Communications

Direct Intercalation of Poly(vinylpyrrolidone) into Kaolinite by a Refined Guest Displacement Method

Yoshihiko Komori,[†] Yoshiyuki Sugahara,[†] and Kazuyuki Kuroda*[,†,‡]

Department of Applied Chemistry,
School of Science and Engineering,
Waseda University, Ohkubo-3, Shinjuku-ku,
Tokyo 169-8555, Japan, and Kagami Memorial
Laboratory for Materials Science and Technology,
Waseda University, Nishiwaseda-2, Shinjuku-ku,
Tokyo 169-0051, Japan

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Inorganic−organic multilayer nanocomposites have attracted considerable attention in recent years. In particular, intercalation of polymers into inorganic layered host lattices is an effective way to construct inorganic−organic nanosystems.[1,2] The constrained environment provided by layered hosts is expected to lead to a higher degree of polymer ordering and to useful optical and mechanical properties. Clay minerals are a group of common host materials for intercalation chemistry,[2−4] and various clay−polymer intercalation compounds have been prepared by using the smectite group of clay minerals such as montmorillonite.[5−9] Kaolinite, a clay mineral with the 1:1-type layered structure, is another candidate for a host material of nanocomposites because of its high crystallinity and unique structure; namely, one side of the interlayer space is covered with hydroxyl groups of the $AlO_2(OH)_4$ octahedral sheets and the other side is covered by oxygens of the SiO_4 tetrahedra.[10] However, due to the hydrogen-bonding between the layers, only a limited number of polar guest species such as *N*-methylformamide (NMF) and dimethyl sulfoxide (DMSO) can directly be intercalated. Thus, intercalation reactions of kaolinite have been extended by a guest displacement method in which new guest species can be intercalated by displacing previously intercalated species.[4,11,12] Various intermediates have been utilized so far such as a kaolinite−NMF intercalation compound,[13−15] a kaolinite−ammonium acetate intercalation compound,[11,16−18] a hydrated kaolinite,[19−21] and a kaolinite−methanol intercalation compound.[22]

We have already succeeded in preparing several kaolinite−polymer intercalation compounds such as a kaolinite−poly(acrylonitrile),[16] a kaolinite−poly(acrylamide),[13] and a kaolinite−poly(vinylpyrroridone) (PVP) intercalation compound.[18] In those reports, the appropriate monomers were first intercalated and then polymerized by thermal treatment (in situ polymerization method). One of the issues to be resolved for this procedure is the control of the degree of polymerization of the intercalated polymers. If polymers can be directly intercalated into kaolinite, it is easier to tune the degree of polymerization of polymers. Tunney et al. have recently succeeded in direct intercalation of poly(ethylene glycol) from the polymer melt at temperatures between 150 and 200 °C using a kaolinite−NMF (or −DMSO) intercalation compound as the intermediate.[23] To separate the products from the polymer matrix after the reaction, the excess polymers must be removed inevitably by washing. This procedure sometimes may lead to the removal of polymers not only on the external surface but also in the interlayer space of the kaolinite.

Here, we report the direct intercalation of a polymer into kaolinite at room temperature in a simple way by a refined displacement method which we have developed recently (Figure 1). The product can be easily separated from the polymer solution by centrifugation. As a polymer guest, we selected PVP, which has already been known to form an intercalation compound with kaolinite by in situ polymerization between the layers.[18]

By utilizing a kaolinite−ammonium acetate intercalation compound as the intermediate, we attempted the intercalation of PVP dissolved in water. The displace-

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[‡] Kagami Memorial Laboratory for Materials Science and Technology.
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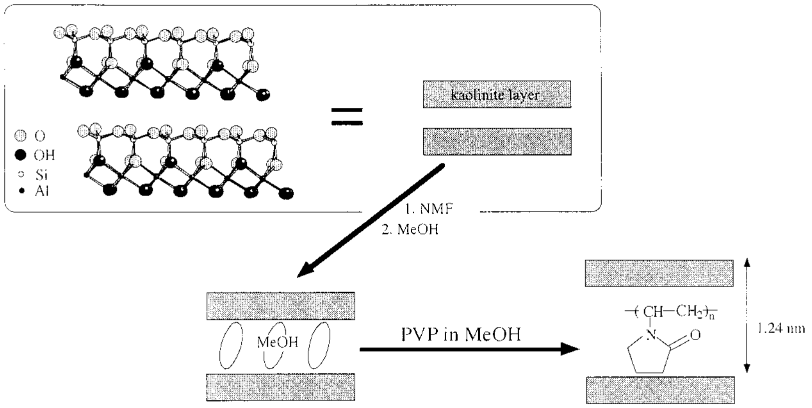

Figure 1. Schematic view of intercalation of PVP into kaolinite by guest displacement.

ment reaction between PVP and ammonium acetate was unsuccessful, resulting in deintercalation of ammonium acetate. Thus, the key for the intercalation reaction is to find a suitable selection for an intermediate and a solvent. On the basis of the description above, we selected a kaolinite–methanol intercalation compound as the intermediate and methanol as the solvent for PVP. The guest displacement ability of the kaolinite–methanol intercalation compound was previously proved to be excellent.[22] Furthermore, the solvent was the same as the intercalated guest in the intermediate, which was expected to suppress spontaneous deintercalation of methanol and facilitate the guest displacement reaction between the methanol and PVP.

The kaolinite used in the present study was KGa1, a well-crystallized Georgia kaolinite obtained from the Source Clays Repository of the Clay Minerals Society (U.S.A.). A small amount of anatase was detected as an impurity by X-ray powder diffraction (XRD). Poly(vinylpyrrolidone) (PVP, Tokyo Kasesi Co.; MW =10 000) was used as received. The intercalation of PVP was achieved by using a wet kaolinite–methanol intercalation compound as the intermediate. The kaolinite–methanol intercalation compound was prepared as reported previously;[22] at first, a kaolinite–NMF intercalation compound was prepared,[24] and then the guest displacement reaction between NMF and methanol was conducted. Ten grams of PVP was dissolved in 10 mL of MeOH, and the PVP solution was added to the wet kaolinite–methanol intercalation compound. After the reaction mixture was stirred for 1 day at room temperature, the product was centrifuged and yellowish white powders were obtained without a washing procedure. Kaolinite, the intermediates, and the product were analyzed by XRD, ^{13}C CP/MAS NMR, IR, ^{29}Si CP/MAS NMR, TG, and elemental (CHN) analyses.

The basal spacing of the kaolinite–NMF intercalation compound increased to 1.08 nm from that of kaolinite (0.72 nm) (Figure 2a,b). After the treatment of the kaolinite–NMF intercalation compound with methanol, the basal spacing slightly increased to 1.11 nm under wet conditions (Figures 2c), which was the same as in our previous report.[22] After the wet kaolinite–methanol intercalation compound was treated with a methanol solution of PVP, the basal spacing increased further to 1.24 nm (Figure 2d), indicating the intercalation of PVP into kaolinite. Because the difference in the basal spacings between the final product and raw kaolinite is about 0.52 nm, PVP is arranged mostly as a monolayer between the layers of kaolinite.

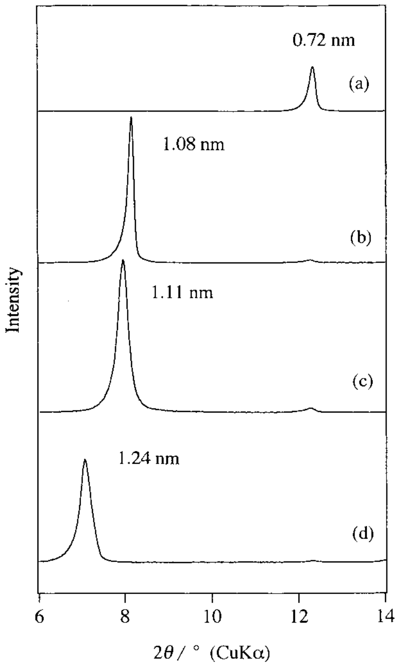

Figure 2. XRD patterns of (a) kaolinite, (b) kaolinite–NMF intercalation compound, (c) kaolinite–methanol intercalation compound, and (d) kaolinite–PVP intercalation compound. The samples of b, c, and d were measured under wet conditions.

The ^{13}C CP/MAS NMR spectrum of the kaolinite–PVP intercalation compound is shown in Figure 3a. The signals due to the CH and CH_2 groups were observed at around 18–44 ppm.[25] The profile in this region was almost the same as that of PVP in the solid state (Figure 3b). On the other hand, two signals assigned to carbonyl groups were detected at 176.2 and 182.9 ppm. The first signal at 176.2 ppm was observed at almost the same chemical shift in the spectrum of PVP and was also detected in the spectrum for the in situ polymerization sample.[18] The second signal was a peculiar one which was neither detected in the spectrum of PVP nor in the spectrum of the in situ polymerization sample. The constant length between carbonyl groups of PVP may

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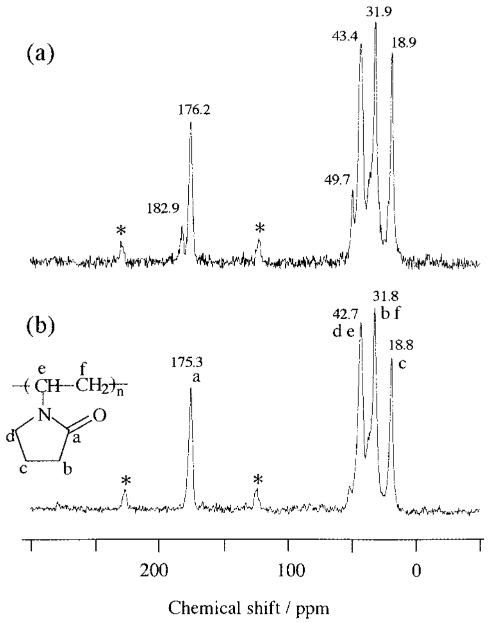

Figure 3. ^{13}C CP/MAS NMR spectra of (a) kaolinite−PVP intercalation compound and (b) PVP, measured at 100.40 MHz. Spinning sidebands are marked by asterisks.

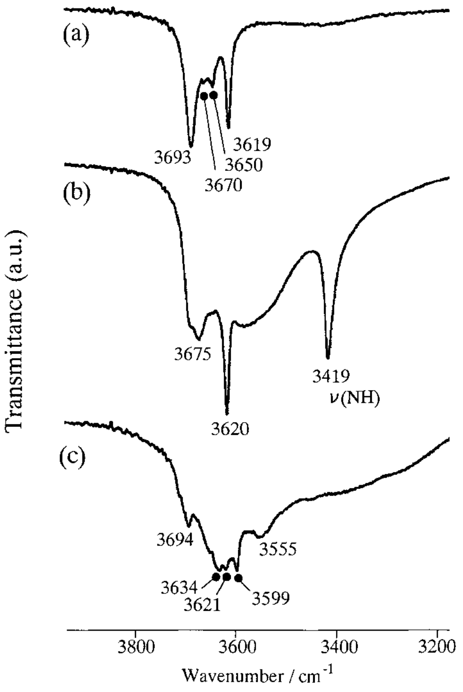

Figure 4. IR spectra (around OH-stretching region) of (a) kaolinite, (b) kaolinite−NMF intercalation compound, and (c) kaolinite−PVP intercalation compound. The samples were prepared as KBr pellets. The pellet of sample c was heated at 120 °C before the measurement.

force the formation of new interactions between the carbonyl groups and hydroxyl groups in kaolinite. The small signal at 49.7 ppm could be assigned to the methyl carbon of methanol, suggesting that a small amount of methanol was adsorbed onto the PVP or still remained in kaolinite. On the other hand, no signals due to NMF were observed.

The IR spectra around the OH-stretching region are shown in Figure 4, although the spectrum of the kaolinite−methanol intercalation compound could not be obtained because of the instability of methanol in the interlayer space under ambient conditions. Kaolinite shows four OH-stretching bands, and three of them at 3693, 3670, and 3650 cm^{-1} are perturbed by the guest species.[4] Hydrogen-bonded hydroxyl groups show new bands at lower wavenumbers, which depends on the strength of hydrogen-bonding with the guest species. On intercalation of NMF molecules, the new bands that appeared at 3675 and 3419 cm^{-1} are assigned to hydrogen-bonded OH stretching and NH stretching, respectively. After the methanol intercalation and the following PVP treatment, these bands disappeared and the bands assigned to hydrogen-bonded OH stretching were detected at 3634, 3599, 3555 cm^{-1}. The appearance of the new bands indicates the formation of characteristic hydrogen-bonding between PVP and kaolinite. The band at 3599 cm^{-1} was a characteristic one which was not observed in the spectrum of the in situ polymerization sample, which may be related with the unique signal at 182.9 ppm due to carbonyl groups in the ^{13}C NMR spectrum. The disappearance of the bands due to NMF molecules indicated the deintercalation of NMF by the displacement reaction, consistent with the results of ^{13}C NMR spectroscopy.

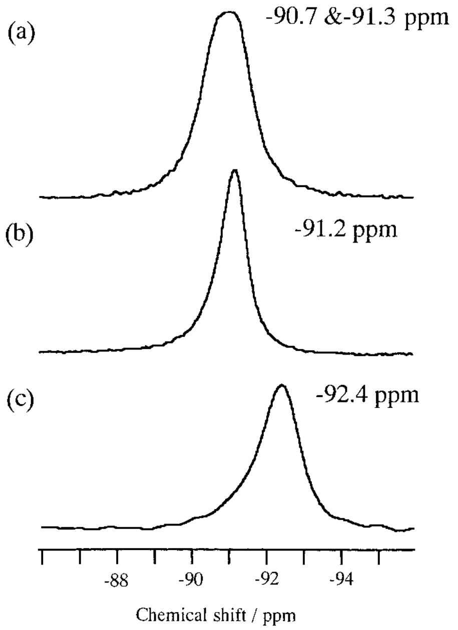

Figure 5. ^{29}Si CP/MAS NMR spectra of (a) kaolinite, (b) kaolinite−NMF intercalation compound, and (c) kaolinite−PVP intercalation compound, measured at 79.30 MHz.

The ^{29}Si CP/MAS NMR signals of kaolinite, shown in Figure 5, are also affected by intercalation. The spectrum of raw kaolinite can be simulated much better by two line shapes than by one. The chemical shifts of the two signals were −90.7 and −91.3 ppm, in line with previous reports.[26,27] The spectrum of the kaolinite−NMF intercalation compound showed a narrow singlet at −91.2 ppm. After the methanol intercalation and the following PVP treatment, the signal further shifted to −92.4 ppm, which was much lower than that at −91.4 ppm for the in situ polymerization sample.[18] The difference may be caused by the peculiar interaction

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between PVP and kaolinite, corresponding to the results of ^{13}C NMR and IR.

The CHN analysis showed that the number of PVP units (C_6H_9NO) per kaolinite unit [$Al_2Si_2O_5(OH)_4$] was 1.9. The TG measurement of the product corresponded to this result. When the kaolintie−PVP intercalation compound was washed with ethanol or water, PVP was quickly deintercalated even after a few minutes of washing, which was confirmed by the disappearance of the XRD peak at 1.24 nm. Therefore, it is very difficult to remove only adsorbed PVP on the external surface from the kaolinite−PVP intercalation compound. Thus, to estimate the amount of PVP adsorbed on the external surface, we conducted an additional experiment to mix raw kaolinite and a PVP−methanol solution with the same concentration in this study (10 g of PVP in 10 mL of methanol) because PVP is not intercalated into raw kaolinite directly. Although there was a previous report showing that PVP adsorbed on the surface of kaolinite,[28] the concentration of PVP used in this report was much lower than that used in this study. After centrifugation and removal of the supernatant, the number of adsorbed PVP units was estimated to be 1.1 per kaolinite unit. Consequently, the number of PVP units in the interlayer space was estimated to be 0.8, and some polymers were present on the external surface and some portions of the intercalated PVP chains would be out of the interlayer space. However, the adsorbed polymers do not affect the aforementioned discussion of the spectroscopic results, because the OH region of the IR spectra and the ^{29}Si NMR spectra are not affected by polymers on the external surface. Additionally, in the ^{13}C NMR spectra, we have discussed the peculiarity of the peak which has not been observed in the spectrum of PVP itself. Considering the volume of interlayer space of kaolinite, the degree of packing of PVP is 0.8 PVP/119 Å^3, which is almost equal to 0.76 PVP/129 Å^3 for the MoS_2−PVP system.[29] Furthermore, this value is close to the typical values of ∼1 for other kaolinite−organic intercalation compounds[30−32] and still larger than 0.4 for the sample obtained by in situ polymerization.[18]

In conclusion, direct intercalation of PVP into the interlayer space of kaolinite at room temperature has been achieved by utilizing both a kaolinite−methanol intercalation compound and PVP dissolved in methanol. This procedure is superior to the in situ polymerization of monomers between the layers from the viewpoint of the possibility of controlling the degree of polymerization by choosing polymers with appropriate molecular weight. Since we have prepared various kaolinite−polymer intercalation compound by an “in situ” method, the kind of polymers can be varied by employing appropriate conditions.

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