffractometer with monochromated Cu Kα radiation. Solid-state ^{13}C and ^{29}Si CP/MAS NMR measurements were performed on a JEOL GSX-400 spectrometer with a spinning rate of 5 kHz. The Larmor frequencies of ^{13}C and ^{29}Si were 100.40 MHz and 79.30 MHz, respectively. The chemical shifts were expressed with respect to tetramethylsilane. Infrared spectra (IR) were recorded on a Perkin-Elmer Spectrum ONE FTIR spectrometer using the KBr-disk technique. The amounts of organic fractions were determined by a CHN analysis using a Perkin-Elmer PE-2400II apparatus. TG and DTA curves were obtained on a Mac Science 2000S instrument. The heating rate was 10 °C min^{-1} under a nitrogen flow. A TG-MS analysis was performed on a combined Shimadzu TGA-50 and GCMS-QP1100EX under a He atmosphere at a heating rate of 10 °C min^{-1}.

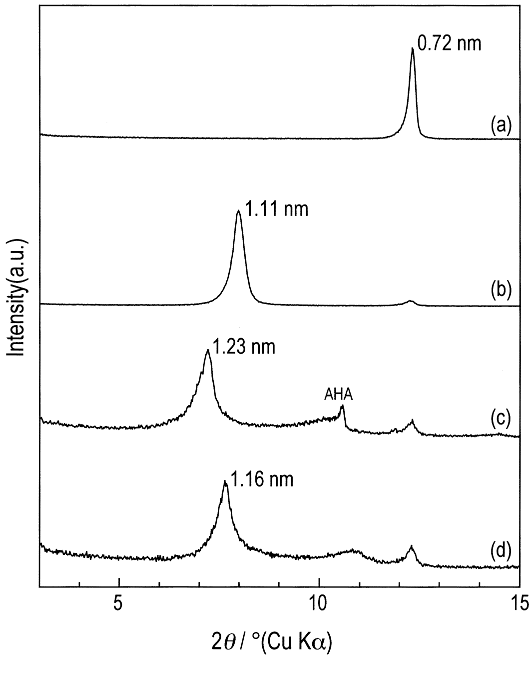

Fig. 1. XRD patterns of (a) kaolinite, (b) kaolinite–methanol intercalation compound under wet conditions, (c) kaolinite–AHA intercalation compound, and (d) kaolinite–AHA intercalation compound heated at 250 °C.

Results and Discussion

Preparation of a Kaolinite–AHA Intercalation Compound. Figure 1c shows the XRD pattern of the product. The basal spacing of the product is 1.23 nm, which is larger than those of kaolinite (0.72 nm; Fig. 1a) and the kaolinite–methanol intercalation compound (1.11 nm; Fig. 1b), indicating the intercalation of AHA into kaolinite. Higher order diffraction peaks (002, 003, and 004) are also observed (not shown). The intensities of the peak at 10.6° (0.84 nm) due to crystalline AHA adsorbed on the surface and the broad peak at around 10° (~ 0.86 nm) due to an unreacted phase (dried kaolinite–methanol intercalation compound)[29] are very weak. On the basis of both the interlayer distance of the product (0.51 nm) and the molecular size of AHA (ca. 0.42 × 0.51 × 1.00 nm), it is very likely that AHA molecules take a monolayer arrangement between the layers of kaolinite. The value of the basal spacing (1.23 nm) is larger than those of the kaolinite intercalation compounds with ω-amino acids containing shorter carbon chains (β-alanine, 1.17 nm; γ-aminobutyric acid, 1.20 nm; δ-aminovaleric acid, 1.21 nm).[21,26] However, the slight degree of the increment with the chain length indicates that the direction of the carbon chains of ω-amino acids is basically parallel to the plane of the layers.

Figure 2b shows the ^{13}C CP/MAS NMR spectrum of the kaolinite–AHA intercalation compound. The signals due to CH_2 groups of AHA appear at ca. 27–30 and 40 ppm. They are broader than those of bulk AHA (Fig. 2a), suggesting that the methylene chains are distorted by a restriction in the interlayer space of kaolinite. The signal at 50 ppm is due to the methoxy groups bound to hydroxy groups of kaolinite.[29] On the other hand, two signals due to C=O groups at 182.3 and 185.0 ppm are detected. The chemical shift of the first signal at 182.3 ppm is very similar to that in the spectrum of AHA (Fig. 2a; 182.4 ppm). The second signal is a peculiar one for an intercalation compound, which may be related to the AHA molecules, distorted by the restriction. The presence of two kinds of carbonyl groups has also been reported for a kaolinite–poly(vinylpyrrolidone) (PVP) intercalation compound,[16] in which signals at 176.2 and 182.9 ppm were observed (175.3 ppm for bulk PVP).

Figure 3 shows the IR spectra in the range between 1200 and 1800 cm^{-1}. In the spectrum of the kaolinite–AHA intercalation compound, the bands due to $\delta_{as}(NH_3^+)$ (1623 and 1652 cm^{-1}), $\delta_s(NH_3^+)$ (1539 cm^{-1}) and $\nu(COO^-)$ (1390 and 1561 cm^{-1}) are observed.[30] Because the intensity of the bands due to $\nu(NH_2)$ (3279 and 3433 cm^{-1}; not shown) and $\nu(COOH)$ (1681 cm^{-1}) are very small, most of AHA molecules are present as zwitterions. The positions of these bands are very similar to those of the crystalline state, indicating that the hydrogen bondings of these functional groups are similar to those in the crystalline state. Interactions among the AHA molecules are possibly strong, even in the intercalation compound.

Figure 4 shows the IR spectra in the OH stretching region.

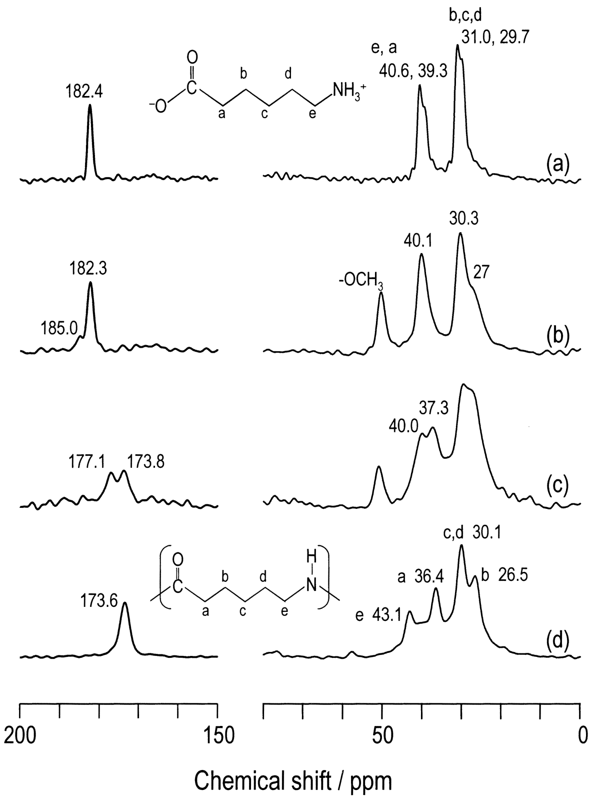

Fig. 2. ^{13}C CP/MAS NMR spectra of (a) AHA, (b) kaolinite–AHA intercalation compound, (c) kaolinite–AHA intercalation compound heated at 250 °C , and (d) AHA heated at 250 °C (nylon 6).

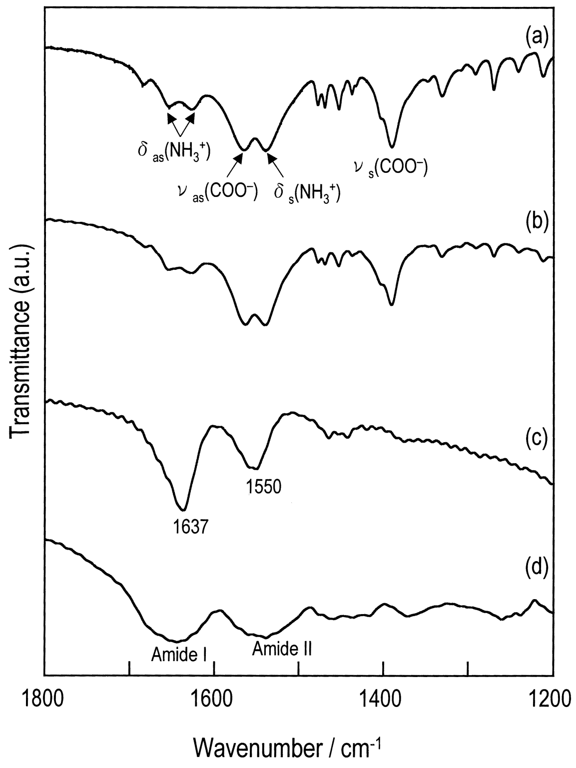

Fig. 3. IR spectra of (a) AHA, (b) kaolinite–AHA intercalation compound, (c) kaolinite–AHA intercalation compound heated at 250 °C, and (d) AHA heated at 250 °C (nylon 6).

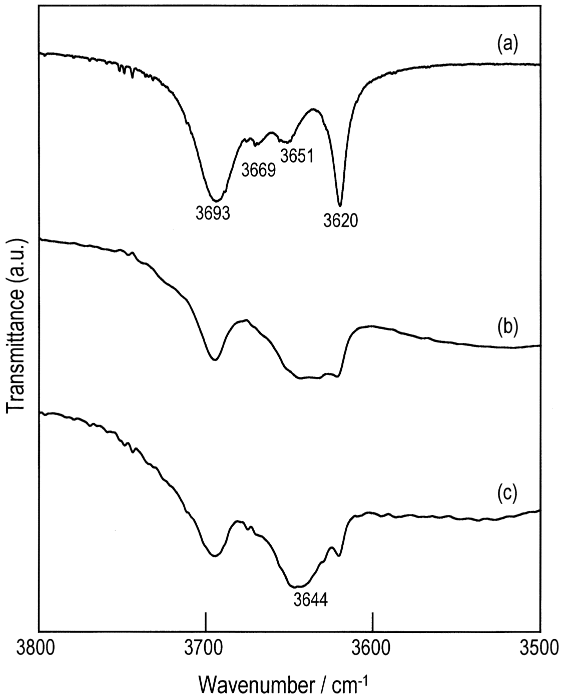

Fig. 4. IR spectra of (a) kaolinite, (b) kaolinite–AHA intercalation compound, and (c) kaolinite–AHA intercalation compound heated at 250 °C.

In the spectrum of kaolinite, four bands at 3620, 3651, 3669, and 3693 cm^{-1} appear (Fig. 4a). The band at 3620 cm^{-1} is assigned to an internal OH group, and the others to outer surface OH groups. By intercalation reactions, the outer OH groups may be perturbed and the OH groups hydrogen-bonded with guest species show new bands at lower wavenumbers, whereas the internal OH group is not influenced.[10] Thus, taking the band at 3620 cm^{-1} as a reference, interactions between OH groups and guest species can be observed. By the intercalation of AHA, the intensity of the band at 3693 cm^{-1} decreases and a broad band at around 3640 cm^{-1} appears (Fig. 4b), indicating the formation of new hydrogen bonds between the OH groups and the AHA molecules. Compared with a kaolinite–*β*-alanine intercalation compound,[21] a relatively large band at around 3640 cm^{-1} appears, whereas the band at 3603 cm^{-1} is not detected. Therefore, the hydrogen bonds of the OH groups with AHA molecules may be weaker than that with *β*-alanine.

The Si environments of kaolinite are influenced by the intercalation of guest species. In the ^{29}Si NMR spectrum of the kaolinite–AHA intercalation, the signal at −91.4 ppm is observed (Fig. 5b), whereas kaolinite shows a doublet at −90.7 and −91.3 ppm (Fig. 5a). As for a kaolinite–*β*-alanine intercalation compound, the signal at −90.4 ppm has been reported.[21] Therefore, the signal at −91.4 ppm for the kaolinite–AHA intercalation compound denotes that the interactions between the silicate sheets and AHA molecules are different from those in the case of *β*-alanine.

The amount of AHA was estimated by a CHN analysis (Table 1). The contents of the carbon and nitrogen are 20.8 and

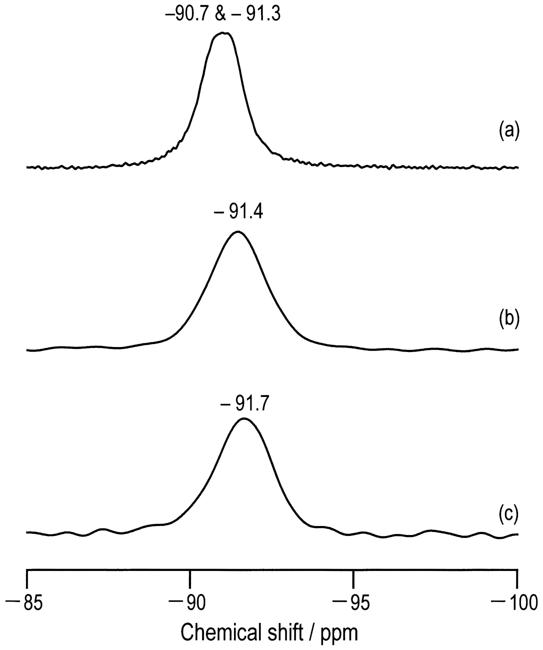

Fig. 5. ^{29}Si CP/MAS spectra of (a) kaolinite, (b) kaolinite–AHA intercalation compound, and (c) kaolinite–AHA intercalation compound heated at 250 °C.

Table 1. CHN Data of the Kaolinite–AHA Intercalation Compounds before and after the Heat Treatment at 250 °C

	Content/mass%		C/N (molar ratio)
	C	N	
Kaolinite–AHA	20.8	3.8	6.3
heat treated product	12.3	2.3	6.2

3.8 mass%, respectively, and the molar ratio of C/N is found to be 6.3. The slight deviation from 6.0 for the chemical composition of AHA is explained by the presence of methoxy groups bound to kaolinite.[29] On the basis of the nitrogen content, 1.2 molecules of AHA per a kaolinite unit of $Al_2Si_2O_5(OH)_4$ are present. On the other hand, the amount of AHA on the surface of kaolinite is estimated to be 0.3 molecules per the unit, which was deduced from a sample prepared by mixing kaolinite with AHA dissolved in the solvent. Consequently, the amount of AHA in the interlayer space of kaolinite is 0.9 molecules per $Al_2Si_2O_5(OH)_4$. When DMSO, a much smaller molecule, is intercalated into kaolinite, the amount of DMSO is 1 molecule per the unit.[31] The basal spacing of kaolinite–DMSO intercalation compound is 1.12 nm, which is not so larger than that of kaolinite–AHA (1.23 nm). On the other hand, an intercalation compound of kaolinite with ε-caprolactam (basal spacing 1.31 nm) has 0.7 molecules per the unit. Consequently, it is suggested that the AHA molecules are closely packed in the interlayer space.

The intercalation of AHA into kaolinite is more difficult than those of ω-amino acids with shorter carbon chains, such as β-alanine.[21,26] Thus, a guest displacement reaction using the kaolinite–methanol intercalation compound as an intermediate was required. When the intermediate was stirred in a saturated solution of AHA in methanol, no reaction took place because of low solubility of AHA in methanol (8 g L^{-1}). Although the use of an aqueous solution of AHA was advantageous for increasing the concentration of AHA, water molecules were selectively intercalated. Therefore, AHA dissolved in the mixed solvent of methanol and water (1:3) was utilized. The long carbon chain of AHA molecules, whose direction is almost parallel to the layer, may be disadvantageous for forming an intercalation compound.

In situ Polymerization of the Kaolinite–AHA Intercalation Compound. The thermal behavior of the kaolinite–AHA intercalation compound under a nitrogen flow was investigated by TG-DTA (Fig. 6). An endothermic reaction with mass loss starts at 190 °C. Because the start of melting and polymerization of bulk AHA is about 210 °C, the endothermic peaks are assigned to the melting and polymerization of AHA. The lower endothermic temperature than that of bulk AHA indicates the peculiar environment of AHA molecules between the layers of kaolinite. The experimental mass loss between 190 and 330 °C (24 mass%) is much larger than that calculated by simple polycondensation of AHA (5 mass%). Additionally, the mass chromatograph between 180 and 260 °C by TG-MS analysis shows the signals of the parent ion of AHA and its fragments (e.g. m/e = 55, 85 and 113). These results indicate that partial volatilization of AHA took place with almost simultaneous melting and a polycondensation reaction. Above 370 °C, the endothermic peaks with mass loss due to the decomposition of organic substances and the dehydroxylation of kaolinite are observed. Based on the thermal behavior, we carried out the polymerization of AHA by a thermal treatment at 250 °C for 1 h.

The polymerization of AHA was confirmed by an IR analysis. In the spectrum of the product after a heat treatment (Fig. 3c), the bands due to $\delta_{as}(NH_3^+)$, $\delta_s(NH_3^+)$, and $\nu(COO^-)$ disappear and amide I (1637 cm^{-1}) and amide II (1550 cm^{-1}) are

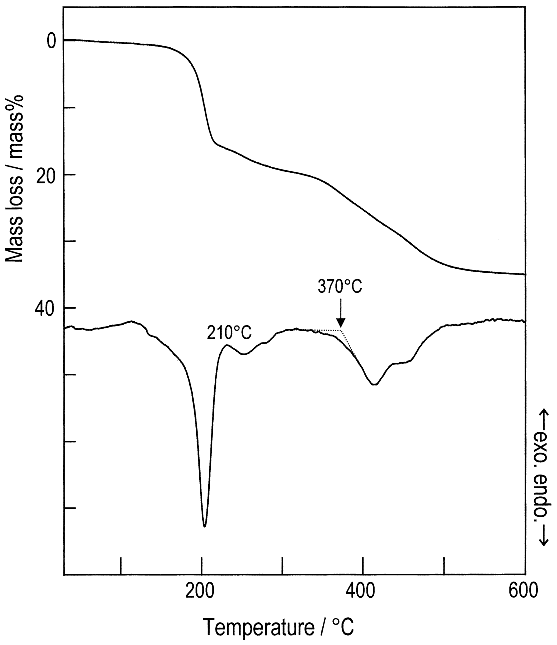

Fig. 6. TG-DTA curves of the kaolinite–AHA intercalation compound.

observed, indicating the formation of nylon 6 by the amide bond (–CONH–).[32] Compared with those of bulk nylon 6, which is prepared by heating AHA molecules under the same conditions (Fig. 3d), the bandwidths due to the amide I and II are obviously narrow. Therefore, the interactions among the guest molecules in the confined region are limited, compared with those in the bulk state, where three dimensional interactions are present.

Figure 4c shows the OH stretching bands of the heated product. In the spectrum, the characteristic band at 3644 cm^{-1} is observed and its width is narrower than that of the product before the heat treatment, indicating that characteristic hydrogen bonds between OH groups and the guest species is present. Because the band at 3645 cm^{-1} is observed in the spectra of kaolinite–2-pyrrolidone[20] and ε-caprolactam intercalation compound,[15] the band may be assigned to the hydrogen bonds between the OH groups and the amide groups.

The basal spacing of the thermally treated product was 1.16 nm (Fig. 1d). Judging from the interlayer distance of 0.44 nm, nylon 6 takes a monolayer arrangement between the layers. The value of the basal spacing is smaller than that before the heat treatment (1.23 nm), and the decrease by 0.07 nm is comparable to that in the case for β-alanine (0.06 nm).[21] Therefore, the decrease in the basal spacing is caused by a polycondensation reaction and a simultaneous rearrangement of the hydrogen bondings between the OH groups and the guest species.

In the ^{13}C CP/MAS NMR spectrum of the heated product (Fig. 2c), the signals due to CH_2 groups at 37.3, 40.0 and around 30 ppm and $C=O$ groups at 173.8 and 177.1 ppm are observed. All of the signals are due to nylon 6.[33] No signals, except for those related to the nylon 6 and methoxy groups (50 ppm), are observed, indicating no side reactions by the heat treatment. The deviation in the chemical shift from the bulk nylon 6 (Fig. 2d) may be due to interactions between kaolinite and nylon 6. Especially, the signal at 177.1 ppm is a peculiar one for an intercalation compound, indicating unique interactions between the OH groups of kaolinite and the $C=O$ groups of nylon 6, as well as the kaolinite–AHA intercalation compound.

The ^{29}Si CP/MAS NMR spectrum of the heated product shows a change in the interaction between the silicate sheets and the guest molecules (Fig. 5c). By a heat treatment, the signal at -91.4 ppm with a full width at half maximum (FWHM) of 1.74 ppm changed to a signal at -91.7 ppm with a FWHM of 1.70 ppm. The change in the chemical shift by the polymerization reaction denotes a new interaction between the silicate sheets and nylon 6. On the other hand, the FWHM of the signal was very similar to that before the heat treatment, indicating well-ordered interactions between the silicate sheets and nylon 6 as the kaolinite–AHA intercalation compound.

The amount of organics was estimated. The contents of carbon and nitrogen atoms were 12.3 and 2.3 mass%, respectively (Table 1). On the basis of the nitrogen content, 0.5 unit of nylon 6 [$-CONH(CH_2)_5-$] per a kaolinite unit [$Al_2Si_2O_5(OH)_4$] was present. The molar ratio of C/N was 6.2, which is very similar to as that of the intercalation compound before the heat treatment. These results indicate that no decomposition reactions occurred, although some amounts of organic materials were reduced by volatilization.

The reaction of kaolinite with AHA is comparable to those of the smectite group, such as montmorillonite (mont).[27] The basal spacings of the mont–AHA intercalation compounds are 0.41–0.82 nm depending on the kind of the interlayer cations. When they were heated at 240–250 °C, AHA molecules in the interlayer space were polymerized to form nylon 6. Although the interlayer distance of 0.46–1.32 nm of the mont–nylon 6 intercalation compounds are larger than that of the kaolinite–nylon 6 intercalation compound, the layers of mont are not exfoliated.[35] On the other hand, when montmorillonite modified with large organic cations, such as alkylammonium cations or ω-amino acid, with long chains were used, the formation of nylon-mont hybrids with exfoliation of the layers has been reported.[7,8,23] As for kaolinite, the layers are neutral and immobilizing organic cations in the interlayer space by charge balance is impossible. However, a modification of hydroxy groups with methanol has been reported recently.[29,34] In the future, if the kaolinite modified with large organic species is available, the formation of polymer–kaolinite hybrids may be produced.

Conclusions

A kaolinite–nylon 6 intercalation compound was prepared by an in situ polymerization of AHA. The intercalation of AHA was achieved by using both a kaolinite–methanol intercalation compound and AHA dissolved in a mixed solvent of methanol and water (1:3). AHA molecules were present in a zwitterion form and took a monolayer arrangement between the layers of kaolinite. By a heat treatment at 250 °C under a nitrogen flow, AHA molecules were polymerized to form a kaolinite–nylon 6 intercalation compound. The preparation of kaolinite intercalation compounds with ω-amino acid with longer carbon chains and their polymerization reactions is feasible under improved experimental conditions. Future applications of these organically modified kaolinites for polymer–clay nanocomposites are expected.

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