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Solvent free synthesis of polyaniline–clay nanocomposites from mechanochemically intercalated anilinium fluoride

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Nanocomposites consisting of conducting polyaniline and clay minerals were successfully synthesized from mechanochemically intercalated anilinium fluoride; the nanocomposites prepared by the mechanochemical intercalation method contained much more polyaniline in the clay layers than those prepared by a conventional solution method.

Polymer intercalation nanocomposites prepared by using layered materials have received considerable attention because they are expected to lead to a high degree of polymer ordering and exhibit thermal stability and enhanced mechanical properties.[1] The encapsulated conducting polymers in the interlayer spaces of organic layered materials may provide different characteristics and unique structure, which cannot be attained with a pristine conducting polymer. Therefore, nanocomposites consisting of conducting polyaniline (PANI) with various layered materials, such as FeOCl,[2] MoO_3,[3,4] V_2O_5[5] and clay minerals[6–8] have been extensively studied. Among these nanocomposites, PANI–clay nanocomposites have been especially studied because clay minerals have attractive advantages such as large surface area and ion-exchange properties. PANI–clay nanocomposites are usually prepared from mixtures of aniline and clays in an aqueous solution. However, we found that a mechanochemical reaction was an effective method for the preparation of PANI–clay nanocomposites. A mechanochemical reaction has obvious advantages such as being an environmentally benign process not using any solvents as well as a simple process. Ogawa *et al.* reported that solid-state reactions are useful ways to introduce organic guest species into the interlayer spaces of clay minerals.[9,10] In this communication, we report the successful synthesis of nanocomposites containing much PANI in the clay layers from mechanochemically intercalated anilinium fluoride.

Sodium montmorillonite (MMT) with a cation exchange capacity (CEC) of 115 meq/100 g (Kunipia F, Kunimine Ind. Co.) was used as a host material. Anilinium fluoride (AF) was synthesized by the reaction of aniline with hydrofluoric acid in water and was used after recrystallization from THF. The mixtures of sodium MMT and AF were mechanochemically ground with a mortar and a pestle at room temperature for 10 min. The grinding operation was carried out manually. The loading of AF varied from 1.15 to 17.25 mmol/1g of MMT. After grinding, a sufficient amount of ammonium peroxodisulfate, the molar ratio of ammonium peroxodisulfate to AF being 1.5, was added to the mortar and the polymerization was also performed manually for 30 min by mechanochemical grinding with a pestle. After standing for 72 hours, the obtained dark green powder was washed with distilled water and repeatedly centrifuged. The final product was dried under vacuum and the PANI–MMT nanocomposite was obtained.

The XRD patterns of the products before and after polymerization and the plots of the basal spacing calculated from XRD against the amount of added AF are shown in Figs. 1 and 2, respectively.

At first, sodium MMT was ground with a mortar and a pestle for 10 min as reference. However, there are no changes in the XRD patterns of MMT before and after grinding. Therefore, the grinding does not affect the crystallinity of the MMT itself. The intercalation of AF into MMT provided red or orange solids. As shown in Fig. 1 (A), the (001) diffraction peaks of AF-intercalated MMT were observed at 2θ = 5.9° when the amounts of added AF were 1.15, 2.3 and 3.45 mmol/1g of MMT. The basal spacing increased from 0.96 to 1.48 nm, indicating the expansion of the interlayer space (*d*-expansion) by 0.52 nm and the successful intercalation by the mechanochemical intercalation method. (The basal spacing of dried sodium MMT was 0.96 nm.) Furthermore, the (001) diffraction

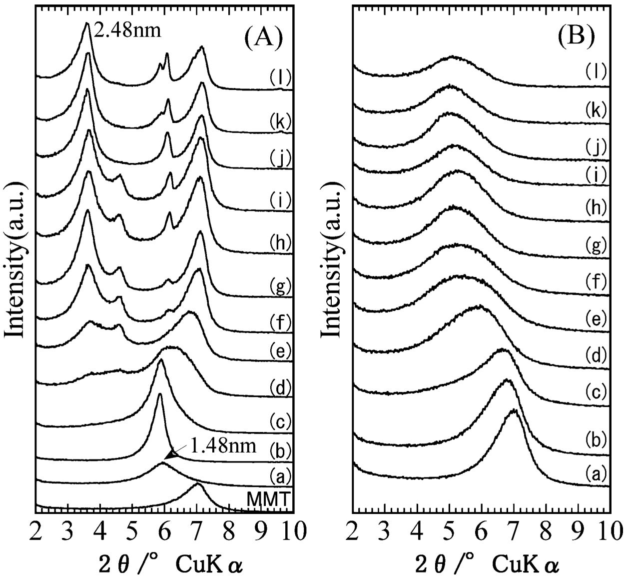

Fig. 1 X-ray diffraction patterns of AF-intercalated MMT with various amounts of added AF (A) before and (B) after polymerization, together with sodium MMT after grinding for 10 min. (a) 1.15, (b) 2.3, (c) 3.45, (d) 4.6, (e) 5.75, (f) 6.9, (g) 8.05, (h) 9.2, (i) 10.35, (j) 11.5, (k) 13.8 and (l) 17.25 (mmol/1g of MMT).

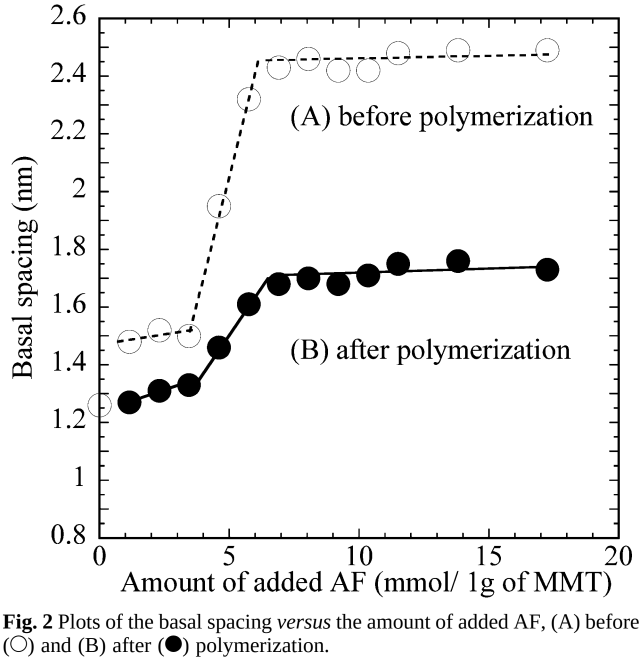

Fig. 2 Plots of the basal spacing *versus* the amount of added AF, (A) before (○) and (B) after (●) polymerization.

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peaks of the products were shifted to a lower angle by grinding higher amounts of AF with MMT and the sharp peaks were clearly observed at $2\theta = 3.6°$ when the amounts of added AF were higher than 6.9 mmol/1g of MMT. The basal spacing of the products drastically increased to 2.48 nm as shown in Fig. 2 (A), indicating *d*-expansion by 1.52 nm. This *d*-expansion (1.52 nm) is about three times greater than the value of 0.52 nm. The large *d*-expansion suggests that a greater amount of guests has been intercalated in the interlayer spaces of MMT by grinding an excess amount of AF. In the TG curve for AF-intercalated MMT with *d*-expansion of 1.52 nm, weight loss was observed in the temperature range 120–200 °C. This weight loss is ascribed to the vaporization of AF. It is thus expected that AF-intercalated MMT obtained by grinding an excess amount of AF contained both anilinium cations and AF molecules, and that the driving force for the intercalation of the former was the ion exchange reactions of the interlayer exchangeable cations and that of the latter was the hydrophobic interactions between anilinium–MMT obtained by ion exchange reaction and AF itself. The basal spacing of the products was constant even when higher amounts of AF were added, indicating that the amount of AF intercalated into MMT had limitations. In Fig. 1 (A), intense peaks at approximately $2\theta = 7°$ correspond to the (002) diffraction peaks. The other small peaks cannot be easily assigned at present.

The XRD patterns of the products after washing with distilled water showed a decrease in the basal spacing due to desorption of the intercalated AF molecules. Consequently, the amount of the intercalated species could not be determined correctly. However, the XRD results suggest that the basal spacing of the product prepared by the mechanochemical intercalation method increases with an increase in the amount of AF added up to 6.9 mmol/1g of MMT (6-fold the CEC of MMT). This indicates that most of the AF used was intercalated into MMT when the amount of AF added was not more than 6.9 mmol/1g of MMT. In contrast, the basal spacing of the product prepared by a conventional solution method was 1.45 nm and did not further increase even when higher amounts of AF were added. Furthermore, the TG result for this product prepared by the solution method revealed that the amount of intercalated species was about equal to the CEC of MMT. Therefore, it is thought that the maximum amount of guests intercalated by the mechanochemical intercalation method is approximately six times that by a solution method. In addition, the (001) diffraction peaks of the products prepared by the mechanochemical intercalation method were sharper than the peaks of products prepared by the solution method. The sharpness of these peaks indicates that the resulting intercalation compounds prepared by the mechanochemical intercalation method constitute an organized stacking arrangement. A similar large *d*-expansion (1.51 nm) was observed for the mechanochemical intercalation method when anilinium chloride was used as a guest compound, though the maximum amount of intercalated species was approximately only 4.6 mmol/1g of MMT. Additionally, when using anilinium bromide and anilinium iodide, those were approximately 1.15 and less than 1.15 mmol/1g of MMT, respectively. These results suggest that the size of counter anions has an effect on the conformation of intercalated species and the smaller molecules are easily intercalated in the clay layers for the mechanochemical intercalation method.

The (001) diffraction peaks of the products after polymerization were shifted to a higher angle than those before polymerization as shown in Fig. 1 (B), indicating the synthesis of PANI in the clay layers. With an increase in the added AF amount, these peaks gradually shifted to a lower angle and became broad. The *d*-expansion for the samples after polymerization increased with increasing the added amount of AF up to 6.9 mmol/1g of MMT as shown in Fig. 2 (B). However, the *d*-expansion was constant and did not further increase even when higher amounts of AF were added. These results suggest that the amount of PANI synthesized in the interlayer spaces was limited when the amount of added AF was 6.9 mmol/1g of MMT.

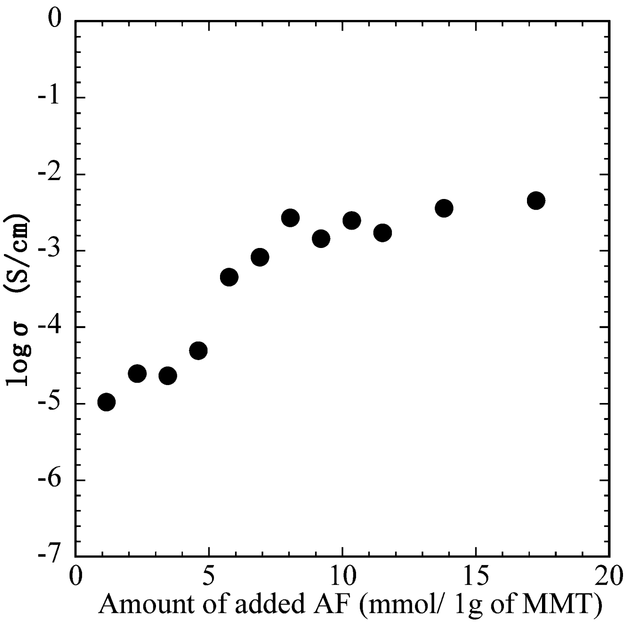

Fig. 3 Conductivities of PANI–MMT nanocomposites.

The FT-IR spectra confirm the presence of the conductive form of PANI in the clay layers. In the FT-IR spectra, the peaks of the characteristic vibrations of conducting PANI at 1247(ν(C–N)), 1301(ν(C–N)), 1491(δ(N–H)), 1570(δ(N–H)) and 3452(ν(N–H)) cm^{-1} are observed.

The conductivities of the synthesized PANI–MMT nanocomposite particles in pressed pellets were measured using the four-probe method. Fig. 3 shows the plots of the conductivities of PANI–MMT nanocomposites against the amount of added AF. The conductivities of the samples in pressed pellets ranged in the order of between 10^{-5} and 10^{-3} S cm^{-1}. They had a tendency to increase with increasing amount of added AF. This can be explained by an increase in the extent of conducting PANI contained in the nanocomposites.

In conclusion, we have shown the synthesis of PANI–MMT nanocomposites by the mechanochemical intercalation method. This method enables us to synthesize nanocomposites that contain much PANI in the clay layers. Consequently, the mechanochemical intercalation method provides a new and effective method for the preparation of PANI–clay nanocomposites.

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