

PREPARATION OF A KAOLINITE-POLYACRYLAMIDE INTERCALATION COMPOUND

YOSHIYUKI SUGAHARA, SHIGEO SATOKAWA, KAZUYUKI KURODA,
AND CHUZO KATO

Department of Applied Chemistry, School of Science and Engineering
Waseda University, Ohkubo 3, Shinjuku-ku, Tokyo, 169 Japan

Abstract—Acrylamide has been polymerized between the layers of kaolinite by heat treatment. Acrylamide monomer was first intercalated by the displacement reaction between a kaolinite-N-methylformamide (NMF) intercalation compound and a 10% acrylamide aqueous solution. The resulting intercalation compound showed a basal spacing of 11.3 Å. Infrared (IR) spectroscopy and ¹³C nuclear magnetic resonance spectroscopy with cross polarization and magic angle spinning (¹³C CP/MAS-NMR) indicated the replacement of NMF by acrylamide. IR spectroscopy also showed the formation of hydrogen bonds with the hydroxyls of kaolinite. When the kaolinite-acrylamide intercalation compound was heated at 300°C for 1 hr, the basal spacing increased to 11.4 Å, and IR and ¹³C CP/MAS-NMR showed the disappearance of C=C bonds, indicating the polymerization of acrylamide. The heat-treated kaolinite-acrylamide intercalation compound was resistant to 30 min-washing with water, whereas the untreated kaolinite-acrylamide intercalation compound collapsed after the same treatment, an observation consistent with acrylamide polymerization between the layers of kaolinite. IR spectroscopy revealed that polyacrylamide was hydrogen bonded to kaolinite, but in a manner different from the hydrogen bonding of acrylamide.

要旨—アクリルアミドは、カオリンの層間に熱処理により、N-メチルホルムアミド(NMF)とアクリルアミドの置換反応によって導入された。導入されたアクリルアミドは、10%のアクリルアミド水溶液と反応して、カオリン-アクリルアミドの層間化合物を形成した。この層間化合物の基底間隔は11.3 Åであった。赤外線(IR)分光法と¹³C核磁気共鳴分光法(CP/MAS-NMR)は、NMFがアクリルアミドに置換されたことを示した。IR分光法は、カオリンのヒドロキシル基とアクリルアミドのカルボニル基との間に水素結合が形成されたことを示した。300°Cで1時間加熱した際、基底間隔は11.4 Åに増加し、IRと¹³C CP/MAS-NMRは、C=C結合の消失を示し、アクリルアミドの重合を示した。加熱処理したカオリン-アクリルアミドの層間化合物は、30分間の水洗いに対して安定であった。一方、未処理のカオリン-アクリルアミドの層間化合物は、同様の処理後に崩壊した。この観察は、カオリンの層間にアクリルアミドの重合が起こったことを示している。IR分光法は、アクリルアミドがカオリンと水素結合を形成していることを示したが、それはアクリルアミドの水素結合とは異なるものである。

Key Words—Acrylamide, Infrared spectroscopy, Intercalation, Kaolinite, Nuclear magnetic resonance, Polymerization, Thermal treatment.

INTRODUCTION

Kaolinite is known to take up certain molecules to form intercalation compounds. Guest molecules are stabilized mainly by hydrogen bonding. Hydrogen bond formation results in the perturbation of OH-stretching bands at 3695, 3670, and 3655 cm⁻¹, while the 3620-cm⁻¹ band is not affected (Theng, 1974). Intercalation of guest molecules also influences ²⁹Si NMR signals. Thompson (1985) observed slight shifts of the ²⁹Si NMR signals to a higher field because of the additional shielding by the intercalated molecules.

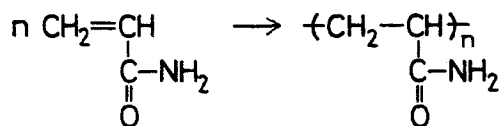
Guest molecules (e.g., amides) contain groups that strongly interact with the kaolinite hydroxyl groups, such as carbonyl groups. To date, six amides have been intercalated; formamide (FA), N-methylformamide

(NMF), N,N-dimethylformamide (DMF), acetamide, N-methylacetamide (NMA), and N,N-dimethylacetamide (DMA) (Weiss *et al.*, 1963; Ledoux and White, 1966; Weiss *et al.*, 1966; Cruz *et al.*, 1969; Olejnik *et al.*, 1970; Olejnik *et al.*, 1971a, 1971b; Adams *et al.*, 1976; Adams, 1978a, 1978b). Similarly, the intercalation of lactams, which also have a NHC=O group, has been reported (Sugahara *et al.*, 1986).

In a related field, the polymerization of organic monomers in the interlayer space of smectites has attracted considerable attention (Theng, 1979). Recently, the present authors reported the polymerization of acrylonitrile between the layers of kaolinite after intercalating acrylonitrile by using ammonium acetate intercalation as the intermediate step (Sugahara *et al.*,

1988). The polymerization process was complicated, because both the acrylonitrile monomer and ammonium acetate were present between the layers.

The present study deals with the polymerization of acrylamide between the layers of kaolinite. Acrylamide possesses both amide and vinyl groups and is easily polymerized as follows:



In this study, acrylamide was intercalated into kaolinite by the displacement of an intermediate intercalated compound and was subsequently polymerized by heat.

EXPERIMENTAL

Materials

Kaolinite (API clay standard No. 9, Mesa Alta, New Mexico) was ground to pass a 100-mesh sieve. No crystalline impurities were detected by X-ray powder diffraction (XRD) analysis. Acrylamide (Wako Pure Chemical Industries, Osaka) was purified by recrystallization. Polyacrylamide was obtained from a commercial 10% polyacrylamide aqueous solution (Wako Pure Chemical Industries).

Preparation

The kaolinite-NMF intercalation compound was prepared by the method reported by Olejnik *et al.* (1970). Direct treatment with aqueous 10% acrylamide solution produced no intercalation.

The kaolinite-acrylamide intercalation compound was produced by reacting the kaolinite-NMF intercalation compound with aqueous 10% acrylamide solution. This was achieved by stirring about 1 g of the kaolinite-NMF compound in 100 ml of the 10% acrylamide solution for 30 min. Solid and liquid were separated by centrifugation, and the solid was stirred again in 100 ml of the same solution for 24 hr. After centrifugation, the solid product was dried under reduced pressure, then stirred twice in 100 ml CCl_4 for 30 min to remove excess acrylamide on the external surface.

The effect of the concentration of the acrylamide aqueous solution was studied by stirring ~1 g of the kaolinite-NMF compound with aqueous solutions of 1–12% acrylamide for 24 hr. These products were centrifuged and dried as before. The washed product prepared with aqueous 10% acrylamide solution was heated in the range 100° to 400°C for 1 hr to induce polymerization.

The kaolinite-acrylamide intercalation compounds (100-mg quantities) were washed with 10 ml of water for 30 min before and after the heat treatment to study the resistance of the intercalated species to washing.

Analyses

XRD patterns of the products were obtained using a Rigaku RAD-IB instrument and Ni-filtered $\text{CuK}\alpha$ radiation. Infrared (IR) spectra of the products were recorded on a JASCO FT/IR-5M spectrophotometer (KBr method, ~0.5 wt. %). Solid state ^{13}C and ^{29}Si nuclear magnetic resonance spectra with cross polarization and magic angle spinning (^{13}C and ^{29}Si CP/MAS-NMR) of the products were collected using a JEOL GSX-270 instrument. The frequencies were 67.74 and 53.67 MHz for ^{13}C and ^{29}Si nuclei, respectively. Repetition time was 5 s, and 72–808 free induction decays were accumulated. Chemical shifts were reported relative to tetramethylsilane used as an external reference.

RESULTS AND DISCUSSION

Preparation of the kaolinite-acrylamide intercalation compound

Figure 1 shows XRD patterns of the products. The kaolinite-NMF intercalation compound had a basal spacing of 10.8 Å, similar to those reported previously for the same complex (10.76 Å, Weiss *et al.*, 1966; 10.6 Å, Cruz *et al.*, 1969; 10.7 Å, Olejnik *et al.*, 1970). After treatment with the aqueous 10% acrylamide solution, the 001 peak shifted to 11.3 Å and the intensity decreased, suggesting a decrease in the stacking order.

The IR spectrum of the kaolinite-NMF intercalation compound (Figure 2b) was similar to those reported earlier (Cruz *et al.*, 1969; Olejnik *et al.*, 1971a). After the 10% acrylamide treatment, the IR spectrum changed drastically, as characteristic bands of NMF (e.g., at 3420 and 1529 cm^{-1}) disappeared and new bands due to adsorbed acrylamide appeared (Figure 2c). These bands were identified by a comparison with the band positions of acrylamide dissolved in CHCl_3 (Table 1). The band positions of a saturated acrylamide CHCl_3 solution were reported by Jonathan (1961). Most of these acrylamide bands were observed in the spectrum of the product; however, more bands were observed in the NH-stretching region of the product than in the same region of the dilute acrylamide CHCl_3 solution, evidently due to the presence of several environments of the amide groups in the product. The presence of a small amount of acrylamide on external surfaces may also have complicated this spectral region.

The ^{13}C NMR spectroscopy also supported the presence of acrylamide in the product. Figure 3a shows a ^{13}C CP/MAS-NMR spectrum of the product, and Figure 3b depicts the spectrum of acrylamide. The spectra are similar, indicating that acrylamide was present in the product.

These observations clearly indicate the formation of a kaolinite-acrylamide intercalation compound, formed by replacing NMF by acrylamide and increasing the basal spacing slightly from 10.8 to 11.3 Å.

Table 1. Infrared assignments of acrylamide and kaolinite-acrylamide intercalation compound.

Wavenumber (cm ⁻¹)			
Acrylamide (in CHCl ₃)		Kaolinite- acrylamide intercalation compound	Assignments ¹
Observed in this study ²	Observed by Jonathan (1961) ³		
		3695	} $\nu(\text{OH})$ (Kaolinite)
		3651	
		3627	} Hydrogen-bonded $\nu(\text{OH})$ (Kaolinite)
		3600	
		3566	
		3546 ⁴	
3530	3540 3502	3489	$\nu_{\text{as}}(\text{NH}_2)$ (monomeric)
3514	3423	3468	$\nu_{\text{sym}}(\text{NH}_2)$ (monomeric)
	3335	3359	$\nu_{\text{as}}(\text{NH}_2)$
	3189	3202	$\nu_{\text{sym}}(\text{NH}_2)$
	3021		$\nu_{\text{sym}}(\text{CH}_2)$
1688	1686	1685	$\nu(\text{C}=\text{O})$
1644	1647	1658	$\nu(\text{C}=\text{C})$
1618	1618	1621	} $\delta(\text{NH}_2)$
1593	1592	1597	
1413	1416	1430	
1336	1342	1355	$\delta(\text{CH})$
1262	1277	1283	$\nu(\text{CN})$

¹ Jonathan (1961).² Concentration: 0.01 mole/liter.³ Saturated solution.⁴ This can be assigned to both hydrogen-bonded $\nu(\text{OH})$ and $\nu(\text{NH}_2)$.

The interaction between kaolinite and acrylamide was further studied by monitoring the IR spectrum in the OH-stretching region (Figure 4). In the spectrum of the kaolinite-acrylamide intercalation compound (Figure 4b), the 3694- and 3669-cm⁻¹ bands were perturbed relative to the bands of the raw kaolinite (Figure 4a). New bands due to hydrogen-bonding of hydroxyls with acrylamide appeared at 3651, 3627, 3600, and 3566 cm⁻¹. These observations suggest strong hydrogen bonding, in which the hydroxyls of kaolinite interact with carbonyl or amine groups of acrylamide. No shift of the C=O stretching band was observed after the intercalation (Table 1), suggesting that the C=O group was not involved in hydrogen bonding.

The interaction between kaolinite and acrylamide was also investigated using ²⁹Si CP/MAS-NMR (Figure 5). The raw kaolinite showed a doublet at -91.0 ppm, which is in line with the value reported by Thompson (1985). In the spectrum of the kaolinite-NMF inter-

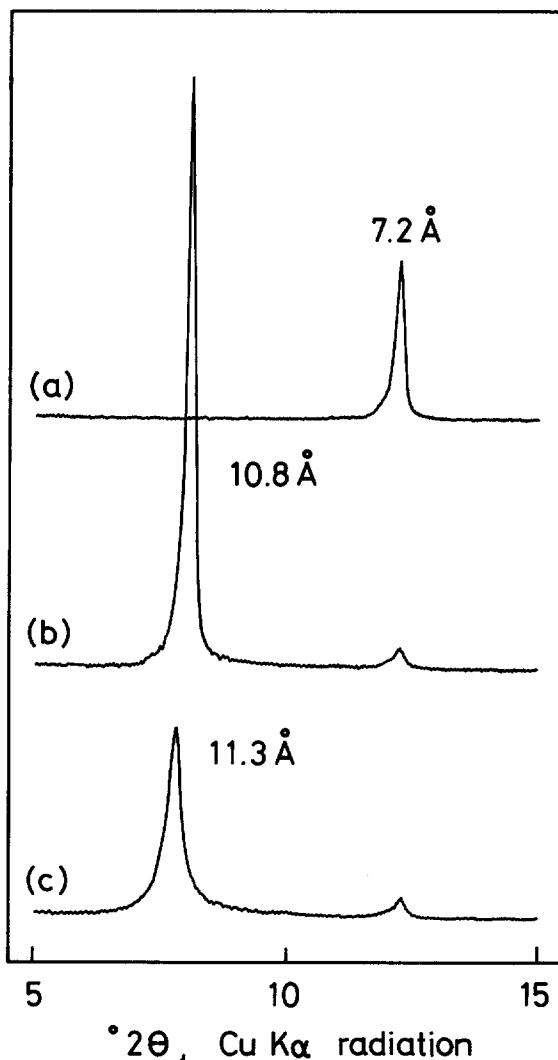


Figure 1. X-ray powder diffraction patterns of (a) raw kaolinite, (b) kaolinite-N-methylformamide intercalation compound, and (c) kaolinite-acrylamide intercalation compound.

calation compound, a singlet was observed at -91.0 ppm. The kaolinite-acrylamide intercalation compound showed a singlet at -91.6 ppm, indicating a change in shielding upon replacement of NMF with acrylamide. Two shoulders at about -91.0 ppm can be ascribed to unexpanded kaolinite.

The effect of the concentration of the aqueous acrylamide solution on intercalate formation is shown in Figure 6. The approximate yield of acrylamide intercalation was estimated on the basis of the ratio of the 001 peaks of the kaolinite-acrylamide intercalation compound and unexpanded kaolinite (Theng, 1974). It should be noted that the stacking order can affect the estimated values. If the aqueous concentration of acrylamide was 1 or 2%, the kaolinite-NMF interca-

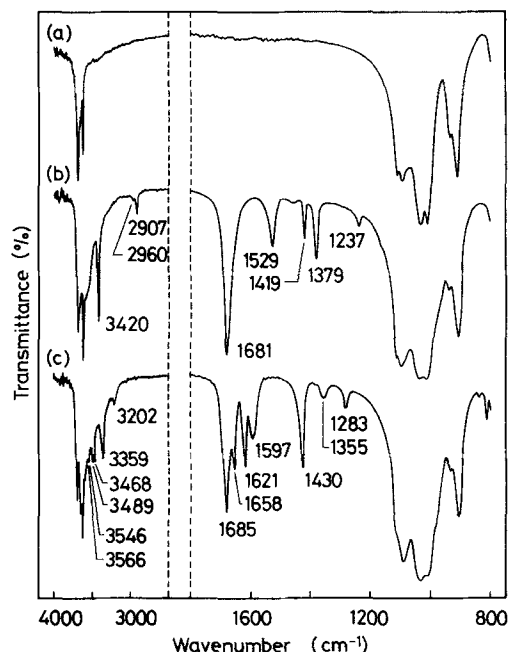


Figure 2. Infrared spectra of (a) raw kaolinite, (b) kaolinite-N-methylformamide intercalation compound, and (c) kaolinite-acrylamide intercalation compound.

lation compound completely collapsed, but 4–12% caused the kaolinite-acrylamide intercalation compound to form readily. The yield increased gradually with an increase in acrylamide within the concentration range of 4–10%, but leveled off at higher concentrations.

These observations suggest two things: (1) If the amount of acrylamide exceeded a particular threshold value, the intercalation reaction proceeded to a considerable extent. (2) A relatively low concentration of acrylamide in aqueous solution was sufficient to obtain the highest yield; the use of a saturated solution was not necessary.

Polymerization of acrylamide between the layers of kaolinite

Acrylamide is usually polymerized in aqueous solutions in the presence of free radicals. Typically, an aqueous 10% acrylamide solution containing 1.2% hydrogen peroxide is heated at 90°C for 150 min (Schulz *et al.*, 1954). In the present study, the kaolinite-acrylamide intercalation compound was thermally polymerized without using an initiator to generate free radicals.

The XRD patterns showed that the layers were still expanded after heat treatments as high as 300°C. Figure 7a shows the XRD pattern of the product heated at 300°C. On heating at 100°C, no change was observed in the XRD pattern. After the heat treatments at 200° and 300°C, the basal spacing increased by 0.1 Å. If the kaolinite-acrylamide intercalation compound was

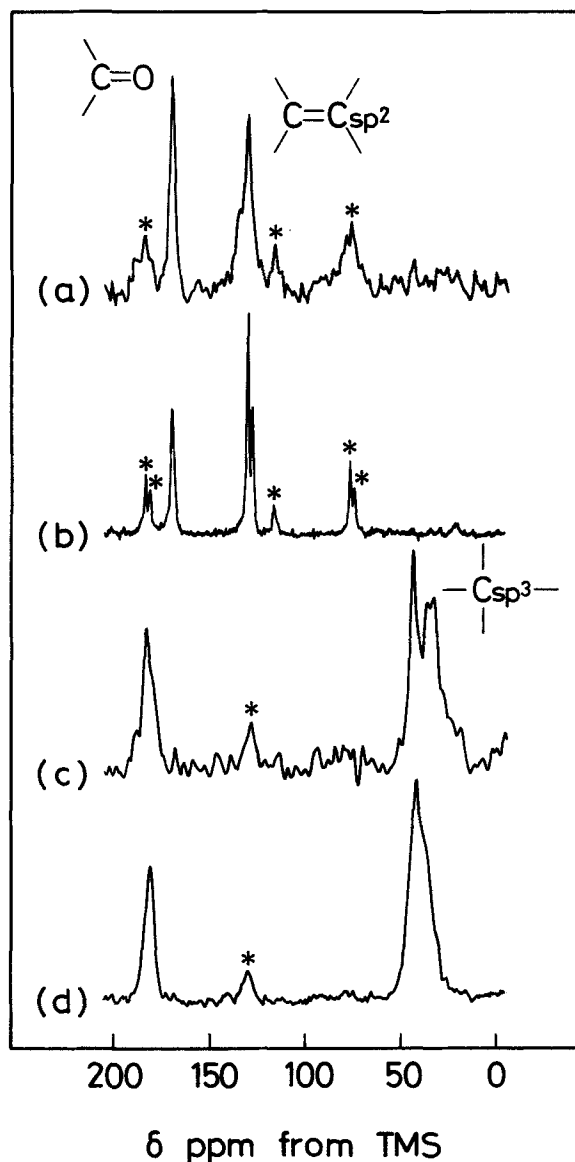


Figure 3. ^{13}C nuclear magnetic resonance spectra with cross polarization and magic angle spinning of (a) kaolinite-acrylamide intercalation compound, (b) acrylamide, (c) kaolinite-acrylamide intercalation compound heated at 300°C for 1 hr, and (d) polyacrylamide. Spinning side bands are marked by asterisks.

heated at 400°C, the layers collapsed to 7.2 Å (Figure 7b).

IR spectra were not affected by heating the sample at 100°C. At 200°C, the C=C stretching band, which is at 1658 cm^{-1} in Figure 2c, decreased in intensity (Figure 8a), and on heating the sample at 300°C, it completely disappeared (Figure 8b). The spectrum of the product was then similar to that of polyacrylamide (Figure 8c), verifying that polymerization was complete at 300°C.

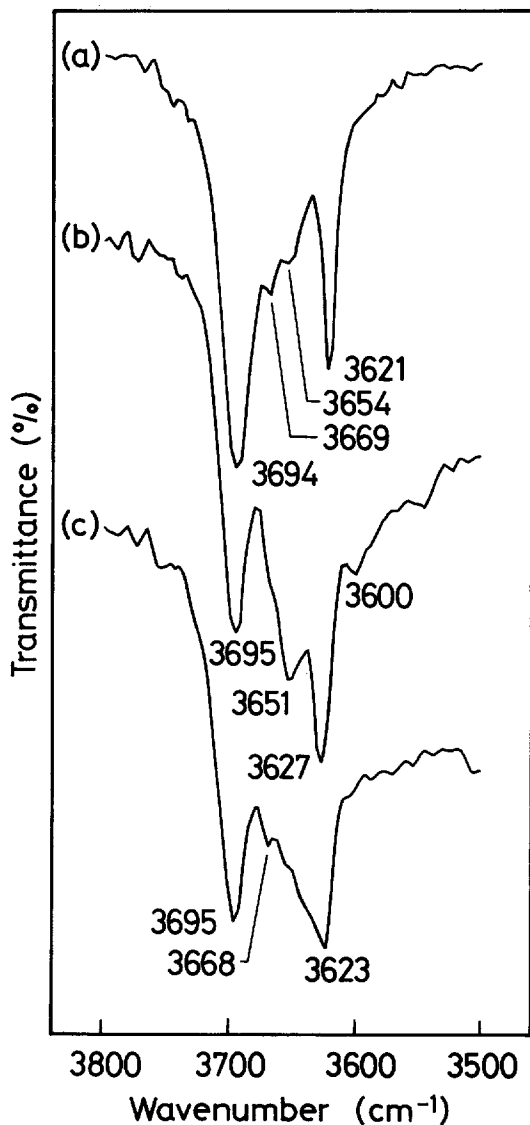


Figure 4. Infrared spectra in the OH-stretching region of (a) raw kaolinite, (b) kaolinite-acrylamide intercalation compound, and (c) kaolinite-acrylamide intercalation compound heated at 300°C for 1 hr.

The ¹³C NMR spectroscopy also indicated the polymerization of acrylamide by the 300°C treatment. Figure 3c shows the ¹³C CP/MAS-NMR spectrum of the kaolinite-acrylamide intercalation compound after the 300°C treatment. A ¹³C NMR signal due to the C=O group (183.0 ppm) and those ascribed to carbon having sp³ hybrid orbitals (34.1, 37.5, and 41.8 ppm) were detected. In the C=C bond region (~130 ppm) only a weak spinning side band was observed. Although a weak peak could have been obscured by the spinning side band, the spectrum indicated that most of the C=C bonds had disappeared. Furthermore, the

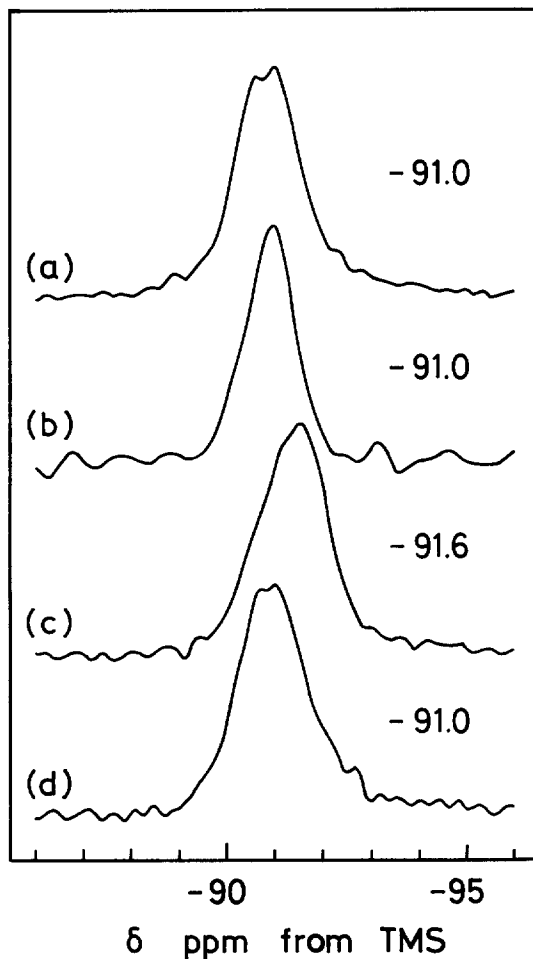


Figure 5. ²⁹Si nuclear magnetic resonance spectra with cross polarization and magic angle spinning of (a) raw kaolinite, (b) kaolinite-N-methylformamide intercalation compound, (c) kaolinite-acrylamide intercalation compound, and (d) kaolinite-acrylamide intercalation compound heated at 300°C for 1 hr.

spectrum was similar to that of polyacrylamide (Figure 3d).

The results taken as a whole indicate that no polymerization occurred at 100°C, although pure acrylamide melts and is subsequently polymerized at ~85°C (Carpenter and Davis, 1957). Between the layers of kaolinite, acrylamide monomers did not polymerize at 100°C, probably because of their restricted motion and intermolecular separation.

If the kaolinite-acrylamide intercalation compound was heated at 300°C, both IR and ¹³C CP/MAS-NMR spectra showed the polymerization of acrylamide. Inasmuch as the layers were still expanded, polymerization must have occurred between the layers. On heating at 400°C, the layers collapsed, indicating the degradation of the polymer.

The polymerization of acrylamide between the layers

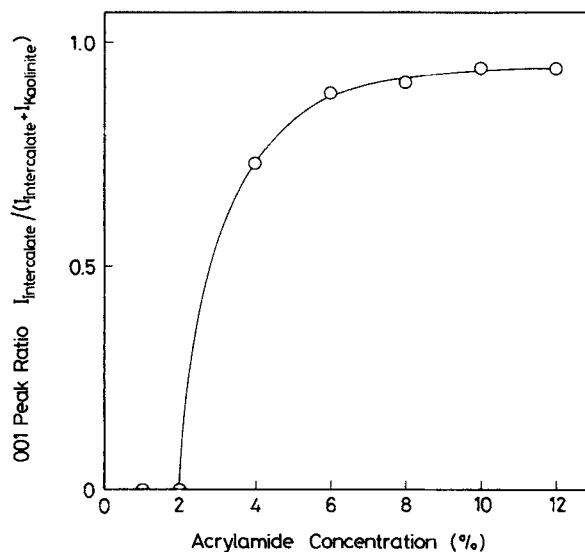


Figure 6. The effect of the concentration of aqueous acrylamide solution on the yield of the kaolinite-acrylamide intercalation compound estimated on the basis of the 001 peak ratio.

of kaolinite was further indicated by the change in resistance to washing with water. When the untreated kaolinite-acrylamide intercalation compound was washed with water, the 11.3-Å peak in the XRD pattern disappeared; a weak broad peak, possibly due to hydrated kaolinite, was detected at ~ 9 Å in addition to the 7.2-Å peak of kaolinite (Figure 7c). On the other hand, the XRD profile barely changed if the kaolinite-acrylamide intercalation compound was heated at 300°C and washed similarly (Figure 7a and 7d). This result is attributed to the very slow deintercalation of the polymer.

The change in the interaction of the guest molecule with kaolinite after the polymerization was studied using IR and ^{29}Si NMR spectroscopy. Polyacrylamide was hydrogen-bonded to the hydroxyls of kaolinite in a manner different from acrylamide. Figure 4c shows the OH-stretching region of the IR spectrum of the kaolinite-acrylamide intercalation compound after heating at 300°C. After the heat treatment, the 3695- cm^{-1} band was still perturbed. However, the relative intensity of the 3669- cm^{-1} band, which was perturbed in the spectrum of the untreated kaolinite-acrylamide intercalation compound (Figure 4b), returned to an intensity comparable to that of the raw kaolinite (Figure 4a), whereas a new OH band appeared at ~ 3630 cm^{-1} . The shifted bands, identified in the spectrum of the untreated kaolinite-acrylamide intercalation compound, disappeared.

The ^{29}Si CP/MAS-NMR spectrum of the kaolinite-acrylamide intercalation compound after heating at 300°C is shown in Figure 5d. The spectrum is similar to that of the raw kaolinite (Figure 5a) displaying a

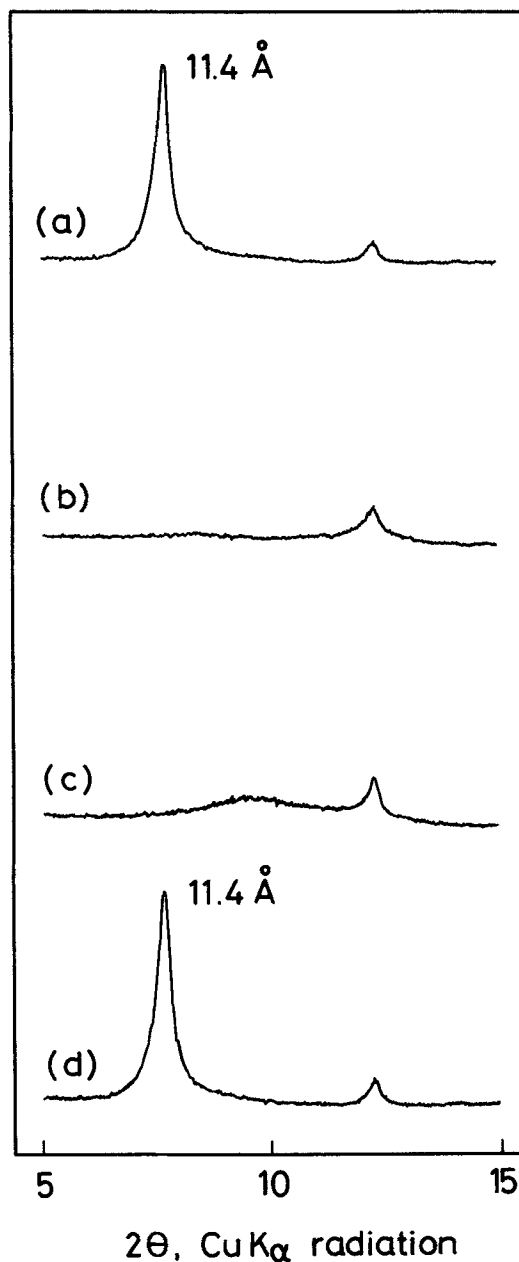


Figure 7. X-ray diffraction patterns of (a) kaolinite-acrylamide intercalation compound heated at 300°C for 1 hr, (b) kaolinite-acrylamide intercalation compound heated at 400°C for 1 hr, (c) kaolinite-acrylamide intercalation compound after washing with water for 30 min, and (d) kaolinite-acrylamide intercalation compound heated at 300°C for 1 hr after washing with water for 30 min.

doublet at -91.0 ppm. The presence of the doublet in the spectrum of the 300°C-heated kaolinite-acrylamide intercalation compound is surprising, because the reported spectra of the intercalation compounds (Thompson, 1985) and the spectra of all the other intercalation compounds in this study showed singlets.

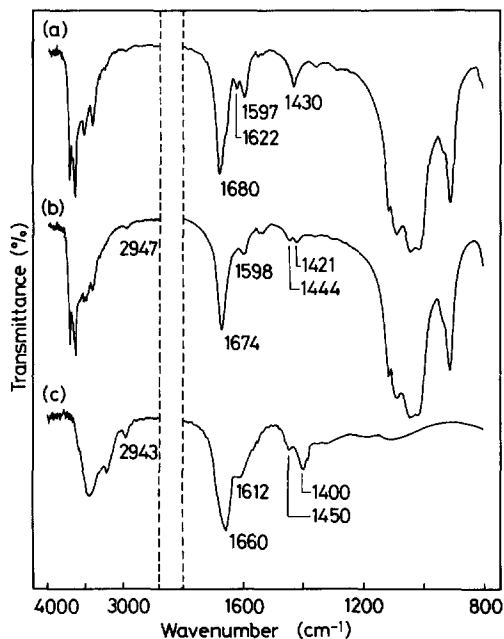


Figure 8. Infrared spectra of (a) kaolinite-acrylamide intercalation compound heated at 200°C for 1 hr, (b) kaolinite-acrylamide intercalation compound heated at 300°C for 1 hr, and (c) polyacrylamide.

Thompson and Barron (1987) assumed that the doublet in the raw kaolinite was due to the presence of two different kinds of Si environment as a result of differences in hydrogen bonding; however, the reason for the appearance of a singlet after intercalation was not explained. Hence, the present observation of a doublet in the ^{29}Si NMR spectrum of the heated kaolinite-acrylamide intercalation compound cannot be interpreted.

SUMMARY AND CONCLUSIONS

Acrylamide, intercalated by displacing NMF, was thermally polymerized between the layers of kaolinite. Polymerization of acrylamide was observed at temperatures as low as 200°C, but a 1-hr treatment at 300°C was required to complete the polymerization. After the heat treatment, the basal spacing slightly increased from 11.3 to 11.4 Å. IR and ^{13}C CP/MAS-NMR confirmed polymerization by detecting the disappearance of the C=C bonds. IR and ^{29}Si CP/MAS-NMR suggested that the hydrogen bonding and surface-organic interactions changed after the polymerization. The resulting kaolinite-polyacrylamide intercalation compound was resistant to decomposition by water washing.

ACKNOWLEDGMENT

The authors express their sincere thanks to K. Deguchi and K. Hioka (JEOL Co. Ltd.) for their skillful NMR work.

REFERENCES

- Adams, J. M., Reid, P. I., Thomas, J. M., and Walters, M. J. (1976) On the hydrogen atom positions in a kaolinite: formamide intercalate: *Clays & Clay Minerals* **24**, 267–269.
- Adams, J. M. (1978a) Differential scanning calorimetric study of the kaolinite: N-methylformamide intercalate: *Clays & Clay Minerals* **26**, 169–172.
- Adams, J. M. (1978b) Unifying features relating to the 3D structures of some intercalates of kaolinite: *Clays & Clay Minerals* **26**, 291–295.
- Carpenter, E. L. and Davis, H. S. (1957) Acrylamide. Its preparation and properties: *J. Appl. Chem.* **7**, 671–676.
- Cruz, M., Laycock, A., and White, J. L. (1969) Perturbation of OH groups in intercalated kaolinite donor-acceptor complexes. I. Formamide-, methyl formamide-, and dimethyl formamide-kaolinite complexes: in *Proc. Int. Clay Conf., Tokyo, 1969, Vol. 1*, L. Heller, ed., Israel Univ. Press, Jerusalem, 775–789.
- Jonathan, N. (1961) The infrared and raman spectra and structure of acrylamide: *J. Mol. Spectrosc.* **6**, 205–214.
- Ledoux, R. L. and White, J. L. (1966) Infrared studies of hydrogen bonding interaction between kaolinite surfaces and intercalated potassium acetate, hydrazine, formamide, and urea: *J. Colloid Interface Sci.* **21**, 127–152.
- Olejnik, S., Posner, A. M., and Quirk, J. P. (1970) The intercalation of polar organic compounds into kaolinite: *Clay Miner.* **8**, 421–434.
- Olejnik, S., Posner, A. M., and Quirk, J. P. (1971a) The i.r. spectra of interlamellar kaolinite-amide complexes—I. The complexes of formamide, N-methylformamide and dimethylformamide: *Clays & Clay Minerals* **19**, 83–94.
- Olejnik, S., Posner, A. M., and Quirk, J. P. (1971b) The infrared spectra of interlamellar kaolinite-amide complexes II. Acetamide, N-methylacetamide and dimethylacetamide: *J. Colloid Interface Sci.* **37**, 536–547.
- Schulz, R., Renner, G., Henglein, A., and Kern, W. (1954) Untersuchungen über die Radikalpolymerisation von Acrylamid: *Makromol. Chem.* **12**, 20–34.
- Sugahara, Y., Kitano, S., Satokawa, S., Kuroda, K., and Kato, C. (1986) Synthesis of kaolinite-lactam intercalation compounds: *Bull. Chem. Soc. Jpn.* **59**, 2607–2610.
- Sugahara, Y., Satokawa, S., Kuroda, K., and Kato, C. (1988) Evidence for the formation of interlayer polyacrylonitrile in kaolinite: *Clays & Clay Minerals* **36**, 343–348.
- Theng, B. K. G. (1974) *The Chemistry of Clay-Organic Reactions*: Adam Hilger, London, 243–260.
- Theng, B. K. G. (1979) *Formation and Properties of Clay-Polymer Complexes*: Elsevier, Amsterdam, 123–147.
- Thompson, J. G. (1985) Interpretation of solid state ^{13}C and ^{29}Si nuclear magnetic resonance spectra of kaolinite intercalates: *Clays & Clay Minerals* **33**, 173–180.
- Thompson, J. G. and Barron, P. F. (1987) Further consideration of the ^{29}Si nuclear magnetic resonance spectrum of kaolinite: *Clays & Clay Minerals* **35**, 38–42.
- Weiss, A., Thielepape, W., Göring, G., Ritter, W., and Schäfer, H. (1963) Kaolinit-Einlagerungs-Verbindungen: in *Proc. Int. Clay Conf. Stockholm, 1963, Vol. 1*, I. Th. Rosenqvist and P. Graff-Petersen, eds., Pergamon Press, Oxford, 287–305.
- Weiss, A., Thielepape, W., and Orth, H. (1966) Neue Kaolinit-Einlagerungsverbindungen: in *Proc. Int. Clay Conf. Jerusalem, 1966, Vol. 1*, L. Heller and A. Weiss, eds., Israel Prog. Sci. Transl., Jerusalem, 277–293.

(Received 26 January 1989; accepted 30 April 1989; Ms. 1875)