JOURNAL OF Materials CHEMISTRY

Synthesis of a kaolinite–poly(β-alanine) intercalation compound

Tetsuro Itagaki,[a] Yoshihiko Komori,[a,b] Yoshiyuki Sugahara[a] and Kazuyuki Kuroda*[a,b]

[a]*Department of Applied Chemistry, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo, 169-8555, Japan. Tel: +81-3-5286-3199; Fax: +81-3-5286-3199; E-mail: kuroda@mn.waseda.ac.jp*
[b]*Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Nishiwaseda-2, Shinjuku-ku, Tokyo, 169-0051, Japan*

Received 22nd January 2001, Accepted 14th August 2001
First published as an Advance Article on the web 9th October 2001

A kaolinite–poly(β-alanine) intercalation compound (kaolinite/poly(β-alanine)) was synthesized by *in-situ* polycondensation of preintercalated β-alanine, which is an initial step toward the extension of the variety of host materials for polymer–clay nanocomposites. β-Alanine was intercalated into kaolinite by a displacement method using kaolinite/ammonium acetate as the intermediate. Zwitterionic β-alanine was ordered in a monolayer arrangement between the layers, which was confirmed by powder XRD, IR and NMR. Although β-alanine was mostly polymerized by thermal treatment of kaolinite/β-alanine at 250 °C for 10 h under an N_2 atmosphere, a part of the guest species was decomposed. Kaolinite/poly(β-alanine) had a higher thermal stability than bulk poly(β-alanine), as evidenced by TG–DTA.

Introduction

The synthesis of layered inorganic–organic nanocomposites based on intercalation of organic species into layered inorganic materials has extensively been investigated because they are applicable to many areas such as adsorption, catalysis, reaction media, packaging, and so on.[1–3] The selection of host materials as well as guest species is important for the design of intercalation compounds and nanocomposites. The smectite group of clay minerals, such as montmorillonite, is frequently used as host materials for the formation of clay–polymer nanocomposites. The layer charge is variable, being dependent on the kind of smectite clay and the composition, which is suitable for controlling the orientation and the amount of intercalated guests.[4–8] Smectites can be exfoliated into polymer matrices *via in-situ* polymerization and clay–polymer nanocomposites exhibit an improvement in the mechanical properties compared with those of the clay alone,[9–11] which has attracted increasing interest over the last ten years.[9–15]

In order to develop these nanocomposites further, other types of clay minerals should also be utilized. However, due to the low intercalation reactivities, other clay minerals have not been recognized as possible hosts for nanocomposite formation. Different types of layered silicates are very interesting because they have different crystallite sizes and aspect ratios. Recently we have reported that the interlayer surface of a layered polysilicate magadiite can be grafted by methacryloxypropylsilyl groups and subsequently copolymerized with methyl methacrylate.[16]

Kaolinite, a 1 : 1 type clay mineral, is unique because the interlayer is sandwiched by hydroxyl groups on one side and oxide layers on the other side which may induce specific guest orientations.[17,18] The size and aspect ratio of kaolinite are larger than those of montmorillonite. Consequently, the interactions at the interfaces between kaolinite and polymers should be very different from those of smectite–polymer systems. Therefore, we have explored the possibility of the formation of various types of kaolinite/organic nanosystems.[19–31] Though the reactivity of kaolinite for intercalation is low, the versatility is greatly improved by the use of an intermediate (for example, kaolinite treated with methanol)[26,31] for displacement reactions.

A very limited number of kaolinite–polymer intercalation compounds have been reported so far.[20,23,25,27,32,33] Direct intercalation of polymers into kaolinite is rather difficult and only a few exceptions, poly(vinylpyrrolidone),[27] poly(ethylene oxide)[32] and polyhydroxybutylate,[33] have been reported. They can directly be intercalated by the displacement of preintercalated guest species. Organic monomers forming hydrogen bonds with the interlayer surface can be intercalated by a displacement method and *in-situ* polymerization of such preintercalated monomers is suitable. Almost all *in-situ* polymerization in kaolinite that has been reported to date is additional polymerization that does not affect so much the hydrogen bonds between guest species and the host.[20,23,25] Consequently, *in-situ* polycondensation between the layers is required because the method is suitable for the formation of many polymers, such as polyamides and polyesters. We recently reported the formation of a kaolinite–nylon 6 intercalation compound.[34] Here we report the synthesis of a new kaolinite–polymer intercalation compound by an *in-situ* polycondensation method. β-Alanine, a simple ω-amino acid, has been selected as a monomer[35] because intercalation of some ω- and α-amino acids into kaolinite has been reported.[22,36] This finding has urged us to pursue the possibility of the formation of kaolinite–polyamide intercalation compounds by an appropriate selection of monomers. Because poly(β-alanine) has a higher density of amide groups than other polyamides, stronger interactions with kaolinite should be expected.

Experimental

Well-crystallized kaolinite from Georgia (KGa-1), obtained from the Source Clays Repository of the Clay Minerals Society (USA), was used after grinding for a few minutes to pass through a 100 mesh sieve. A slight amount of anatase was detected as an impurity by X-ray powder diffraction. β-Alanine and poly(β-alanine) (MW = 9700) were obtained from Tokyo Chemical Industry Co. and Sigma-Aldrich Co., respectively. Reagents were used as received.

First, a kaolinite–ammonium acetate intercalation compound (abbreviated as kaolinite/ammonium acetate hereinafter; other kaolinite–organic intercalation compounds are abbreviated similarly) was prepared as an intermediate, since

DOI: 10.1039/b100746g

β-alanine reacted with neither kaolinite nor kaolinite/*N*-methylformamide (NMF). Kaolinite/NMF was prepared by stirring kaolinite powders and an aqueous NMF solution (90.9 vol%) at rt for 72 h, according to a method reported previously ($d_{001} = 1.08$ nm, Fig. 1B).[37] Kaolinite/NMF was mixed with an aqueous solution of ammonium acetate (50 mass%) and the mixture was stirred for 2 d. The aqueous solution was exchanged with a fresh solution after the reaction for 1 d to displace NMF with ammonium acetate completely. After centrifugation, kaolinite/ammonium acetate ($d_{001} = 1.42$ nm, Fig. 1C) was obtained.

Kaolinite/β-alanine was prepared by the displacement of ammonium acetate with β-alanine. The mixture of kaolinite/ammonium acetate and an aqueous solution of β-alanine (9.1 mass%) was stirred for 1 d, and the product was centrifuged and air-dried. The product was heated at 250 °C for 10 h using an electric furnace under a nitrogen flow to polymerize β-alanine.

XRD patterns were obtained by a MAC Science MXP^3 diffractometer with graphite monochromated Cu Kα radiation. IR spectra were recorded on a Perkin Elmer FT-IR 1640 spectrometer using the KBr-disk technique. Solid-state ^{13}C and ^{29}Si CP/MAS NMR spectroscopies were performed at 100.40 MHz and 79.30 MHz, respectively, with a JEOL NM-GSX-400 spectrometer using a spinning rate of *ca.* 5 kHz. Chemical shifts were quoted with respect to external tetramethylsilane (TMS). DTA and TG curves were obtained with a MAC Science TG-DTA 2010S instrument under an N_2 or a dry air flow (50 ml min^{-1}) with a heating rate of 10 °C min^{-1}. The amounts of organic fractions were determined by using a Perkin-Elmer 2400II CHN analyzer. Thermogravimetry–mass spectrometry (TG–MS; Shimadzu TGA-50 thermobalance coupled with a Shimadzu QP1100EX quadrupole mass spectrometer *via* a stainless capillary column) was performed under a helium flow (40 ml min^{-1}) at a heating rate of 5 °C min^{-1}.

Results and discussion

I. Synthesis of a kaolinite–β-alanine intercalation compound (kaolinite/β-alanine)

The basal spacing of kaolinite/β-alanine was 1.17 nm (Fig. 1D), and the XRD pattern showed seven higher (00*l*) reflections (0.586 nm (d_{002}), 0.390 nm (d_{003}), 0.292 nm (d_{004}), 0.234 nm (d_{005}), 0.195 nm (d_{006}), and 0.167 nm (d_{007})). A small peak at 0.72 nm due to raw kaolinite was detected in the product.

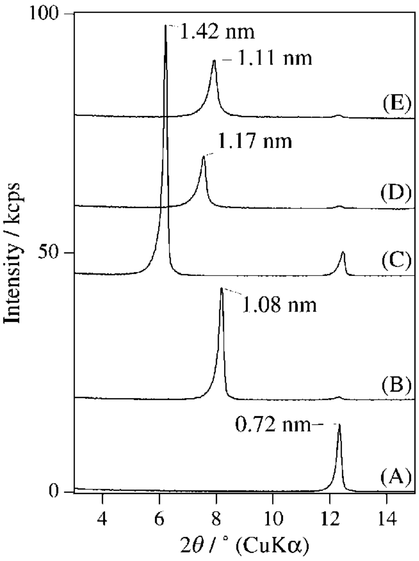


Fig. 1 XRD patterns of (A) kaolinite, (B) kaolinite/NMF, (C) kaolinite/ammoium acetate, (D) kaolinite/β-alanine, and (E) kaolinite/β-alanine heated at 250 °C.

The ^{13}C CP/MAS NMR spectrum of the product (Fig. 2A) shows the resonances attributed to β-alanine at 34.0 and 39.0 ppm (CH_2) and 180.2 ppm (*C*OOH).[38] No resonances attributed to ammonium acetate were detected. The preparation of kaolinite/β-alanine was confirmed by these results. The interlayer distance (0.45 nm) of the intercalation compound indicates a monolayer arrangement of β-alanine between the layers because the distance is too small for multilayer arrangements. In kaolinite/ω-amino acid (NH_3^+–$(CH_2)_n$–COO^- ($n = 1$–5)), a stepwise increase in the interlayer distance with the carbon number was observed,[36] indicating that ω-amino acids including β-alanine ($n = 2$) take inclined arrangements against the aluminosilicate layers.

The IR spectrum of kaolinite/β-alanine revealed that β-alanine took a zwitterionic form between the layers as well as in its crystalline state,[39–42] consistent with the finding reported previously.[36] The characteristic bands due to $\delta_d(NH_3^+)$ at 1636 and 1610 cm^{-1}, $\delta_s(NH_3^+)$ at 1482 cm^{-1}, and $\nu_{as}(COO^-)$ at 1577 cm^{-1} appeared (Fig. 3A and B). However, the interactions of intercalated β-alanine species were different from those in the crystalline state. The $\nu_{as}(NH_3^+)$ band, which is observed at 3105 cm^{-1} in single crystals,[42] appeared at 3314 cm^{-1}. All $\delta(NH_3^+)$ bands were shifted to lower wavenumbers by about 20 cm^{-1} than those of β-alanine crystals. The $\nu_{as}(COO^-)$ band was not shifted. These results show that the NH_3^+ groups between the layers are hydrogen-bonded equivalently as in crystals.

Information on the interactions between kaolinite and β-alanine is also obtained from the OH stretching region. Four characteristic OH stretching bands (3620, 3650, 3670, and 3692 cm^{-1}) are detected for kaolinite (Fig. 4A). The first band is assigned to inner hydroxyl groups, and the others to inner-surface hydroxyl groups.[43] When a guest is intercalated into kaolinite, only the latter three bands can be perturbed by the newly created hydrogen bonds. Thus, the position of these shifted bands depends on the host–guest interactions. Upon intercalation of β-alanine into kaolinite, a new band at 3603 cm^{-1} and a shoulder at around 3620–3671 cm^{-1} appeared, and the intensity of the band at 3992 cm^{-1} decreased

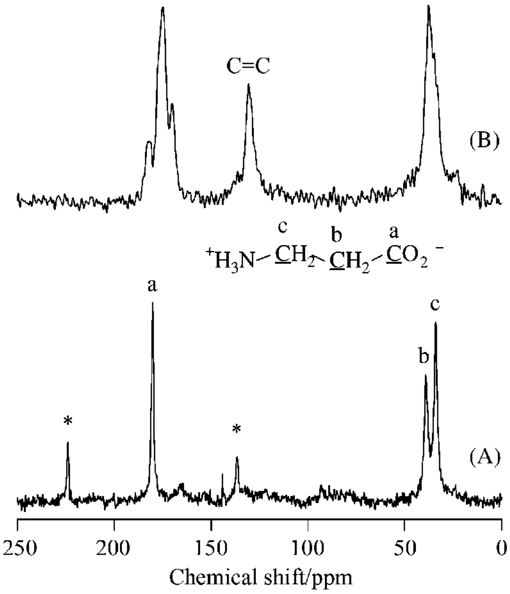


Fig. 2 ^{13}C CP/MAS NMR spectra of (A) kaolinite/β-alanine and (B) kaolinite/β-alanine heated at 250 °C. Spinning side bands are marked by asterisks. The spectrum B was obtained by a TOSS method to remove spinning side bands.

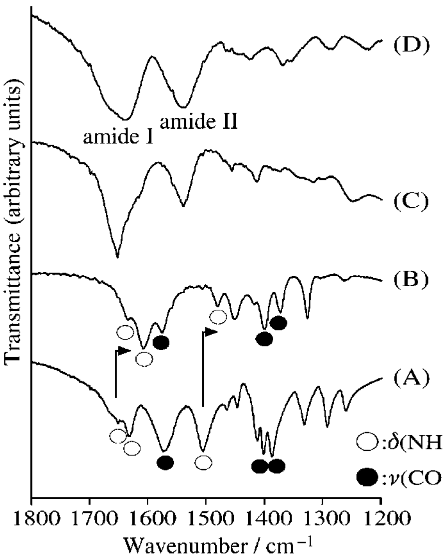


Fig. 3 IR spectra in the 1800–1200 cm^{-1} region of (A) bulk β-alanine, (B) kaolinite/β-alanine, (C) kaolinite/β-alanine heated at 250 °C, and (D) poly(β-alanine).

(Fig. 4B). When kaolinite/methanol and a methanol solution of β-alanine were used for the formation of kaolinite/β-alanine, the IR spectrum of the product (not shown) showed that the intensity of the band at 3603 cm^{-1} was substantially decreased. Thus, the band at 3603 cm^{-1} is possibly due to the OH stretching vibration of hydrated AlOH or cointercalated H_2O because an aqueous solution of β-alanine was used for the normal synthesis. The shoulder is due to new hydrogen bonds between β-alanine and the OH groups of kaolinite.

Kaolinite exhibits two ^{29}Si NMR resonances at −90.7 and −91.3 ppm because of different Si environments induced by interlayer hydrogen bonds or Si–Al distances (Fig. 5A).[44,45] In the spectra of kaolinite–organic intercalation compounds reported so far, the resonances are generally shifted to lower frequencies. This is because the interactions between the SiO_4 tetrahedral sheets and the guests are weaker than the inherent hydrogen bonds between the layers of kaolinite.[46] The spectrum of kaolinite/β-alanine displayed one resonance at −90.4 ppm, a higher frequency than those of kaolinite (Fig. 5B). This shift to higher frequency was observed for the first time in the intercalation compounds of kaolinite.[23,24,26,28,46–52] This shift means that kaolinite/β-alanine has a unique interaction between the guest and SiO_4 sheets. Sato[36] suggested that β-alanine between the layers interacted with both silicate and gibbsitic sheets: COO^- groups interacted with the gibbsitic sheet and NH_3^+ groups with the silicate sheet. This shift may be due to the interactions between SiO_4 tetrahedral sheets and the NH_3^+ groups.

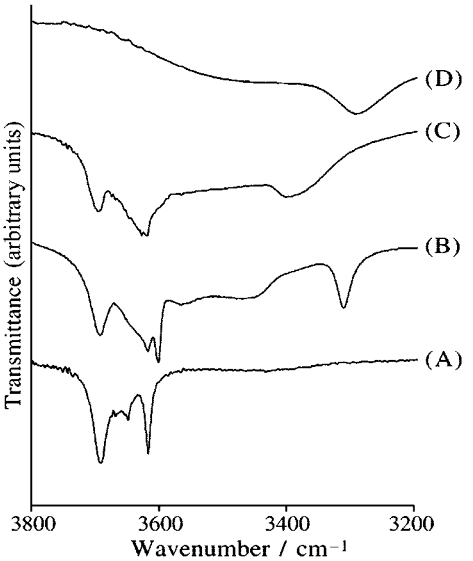


Fig. 4 IR spectra in the 3800–3200 cm^{-1} region of (A) raw kaolinite, (B) kaolinite/β-alanine, (C) kaolinite/β-alanine heated at 250 °C, and (D) poly(β-alanine).

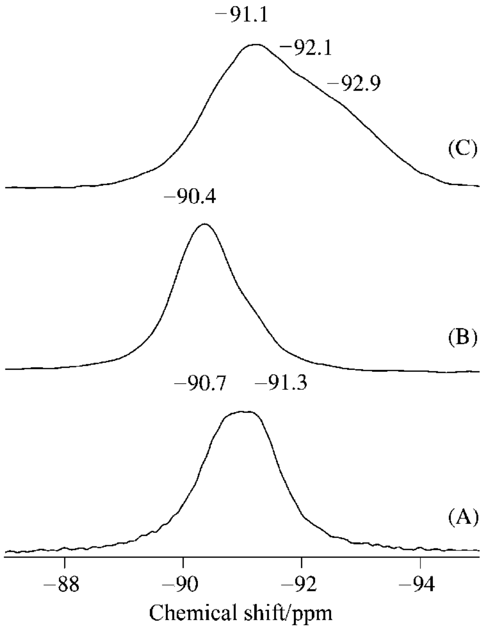


Fig. 5 ^{29}Si CP/MAS NMR spectra of (A) raw kaolinite, (B) kaolinite/β-alanine, and (C) kaolinite/β-alanine heated at 250 °C.

The carbon content of kaolinite/β-alanine is 8.96 mass%, and the formula is described as $Al_2Si_2O_5(OH)_4{\cdot}(NH_3^+CH_2CH_2COO^-)_{0.82}$ (Table 1). Complete guest displacement reaction between ammonium acetate and β-alanine is demonstrated by the results of CHN analysis: the N/C ratio of kaolinite/β-alanine was 0.33, a value equal to that of pristine β-alanine. Based on the basal spacing, spectroscopic data, and organic content, a model of kaolinite/β-alanine is schematically shown in Fig. 6.

II. *In-situ* polymerization of β-alanine

To polymerize β-alanine between the layers, kaolinite/β-alanine was heated at 250 °C under an N_2 flow. The TG–DTA curves of kaolinite/β-alanine under an N_2 atmosphere showed four endothermic peaks with mass losses at 220, 250, 370, and 450 °C (not shown). The peak at 450 °C is mainly due to the dehydroxylation of kaolinite.[53] β-Alanine is normally polymerized by thermal treatment at 180–210 °C in an N_2 flow.[54] The endothermic peak at 220 °C and its shoulder at 250 °C should be due to polymerization of β-alanine between the layers. The endothermic peak at 370 °C is assignable to the decomposition of organic components.

Upon heat treatment of kaolinite/β-alanine, the basal spacing was decreased from 1.17 nm to 1.11 nm (Fig. 1D, E). This interlayer distance (0.39 nm) indicates a monolayer arrangement of poly(β-alanine) in kaolinite. The (060) diffraction peak of kaolinite was not shifted during the intercalation

Table 1 CHN data of kaolinite/β-alanine before and after heat treatment at 250 °C

	C (mass%)	N (mass%)	N/C ratio
Before heat treatment	8.96	3.41	0.33
After heat treatment	7.75	1.97	0.22

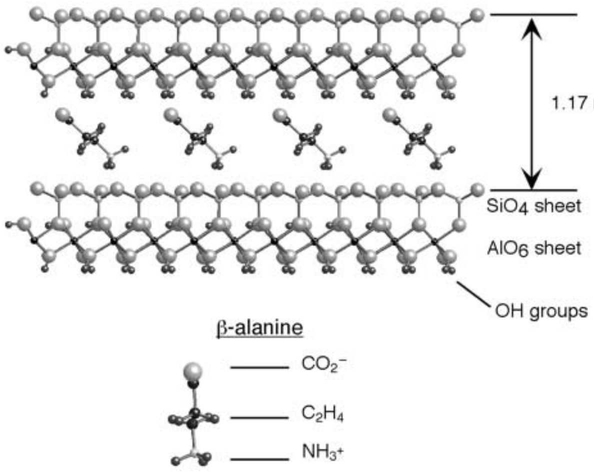


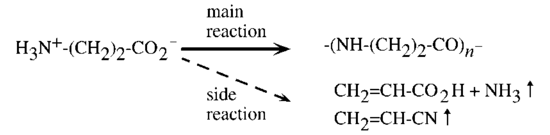
Fig. 6 Structural model of kaolinite/β-alanine.

and *in-situ* polymerization of β-alanine. This shows that aluminosilicate layers of kaolinite are stable during the reactions. The IR spectrum of kaolinite/β-alanine heated at 250 °C revealed that the interactions between the guest and kaolinite were changed. The ν(OH) of the kaolinite/β-alanine band at 3603 cm^{-1} disappeared, and a new ν(OH) band at 3630 cm^{-1} was observed (Fig. 4B, C). These changes in the OH stretching region showed that interlayer H_2O was deintercalated and the hydrogen bonds between the host and the guest were rearranged. The ν(NH) band of the heated sample appeared at 3404 cm^{-1}, at a much higher wavenumber than that of poly(β-alanine) at 3296 cm^{-1} and that of kaolinite/β-alanine at 3314 cm^{-1}, showing that the heated sample had relatively free NH groups compared with bulk poly(β-alanine) and β-alanine between the layers (Fig. 4C, D).

The ^{29}Si NMR spectrum of the product showed that the interactions between the silicate sheets and the guest species were changed. Upon heat treatment, the signal at −90.4 ppm disappeared, and new broad signals at −91.1, −92.1, and −92.9 ppm were detected. These shifts to lower frequencies, compared with those for raw kaolinite and kaolinite/β-alanine, indicate significant changes of the Si environments during the polymerization. The interactions in kaolinite/β-alanine perhaps disappeared during the heat treatment. This implies that the interactions between the silicate sheets and NH_3^+ groups disappeared and that the weak one between the silicate sheets and amide groups appeared, which is in accordance with the IR results.

Besides the polymerization of β-alanine, its partial decomposition was also observed. TG–MS results showed the generation of ammonia, acrylic acid and acrylonitrile as well as H_2O; $m/z = 72$, 55, 45, 43, 27, 26 (acrylic acid) and $m/z = 53$, 52, 26 (acrylonitrile) were detected from *ca.* 240 °C. The presence of acrylic acid between the layers is shown by the ^{13}C NMR and IR spectra of kaolinite/poly(β-alanine). The resonances at *ca.* 170–180 ppm are assignable to C=O due to both poly(β-alanine) and acrylic acid (Fig. 2B); and the C=C signal at 130.5 ppm was detected in the ^{13}C NMR spectrum. A small shoulder due to ν(C=O) was also detected at 1615 cm^{-1} in the IR spectrum (Fig. 3C). These data are consistent with those of a kaolinite–acrylic acid intercalation compound heated at 250 °C.[24]

The carbon content and the N/C ratio of kaolinite/β-alanine decreased after thermal treatment (Table 1). The reduction of the carbon content from 8.96 to 7.75 mass% showed that a small amount of volatile organic components such as acrylonitrile were deintercalated during the heat treatment. The decrease of the N/C ratio from 0.33 to 0.22 is explained by the decomposition of β-alanine to acrylic acid and NH_3 gas.[55]



$$H_3N^+\text{-}(CH_2)_2\text{-}CO_2^- \xrightarrow{\text{main reaction}} \text{-}(NH\text{-}(CH_2)_2\text{-}CO)_n\text{-}$$

$$\xrightarrow{\text{side reaction}} CH_2{=}CH\text{-}CO_2H + NH_3\uparrow \quad CH_2{=}CH\text{-}CN\uparrow$$

Scheme 1 Thermal reactions of β-alanine between the layers of kaolinite.

If all the guests in the heated sample are assumed to be poly(β-alanine) and acrylic acid, about 70% of intercalated β-alanine was polymerized and the rest was decomposed, and the thermal reaction of intercalated β-alanine is described as Scheme 1.

The TG and DTA curves of kaolinite/poly(β-alanine) under a dry air atmosphere were quite different from those of poly(β-alanine) (Fig. 7A, B). In the TG curves, the mass loss of poly(β-alanine) started at 230 °C, but that of kaolinite/poly(β-alanine) does not start until 300 °C. The DTA curve of poly(β-alanine) had four exothermic peaks due to combustion of the polymer, but that of kaolinite/poly(β-alanine) had only one exothermic peak at 340 °C. These findings are explained by the differences of the environments of the polymer. Polymers in kaolinite/poly(β-alanine) should have interactions not only with adjacent polymers but also with kaolinite, thus its thermal stability is higher than that of the polymer alone. Both poly(β-alanine) and acrylic acid seemed to be decomposed at almost the same time.

Conclusions

Kaolinite/β-alanine is prepared by using a displacement method. β-Alanine is present in a zwitterionic form with a monolayer arrangement. By heating kaolinite/β-alanine at 250 °C under an N_2 atmosphere, poly(β-alanine) is synthesized between the layers. The sample exhibited high thermal stability in air. However, the thermal decomposition of β-alanine also proceeded in part. The *in-situ* polycondensation method is a new approach and will be applicable for many kaolinite/polymers such as kaolinite/nylon 6. Kaolinite/polymer systems have unique characteristics such as specific interactions between the host and guest species, which makes this material system very different from other inorganic–polymer intercalation compounds.

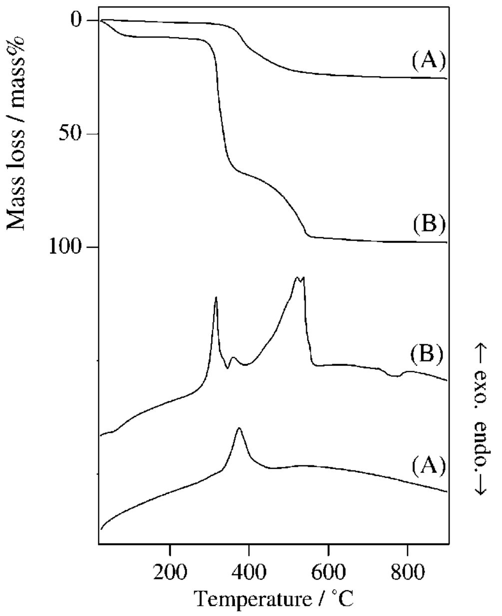


Fig. 7 TG-DTA curves of (A) kaolinite/β-alanine heated at 250 °C and (B) poly(β-alanine) under air atmosphere.

References

1 J. Pinnavaia, *Science*, 1983, **220**, 365.

2 M. Ogawa, *Chem. Rev.*, 1995, **95**, 399.

3 F. Berger, I. Dekany, K. Beneke and G. Lagaly, *Clay Miner.*, 1997, **32**, 331.

4 P. Aranda and E. Ruiz-Hitzky, *Chem. Mater.*, 1992, **4**, 1395.

5 Y. Fukushima, A. Okada, M. Kawasumi, T. Kurauchi and O. Kamigaito, *Clay Miner.*, 1988, **23**, 27.

6 C. Kato, K. Kuroda and M. Misawa, *Clays Clay Miner.*, 1979, **27**, 129.

7 T.-C. Chang, S.-Y. Ho and K.-J. Chao, *J. Chin. Chem. Soc.*, 1992, **39**, 209.

8 M. Sikka, L. N. Cerini, S. S. Ghosh and K. I. Winey, *J. Polym. Sci., Part B: Polym. Phys.*, 1996, **34**, 1443.

9 Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito, *J. Mater. Res.*, 1993, **8**, 1185.

10 Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi and O. Kamigaito, *J. Polym. Sci., Part A*, 1993, **31**, 983.

11 P. C. LeBaron, Z. Wang and T. J. Pinnavaia, *Appl. Clay Sci.*, 1999, **15**, 11.

12 H. Shi, T. Lan and T. J. Pinnavaia, *Chem. Mater.*, 1996, **8**, 1584.

13 K. Yano, A. Usuki, A. Okada, T. Kurauchi and O. Kamigaito, *J. Polym. Sci., Part A*, 1993, **31**, 2493.

14 A. Usuki, M. Kato, A. Okada and T. Kurauchi, *J. Appl. Polym. Sci.*, 1997, **63**, 137.

15 T. J. Pinnavaia and G. Beal, *Polymer–Clay Nanocomposites: Unique Polymers with a Dispersed Nanophase*, John Wiley & Sons Ltd, New York, 2001.

16 K. Isoda, K. Kuroda and M. Ogawa, *Chem. Mater.*, 2000, **12**, 1702.

17 A. Weiss, W. Thielepape, G. Göring, W. Ritter and W. Schäfer, *Int. Clay Conf.*, 1963, **1**, 287.

18 J. G. Thompson and C. Cuff, *Clays Clay Miner.*, 1985, **33**, 490.

19 Y. Sugahara, S. Kitano, S. Satokawa, K. Kuroda and C. Kato, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2607.

20 Y. Sugahara, S. Satokawa, K. Kuroda and C. Kato, *Clays Clay Miner.*, 1988, **36**, 343.

21 Y. Sugahara, S. Satokawa, K.-I. Yoshioka, K. Kuroda and C. Kato, *Clays Clay Miner.*, 1989, **37**, 143.

22 T. Sugiyama, M. Ogawa, Y. Sugahara, K. Kuroda and C. Kato, *Book of Abstracts, 35th Annual Meeting of the Clay Science Society of Japan*, 1990, p. 76.

23 Y. Sugahara, S. Satokawa, K. Kuroda and C. Kato, *Clays Clay Miner.*, 1990, **38**, 137.

24 Y. Sugahara, T. Nagayama, K. Kuroda, A. Doi and C. Kato, *Clay Sci.*, 1991, **8**, 69.

25 Y. Sugahara, T. Sugiyama, T. Nagayama, K. Kuroda and C. Kato, *J. Ceram. Soc. Jpn.*, 1992, **100**, 413.

26 Y. Komori, Y. Sugahara and K. Kuroda, *J. Mater. Res.*, 1998, **13**, 930.

27 Y. Komori, Y. Sugahara and K. Kuroda, *Chem. Mater.*, 1999, **11**, 3.

28 Y. Komori, Y. Sugahara and K. Kuroda, *Appl. Clay Sci.*, 1999, **15**, 241.

29 Y. Komori, A. Matsumura, T. Itagaki, Y. Sugahra and K. Kuroda, *Clay Miner.*, 2000, **11**, 47.

30 K. Kuroda, K. Hiragturi, Y. Komori, Y. Sugahara, H. Mouri and Y. Uesu, *Chem. Commun.*, 1999, 2253.

31 Y. Komori, H. Enoto, R. Takenawa, S. Hayashi and K. Kuroda, *Langmuir*, 2000, **16**, 5506.

32 J. J. Tunney and C. Detellier, *Chem. Mater.*, 1996, **8**, 927.

33 J. E. Gardolinski, L. C. M. Carrera, M. P. Cantão and F. Wypych, *J. Mater. Sci.*, 2000, **35**, 3113.

34 A. Mataumura, Y. Komori, T. Itagaki, Y. Sugahara and K. Kuroda, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 1153.

35 T. Itagaki, K. Yoshihiko, Y. Sugahara and K. Kazuyuki, *Book of Abstracts, 42nd Annual Meeting of the Clay Science Society of Japan*, 1998, p. 74.

36 M. Sato, *Clays Clay Miner.*, 1999, **47**, 793.

37 S. Olejnik, A. M. Posner and J. P. Quirk, *Clay Miner.*, 1970, **8**, 421.

38 G. Schilling and H. R. Kricheldorf, *Makromol. Chem.*, 1975, **176**, 3341.

39 P. Cloos, B. Calicis, J. J. Fripiat and K. Makay, *Proc. Inter. Clay Conf.*, 1966, **1**, 233.

40 J. F. Pearson and M. A. Slifkin, *Spectrochim. Acta, Part A*, 1972, **28**, 2403.

41 C. Garrigou-Lagrange, *Can. J. Chem.*, 1978, **56**, 663.

42 L. I. Berezhinsky, G. I. Dovbeshko, M. P. Lisitsa and G. S. Litvinov, *Spectrochim. Acta, Part A*, 1998, **54**, 349.

43 R. L. Ledoux and J. L. White, *Science*, 1964, **143**, 244.

44 J. G. Thompson, *Clays Clay Miner.*, 1984, **32**, 233.

45 P. Barron, R. L. Frost, J. O. Skjemstad and A. J. Koppi, *Nature*, 1983, **302**, 49.

46 J. G. Thompson, *Clays Clay Miner.*, 1985, **33**, 173.

47 M. J. Duer, J. Rocha and J. Klinowski, *J. Am. Chem. Soc.*, 1992, **114**, 6867.

48 J. J. Tunney and C. Detellier, *Chem. Mater.*, 1993, **5**, 747.

49 J. J. Tunney and C. Detellier, *J. Mater. Chem.*, 1996, **6**, 1679.

50 J. G. Thompson, P. J. R. Uwins, A. K. Whittaker and I. D. R. Mackinnon, *Clays Clay Miner.*, 1992, **40**, 369.

51 X. Xie and S. Hayashi, *J. Phys. Chem. B*, 1999, **103**, 5949.

52 S. Hayashi and E. Akiba, *Chem. Phys. Lett.*, 1994, **226**, 495.

53 G. W. Brindley and M. Nakahira, *J. Am. Ceram. Soc.*, 1959, **42**, 314.

54 J. S. Chirtel and A. M. Mark, US Patent, 1954, 2691643.

55 M. A. Ratcriff-Jr., E. E. Medley and P. G. Simmonds, *J. Org. Chem.*, 1974, **39**, 1481.