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PREPARATION OF MONTMORILLONITE-POLYACRYLAMIDE INTERCALATION COMPOUNDS AND THE WATER ABSORBING PROPERTY

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ABSTRACT

Montmorillonite-acrylamide intercalation compounds were prepared by treating sodium montmorillonite with acrylamide aqueous solutions, the concentrations of which were varied from 4% to 20%. The basal spacings of the compounds prepared from 4% and 20% acrylamide aqueous solutions were ca. 15 Å and 20 Å, respectively. These values suggested that acrylamide was intercalated as monomolecular and bimolecular arrangements in the interlayer space of montmorillonite with the molecular plane perpendicular to the silicate sheet. After the removal of excess acrylamide by washing with nonpolar organic solvents, the intercalated acrylamide was polymerized to form montmorillonite-polyacrylamide intercalation compounds. These compounds absorbed more water than raw sodium montmorillonite.

Key words: Montmorillonite, Intercalation Compound, Polyacrylamide, Water Absorbent

INTRODUCTION

Some layered clay minerals are known to accommodate various organic substances in their interlayer spaces to form intercalation compounds (Theng, 1974). Many studies have been carried out because such clay-organic intercalation compounds have the potential to exhibit unique properties. Montmorillonite, which is a typical swelling clay mineral, has been widely used as a host material. Recently, catalytic (Pinnavaia, 1983), electrochemical (Ghosh et al., 1983), and photochromic (Miyata et al., 1987) properties of montmorillonite-organic intercalation compounds have been investigated.

Montmorillonite-polymer intercalation compounds have attracted much interest in polymer science because the intercalated polymer has a possibility to take an unusual ordered conformation (Theng, 1979). Montmorillonite-polymer intercalation compounds are usually prepared in two ways: by polymerizing an intercalated monomer and by intercalating a polymer directly. The former method has been applied to prepare the intercalation compounds with poly(methyl methacrylate) (Blumstein, 1965), polystyrene (Kato et al., 1981), polyacrylonitrile (Blumstein, 1974), and so on. The application of montmorillonite-polymer intercalation compounds has also been reported. Montmorillonite-polyacrylonitrile intercalation compounds were used as the precursor for

the preparation of non-oxide ceramics (Sugahara et al., 1984, 1986) and graphite (Kyotani et al., 1988).

On the other hand, polyacrylamide, which is a typical hydrophilic polymer, has been used as a flocculating agent of mineral suspensions and a soil aggregate stabilizer (Theng, 1979). From this point of view, montmorillonite-polyacrylamide intercalation compounds have already been prepared by intercalating the polymer directly (Siffert et al., 1977, 1979, Tanihara et al., 1977). Bottero et al., (1988) studied the adsorption of polyacrylamide onto sodium montmorillonite in detail. Friedlander (1964) has reported the formation of montmorillonite-polyacrylamide intercalation compounds by standing montmorillonite in contact with acrylamide above its melting point (84.5°C).

Recently, partly crosslinked polyacrylamide has been applied to a water absorbent. The physical properties of their swollen gels have attracted considerable attention because of their possibility to be applied to a mechanochemical actuator (Tanaka, 1981). Montmorillonite is also known to swell in water to form a thixotropic gel. Consequently, the complexation of montmorillonite and polyacrylamide can be expected to show a novel water absorbing property. As described above, some studies on the preparation of montmorillonite-polyacrylamide intercalation compounds have already been performed. Those compounds, however, have been prepared by the direct intercalation of polyacrylamide and the amount of adsorbed polyacrylamide on to clays was very small. No experiments to examine the water absorbing property of the compounds have been reported. Therefore, montmorillonite-polyacrylamide intercalation compounds were prepared by polymerizing the intercalated acrylamide monomers in the interlayer region of montmorillonite. Subsequently, we investigated the possibility of the montmorillonite-polyacrylamide intercalation compound as a new type of water absorbent.

EXPERIMENTAL

Materials

The clay mineral was sodium-montmorillonite (Kunipia F) obtained from Aterazawa mine (Yamagata, Japan). The chemical composition was the same as described in the previous report (Sugahara et al., 1984). Homoionic (Co-, Ni-, and Cu-) montmorillonites were prepared by ion exchange with aqueous solutions of metal chlorides. After the ion exchange was repeated three times, the excess salts were removed by washing with water. Acrylamide (extra pure grade, WAKO Pure Chemical Industries Co.) was recrystallized from ethyl acetate before use. Benzoyl peroxide (BPO) (WAKO Pure Chemical Industries Co.) was used without further purification.

Preparation of montmorillonite-polyacrylamide intercalation compounds

Sodium montmorillonite (1 g) was dispersed into 50 ml of acrylamide aqueous solution. The concentration of the acrylamide aqueous solution was varied from 4% to 20%. All the mixtures were stirred for 1 day and centrifuged. After drying at 70°C which caused the sublimation of acrylamide to some extent, the products were washed further with CCl_4 or n-heptane to remove excess acrylamide. Then, the intercalated acrylamide was polymerized by heating the intercalation compounds with benzoyl peroxide as an initiator

in n-heptane at 70°C for 1 day.

Characterization

X-ray diffraction (XRD) patterns of the compounds were obtained by using a Rigaku RAD-IIA diffractometer (with Mn filtered Fe Kα radiation). Infrared (IR) spectra of the compounds were recorded on a Perkin Elmer FT IR 1640 Fourier-transform spectrometer by the KBr disk method (sample concentration: 2%). DTA curves were obtained using a Shimadzu DT-20B instrument and α-Al_2O_3 as a reference material. DTA was carried out at a heating rate of 10°C min^{-1}.

The ratio of absorbed water to montmorillonite-polyacrylamide intercalation compounds were determined by TG. Each compound was placed in a large amount of distilled water and allowed to stand for 1 day. After the excess water was removed by filtration, the sample was analyzed by TG. TG curves were recorded on a Shimadzu TGA-40 instrument at a heating rate of 5°C min^{-1}. Since all the absorbed water was desorbed below 120°C, the weight loss up to the temperature was measured.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of unwashed montmorillonite-acrylamide intercalation compounds prepared from various concentrations of acrylamide. With the increase in the concentration, d(001) diffraction peaks shifted to lower 2θ angles, showing two typical peaks which corresponded to the basal spacings of ca. 15 Å and 20 Å. Thus, two types of montmorillonite-acrylamide intercalation compounds were prepared. The compounds with the smaller basal spacing were obtained from lower concentrations of acrylamide. The compounds with the larger spacing were prepared from the higher concentrations. In this paper, the two types of the compounds were designated as the 15 Å compound and the 20 Å compound, respectively. The 15 Å compound prepared from 4% solution and the 20 Å compound from 20% were used for further studies.

The influence of washing with organic solvents on the intercalation compounds was checked by XRD. When the 20 Å compound was used, the intercalated acrylamide was partly desorbed to form the 15 Å compound after washing with CCl_4 or $CHCl_3$, whereas it was stable against washing with n-heptane. Therefore, the 20 Å compound was washed with n-heptane. When the 15 Å compound was employed, the intercalated acrylamide was stable against washing with CCl_4, so it was washed with CCl_4.

Table 1 displays the basal spacings of the washed samples and their C:N data. The C:N ratios of the intercalation compounds are in good agreement with that of acrylamide. The basal spacings of the 15 Å compound and the 20 Å compound indicated the expansion of the interlayer space by 5.4 Å and 9.9 Å, respectively. (The basal spacing of Na-montmorillonite was 9.6 Å).

The infrared spectra of the washed samples are shown in Fig. 2. Table 2 displays the principal infrared absorption bands and their assignments. Comparing the absorption bands of the two types of the compounds, the 15 Å compound and the 20 Å compound, almost all the absorption bands were observed in the same frequencies. For example, in the spectrum of the 15 Å compound, the absorption bands due to N-H stretching vibration

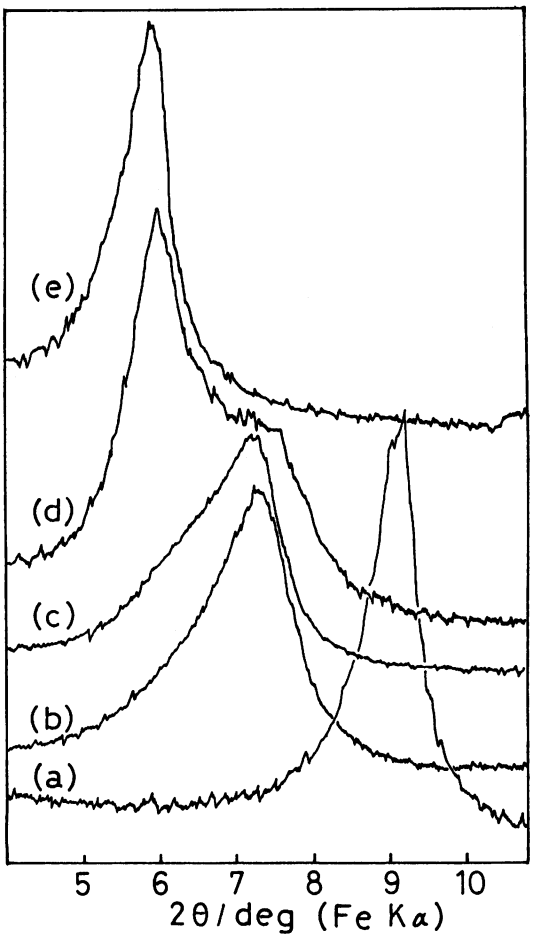

FIG. 1. X-ray powder diffraction patterns of (a) montmorillonite, (b)~(e) montmorillonite-acrylamide intercalation compounds prepared from acrylamide aqueous solutions; (b) 4%, (c) 10%, (d) 16%, and (e) 20%.

TABLE 1. The basal spacings of the intercalation compounds and the amounts of adsorbed organic substances

	d(Å)*	C:N ratio**	Acrylamide/g per 100 g clay
15 Å compound	5.4	2.57 : 1	18
20 Å compound	9.9	2.53 : 1	31

* d = d(001) — 9.6 Å

** The C:N ratio of acrylamide is 2.52:1

at 3488 cm^{-1} and 3397 cm^{-1}, the band assigned to C=O stretching vibration at 1676 cm^{-1}, and the band ascribable to C=C stretching vibration at 1624 cm^{-1} appeared. From both XRD and IR data, it can be concluded that acrylamide monomer was intercalated in the interlayer of montmorillonite. Compared with the bands of acrylamide in $CHCl_3$, which was reported by Jonathan (1961), the bands due to N-H stretching vibration and C=O stretching vibration appeared in lower frequencies. Consequently, these bonds had a certain interaction in the interlayer of montmorillonite.

The reaction between amide and montmorillonite have already been studied. Mortland has described four possible reaction mechanisms which may be involved in the adsorp-

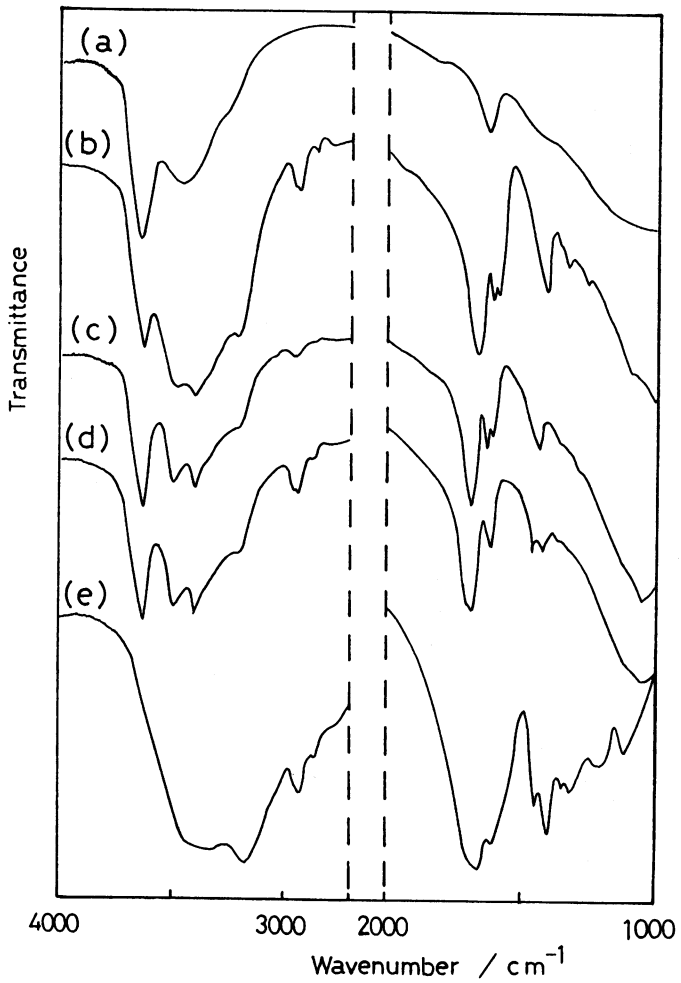

FIG. 2. Infrared spectra of (a) montmorillonite, (b) 20 Å compound, (c) 15 Å compound, (d) polymerized 15 Å compound, (e) polyacrylamide.

TABLE 2. Infrared assignments of acrylamide, copper acrylamide coordination complex, and the montmorillonite acrylamide intercalation compounds

Wavenumber (cm^{-1})					
AAm*	$Cu(AAm)_6(BF_4)$**	15 Å comp.	20 Å comp.	Cu-mont AAm comp.	Assignment**
3540	3445	3488	3488	3478	
3502	3365	3397	3395	3393	
3423	3318			3368	ν(N-H)
3423	3318			3368	
3335	3270			3279	
3189	3220			3198	
3021					
1686	1663	1676	1676	1675	ν(C=O)
1647	1625	1624	1624	1623	ν(C=C)
1618	1580	1602	1599	1594	δ (N-H)
1592	1557(s)			1559(s)	
1277	1287	1282	1282	1283	ν(C-N)

* The data has taken from Jonathan (1961). (saturated $CHCl_3$ solution)

**The data was taken from the report by Farona et al. (1969) and the assignments are based on the same report.

tion phenomenon of amide molecules on to clays (Mortland, 1966, Tahoun et al., 1966). These are ion exchange of interlayer exchangeable cation with protonated amide molecule, hemisalt formation, coordination complex formation with interlayer exchangeable cation, and hydrogen bonding with surface oxygen atom. Since protonation and hemisalt formation usually occur in acid montmorillonite system, these two mechanisms can be excluded. In fact, when protonation or hemisalt formation occurs, the double bond character of the C=O bond will be decreased, and its absorption frequency should be largely decreased accordingly. However, no remarkable decrease in the absorption band due to C=O stretching vibration was observed. In addition, in the case of protonation, CN bond will have a double bond character to some extent, and the new band due to C=N should appear. New band due to C=N, however, could not be detected. Consequently, neither protonation nor hemisalt formation of acrylamide occurred in this case. Thus, the coordination complex formation and hydrogen bonding may play a major role in the reaction of acrylamide with montmorillonite.

Transition metal ion exchanged montmorillonites were used in order to confirm this estimate. By using the same procedure, acrylamide was intercalated into the transition metal montmorillonites. The basal spacings of the compounds were 19.1, 19.0, and 18.7 Å for Co-, Ni-, and Cu-montmorillonites, respectively. Table 2 shows the infrared absorption bands of the Cu-montmorillonite acrylamide intercalation compound and copper acrylamide coordination compound (Farona et al., 1969, Reedijk, 1971). The bands

of the intercalation compound were in good accordance with that of the coordination compound. Thus the coordination complex formation in the interlayer space took place. Acrylamide coordinate to the transition metal ions through oxygen of the carbonyl group (Reedijk, 1971). Therefore, NH_2 groups can form hydrogen bonding with oxygen in the silicate surface. Similar results were obtained when Ni- and Co-montmorillonites were used.

The arrangement of acrylamide in the interlayer space was estimated on the basis of XRD and IR results described above. Acrylamide molecule has a rectangular shape of 4.2 Å × 3.8 Å. The expansion of the interlayer region was ca. 5 Å in the 15 Å compound and ca. 10 Å in the 20 Å compound, respectively. Consequently, it is not likely that acrylamide molecules lie flat in the interlayer space since the molecular thickness is about 2.6 Å. Considering the sizes of both acrylamide and exchangeable cations, acrylamide was probably adsorbed as monomolecular arrangement in the 15 Å compound with its molecular plane perpendicular to the silicate sheet. The IR results, which showed that the interaction between montmorillonite and acrylamide was mainly hydrogen bonding and coordination complex formation, confirmed this estimate. Therefore, it was thought that the carbonyl group of acrylamide was oriented to the exchangeable cation, and the NH_2 group was directed to silicate sheet. In the 20 Å compound, the intercalated acrylamide was probably adsorbed as bimolecular arrangement in a similar manner.

Polymerization of the intercalated acrylamide was confirmed by IR, DTA, and XRD. Figure 2 shows the variation in the infrared spectra of the 15 Å compounds before and

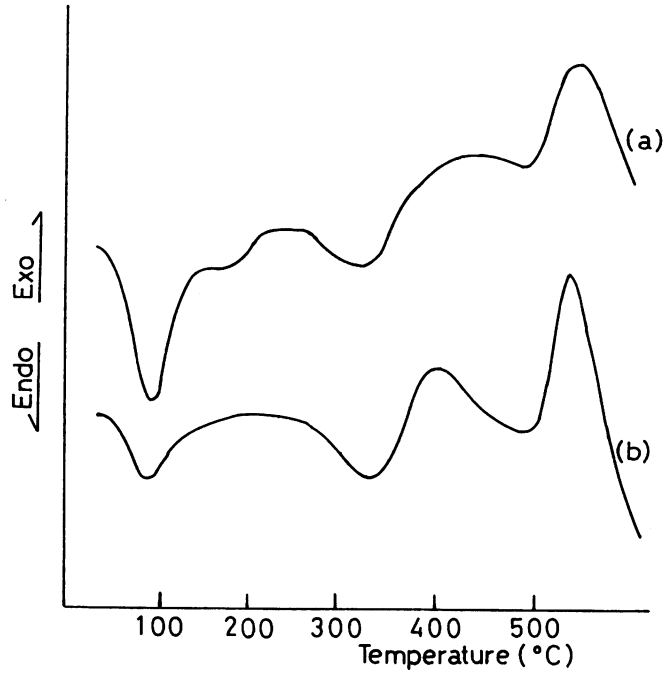

FIG. 3. DTA curves of the 20 Å compounds (a) before and (b) after the heat treatment.

after the heat treatment. After the treatment, the band at 1624 cm^{-1} due to the C=C stretching vibration disappeared. The spectrum became similar to that of polyacrylamide which was polymerized in an aqueous solution. The spectrum of 20 Å compound also showed the absence of C=C bond. Figure 3 shows the DTA curves of the 20 Å compounds before and after the heat treatment. Before the heat treatment, the curve showed a broad exothermic peak around 180°C. After this exothermic reaction, the band due to C=C stretching disappeared in the IR spectra. Consequently, the exothermic peak corresponded to the polymerization of the intercalated acrylamide. After heating, no peak was observed around 180°C in the DTA curve. Similar results were obtained for the 15 Å compound. On the other hand, the basal spacings of the heat treated 15 Å and 20 Å compounds were 15.4 Å and 19.8 Å, respectively. Compared with the basal spacings of the compounds before the heat treatment, which were listed in Table 1, the basal spacings changed only slightly through the reaction. All these results showed that the intercalated acrylamide was polymerized in the interlayer of montmorillonite.

The intercalation compounds were washed with a polar organic solvent like acetone. After the washing prior to the heat treatment, the basal spacings of the compounds decreased and the infrared absorption bands due to the intercalated acrylamide disappeared, suggesting that the intercalated acrylamide was desorbed. However, no changes in the XRD patterns and the IR spectra were observed for the heat treated compounds. This observation also confirmed the polymerization of the intercalated acrylamide.

Table 3 shows the ratios of absorbed water to raw montmorillonite and the intercalation compounds. When the samples were allowed to stand in distilled water, they gradually swelled to form a hydrogel. Whereas polyacrylamide is a water soluble polymer, partly crosslinked polyacrylamide is insoluble in water and can form a hydrogel. In this study, montmorillonite is thought to play a role to prevent the intercalated polyacrylamide from being dissolved in water. The water absorbing power increased with the increase in the ratio of acrylamide in the intercalation compounds: sodium montmorillonite $<$ 15 Å compound $<$ 20 Å compound. This observation suggested that the intercalated polyacrylamide has a certain effect for improving the water absorbing power of montmorillonite.

In conclusion, montmorillonite-acrylamide intercalation compounds formed by treating montmorillonite with acrylamide aqueous solutions. The intercalated acrylamide was polymerized to form montmorillonite-polyacrylamide intercalation compounds. The montmorillonite-polyacrylamide intercalation compounds absorbed more water than raw sodium montmorillonite.

TABLE 3. The amounts of absorbed water to the intercalation compounds

	amount of absorbed water (g per g sample)
Sodium montmorillonite	10
15 Å compound (polymerized)	20
20 Å compound (polymerized)	26

REFERENCES

BLUMSTEIN, A. (1965) J. Polym. Sci., **A-3**, 2653-2664.
BLUMSTEIN, A. (1974) Appl. Polym. Symp., **25**, 81-88.
BOTTERO, J.Y., BRUANT, M., CASES, M., CANET, D. and FIESSINGER, F. (1988) J. Colloid Interface Sci., **124**, 515-527.
FARONA, M.F., AYERS, W.T., RAMSEY, B.G. and GRASSELLI, G. (1969) Inorg. Chim. Acta, **3**, 503-507.
FRIEDLANDER, H.Z. (1964) J. Poly. Sci., Poly. Lett. Ed., **2**, 475-479.
GHOSH, P.K. and BARD, A.J. (1983) J. Am. Chem. Soc., **105**, 5691-5693.
JONATHAN, N. (1961) J. Mol. Spectrosc., **6**, 205-214.
KATO, C., KURODA, K. and TAKAHARA, H. (1981) Clays Clay Miner., **29**, 294-298.
KYOTANI, T., SONOBE, S. and TOMITA, A. (1988) Nature (London), **331**, 331-334.
MIYATA, H., SUGAHARA, Y., KURODA, K. and KATO, C. (1987) J. Chem. Soc. Farady Trans., **1**, 83, 1851-1858.
MORTLAND, M.M. (1966) Clay Miner., **6**, 143-156.
PINNAVAIA, T.J. (1983) Science, **220**, 365-371.
REEDIJK, J. (1971) Inorg. Chim. Acta, **5**, 687-690.
SIFFERT, B. and STUTZMANN, T. (1977) Clays Clay Miner., **25**, 392-406.
SIFFERT, B. and ESPINASSE, P. (1979) Clays Clay Miner., **27**, 279-284.
SUGAHARA, Y., KURODA, K. and KATO, C. (1984) J. Am. Ceram. Soc., **67**, C-247-8.
SUGAHARA, Y., SUGIMOTO, K., KURODA, K. and KATO, C. (1986) Yogyo-Kyokai-Shi, **94**, 38-43.
TAHOUN, S.A. and MORTLAND, M.M. (1966) Soil Sci., **102**, 248-254.
TAHOUN, S.A. and MORTLAND, M.M. (1966) Soil Sci., **102**, 314-321.
TANAKA, T. (1981) Sci. Am., **249**, 124-130.
TANIHARA, K. and NAKAGAWA, M. (1975) Nippon Kagaku Kaishi, 782-789.
THENG, B.K.G. (1974) "The Chemistry of Clay-Organic Reactions", Adam Hilger, London.
THENG, B.K.G. (1979) "Formation and Properties of Clay-Polymer Complexes", Elsevier, Amsterdam.