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EVIDENCE FOR THE FORMATION OF INTERLAYER POLYACRYLONITRILE IN KAOLINITE

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Abstract—A kaolinite-polymer intercalation complex was apparently formed for the first time by the polymerization of acrylonitrile between the kaolinite layers. A kaolinite-ammonium acetate intercalation complex was dispersed in acrylonitrile monomer. The monomer was apparently incorporated between the layers by displacing intercalated ammonium acetate. After the removal of excess monomer, the intercalation complex was heated to cause polymerization. The resulting kaolinite-polyacrylonitrile (PAN) intercalate showed a basal spacing of ~13–14 Å. On heating the complex at 220°C for 1 hr in air, the spacing decreased slightly. The hydrogen bond between the hydroxyls of kaolinite and probably the C≡N group of PAN was not affected after heating at 220°C. Even after heating at 400°C, the layers expanded. Because the starting kaolinite-ammonium acetate intercalation complex decomposed at a much lower temperature, these observations strongly suggest the presence of PAN between the layers.

要旨—アクリロニトリルが層間で重合することによりカオリナイト—ポリマー層間化合物が生成したものと推定された。カオリナイト—酢酸アンモニウム層間化合物をアクリロニトリルモノマー中に分散したところ、モノマーはインターカレートした酢酸アンモニウムを置換することにより層間に侵入したものと推定された。過剰なモノマーを除去した後、層間化合物を重合の為に加熱した。得られたカオリナイト—ポリアクリロニトリル層間化合物は約１３～１４Åの基本面間隔値を示した。この層間化合物を２２０℃にて１ｈ熱処理を行ったところ、基本面間隔は若干減少した。カオリナイトの水酸基はおそらくＰＡＮのＣ≡Ｎ基と水素結合を形成しているものと推定されるが、この結合は２２０℃の熱処理によっては影響を受けなかった。層は４００℃の熱処理後においても依然拡大していた。これに対し、出発物質であるカオリナイト—酢酸アンモニウム層間化合物がかなり低い温度で分解することから、ＰＡＮは層間に存在することが示唆された。

Key Words—Ammonium acetate, Infrared spectroscopy, Intercalation, Kaolinite, Polyacrylonitrile, Polymerization, X-ray powder diffraction.

INTRODUCTION

Intercalates between clay minerals and organic polymers and resulting clay-polymer complexes have attracted wide attention (Theng, 1979). Such intercalation complexes are of interest, because organic polymer layers and inorganic silicate layers are alternatively interstratified at the molecular level. Montmorillonite, having a 2:1 type structure, is generally used as the host material. Such montmorillonite-polymer intercalates are prepared in two ways: by polymerizing intercalated monomers and by intercalating the polymers directly. The former method has been used in the syntheses of the intercalation complexes with polyacrylonitrile (Blumstein *et al.*, 1974), polymethyl methacrylate (Blumstein, 1965), and polystyrene (Kato *et al.*, 1981), whereas intercalation complexes with polyvinyl alcohol (Greenland, 1963) and polyvinyl pyrrolidone (Francis, 1973) have been obtained directly.

On the other hand, no intercalation complexes with polymers have been reported for kaolinite, another potential host mineral having a 1:1 type structure. Kaolinite takes up only a limited number of polar molecules, and although only small molecules such as formamide and dimethylsulfoxide (DMSO) can be intercalated directly, relatively large molecules can easily be incorporated between the layers by displacing smaller molecules which have been already intercalated (i.e., the so-called "displacement method"; Theng, 1974). By using such a displacement method, the present authors obtained kaolinite-lactam intercalation complexes, which apparently did not form by direct reaction of the constituents (Sugahara *et al.*, 1986).

In the present study, the synthesis of a kaolinite-polymer intercalation complex was attempted. That the guest molecules are stabilized between layers mainly due to hydrogen bond formation with hydroxyls of the kaolinite is well known; hence, polymers having functional groups which can form hydrogen bonds should be selected. The C≡N group, as well as C=O and –O–, can act as acceptors in hydrogen bond formation (Shashanka, 1962). Actually, the intercalation of acetonitrile (CH_3–C≡N) has been reported (Camazano and Garcia, 1966). Therefore, polyacrylonitrile

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$(\text{-}CH_2\text{-}CH\text{-})_n$ (PAN) may also be stable between the
C≡N
layers of kaolinite.

For the preparation, the monomer was initially intercalated by the "displacement method." In preliminary experiments, we were unable to incorporate PAN between the layers; however, the acrylonitrile monomer seems to have intercalated and subsequently polymerized between the layers. Because the monomer was not intercalated directly, the "displacement method" was used to intercalate it. As an intermediate, a kaolinite-ammonium acetate intercalate was used to form a kaolinite-PAN intercalation complex. The resulting product was characterized analytically and by its thermal stability.

MATERIALS AND METHODS

Starting materials

The kaolinite used in the present study was API standard clay No. 9 (Mesa Alta, New Mexico). Its X-ray powder diffraction (XRD) analysis revealed the presence of no peaks due to crystalline impurities.

Sample preparation

In the present study, the kaolinite-ammonium acetate intercalate was used as an intermediate for the synthesis of the kaolinite-PAN intercalation complex. Generally, intercalates with smaller organic materials such as formamide and DMSO have been used as intermediates; however, no evidence for the intercalation of the monomer was obtained, when they were used, probably due to their smaller basal spacings. Hence, the kaolinite-ammonium acetate intercalate was used because of its larger spacing (about 14 Å).

The kaolinite-ammonium acetate intercalate was prepared by the "displacement method." Although Weiss *et al.* (1963) first obtained the complex directly by controlling the pH of the ammonium acetate aqueous solution, the displacement method has also been applied for its preparation (Seto *et al.*, 1978). In the present study, the kaolinite-ammonium acetate intercalate was synthesized from a kaolinite-DMSO intercalation complex, which has been prepared by the procedure reported by Olejnik *et al.* (1968). The kaolinite-DMSO intercalate was stirred in a 60 wt. % ammonium acetate aqueous solution (40 ml/1 g kaolinite) for 10 min and subsequently separated by centrifugation twice. The product was then dried at 40°C for 48 hr.

To introduce the acrylonitrile monomer between the layers, the kaolinite-ammonium acetate intercalate was dispersed in the acrylonitrile monomer containing 0.7 wt. % of benzoyl peroxide as an initiator (200 ml acrylonitrile/1 g kaolinite), and the suspension was stirred for 24 hr. After the suspension had been allowed to stand for a few hours, most of a supernatant acrylonitrile monomer was removed. The further removal of the monomer resulted in the collapse after the polymerization. The crude product was subsequently heated at 50°C for 24 hr to cause polymerization. Hence, a certain amount of PAN was also apparently present on the external surface of the particles, although the monomer was evaporated during the polymerization. Both the product and the kaolinite-ammonium acetate intercalate were then further heated at 220°C and 400°C for 1 hr in air to investigate their thermal stability.

Analyses

X-ray powder diffraction (XRD) patterns of the products were obtained using a Rigaku RAD I-B diffractometer and Ni-filtered CuKα radiation (scan speed: 2°2θ/min). Infrared (IR) spectra of the products were recorded on a Shimadzu IR-435 double-beam spectrophotometer and a JASCO FT/IR-5M Fourier-transform spectrophotometer by the KBr disk method (concentration: 0.5 wt. %). Differential thermal analysis (DTA) curves of the products were obtained using a Shimadzu DT-20B instrument and α-Al_2O_3 as reference material.

RESULTS AND DISCUSSION

X-ray powder diffraction

Figure 1 shows the XRD patterns of the products. With the intercalation of ammonium acetate, the basal spacing increased from 11.3 Å, for the DMSO complex, to 14.3 Å (Figures 1b and 1c). The observed spacing was slightly larger than that reported previously (14.05 Å) by Weiss *et al.* (1963). The presence of high orders (at d = 7.2, 4.7, 3.6, 2.8, 2.4, and 2.0 Å) indicates the high stacking order in the kaolinite-ammonium acetate intercalation complex.

A typical XRD pattern after polymerization is shown in Figure 1d. A broad peak at about 13–14 Å can be ascribed to the 001 reflection of the suspected kaolinite-PAN intercalation complex. (Evidence for the presence of PAN between the layers will be presented below.) An 11.1-Å peak due to another phase was observed in some products in addition to the peak at about 13–14 Å. This phase might be a dehydrated kaolinite-ammonium acetate complex. A peak at 7.2 Å was ascribed to the non-expanded kaolinite, because it was too strong for the 002 peak of the 14-Å phase. A peak which can be ascribed to the suspected kaolinite-PAN intercalation complex was always detected at about 13–14 Å, although its precise position, its profile, and its intensity varied among the syntheses under the same conditions. The variation in the basal spacing may be due to the presence of ammonium acetate in the product, which will be shown below by IR data. The intercalated ammonium acetate was probably more resistant to its removal by the acrylonitrile monomer during the stirring than ammonium acetate adsorbed on the external

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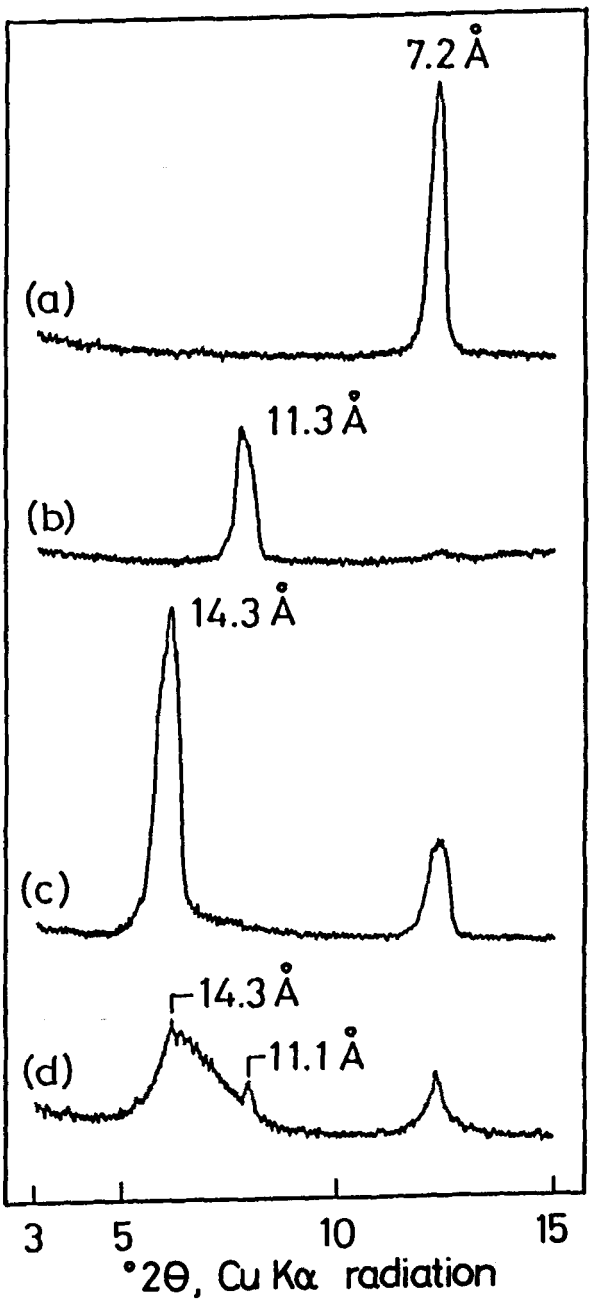


Figure 1. X-ray powder diffraction patterns of (a) untreated kaolinite, (b) kaolinite-dimethylsulfoxide intercalation complex, (c) kaolinite-ammonium acetate intercalation complex, and (d) kaolinite-polyacrylonitrile intercalation complex.

surface; some ammonium acetate between the layers could have been present even after the removal of ammonium acetate on the external surface by the acrylonitrile monomer and the intercalation of the acrylonitrile monomer; therefore, it may have hindered the ordered orientation of the acrylonitrile monomer and led to the formation of the oligomeric species. Thus, the variation in the basal spacing was possible.

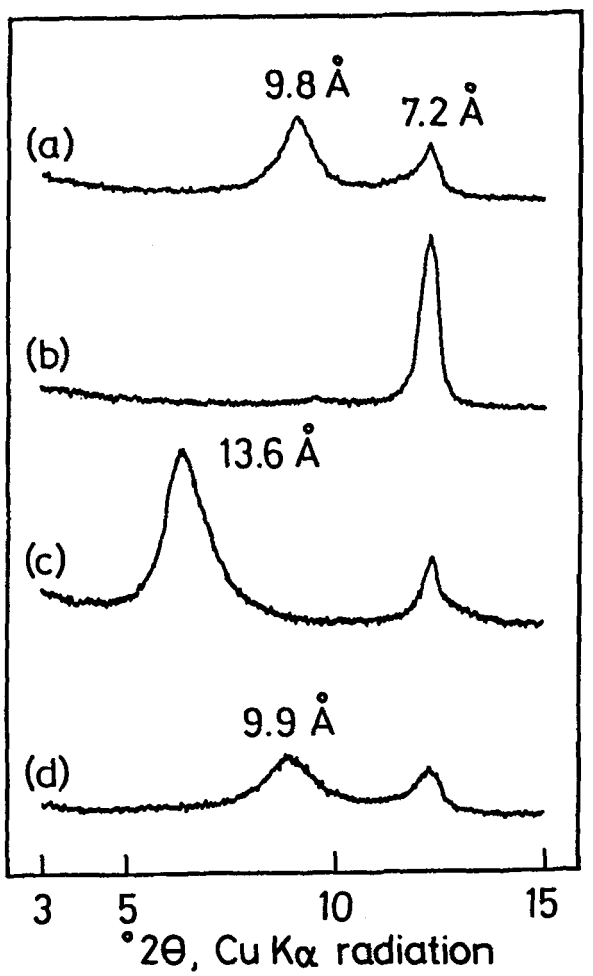


Figure 2. X-ray powder diffraction patterns of the product heated in air for 1 hr. (a) and (b) from the kaolinite-ammonium acetate intercalation complex; (a) at 220°C and (b) at 400°C. (c) and (d) from the kaolinite-polyacrylonitrile intercalation complex; (c) at 220°C and (d) at 400°C.

Thermal decomposition of the kaolinite-organic intercalates

The presence of PAN between the layers is strongly suggested by a comparison of the thermal decomposition of the suspected kaolinite-PAN intercalate with that of the kaolinite-ammonium acetate intercalate. The suspected kaolinite-PAN intercalate showed a broad DTA exothermic peak at about 300°C, which can be assigned to the oxidation (and possibly cyclization) of PAN (Grassie and McGuchan, 1970). The DTA curve of the kaolinite-ammonium acetate intercalate showed two strong endothermic peaks at about 100°C. Both intercalates were heated at 220°C and 400°C for 1 hr in air. Absorbed ammonium acetate decomposes at <220°C and only polymers are stable at >400°C.

Figure 2 shows the XRD patterns of the heat-treated products from both the intercalation complexes. The

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kaolinite-ammonium acetate intercalate collapsed to kaolinite on heating at 400°C. On heating the kaolinite-ammonium acetate intercalate to 220°C, the basal spacing decreased from 14.3 to 9.8 Å (Figure 2a). On heating it to 400°C, no peaks due to expanded phases were detected (Figure 2b).

In contrast, the suspected kaolinite-PAN intercalation complex still expanded even after heating at 400°C. On heating the suspected kaolinite-PAN intercalate to 220°C, the basal spacing slightly decreased (Figure 2c), typically from 14.3 to 13.6 Å. The peak was always more symmetric than that of the corresponding unheated material, possibly due to the decomposition of co-intercalated ammonium acetate, as shown above. After heating at 400°C, a broad peak was observed at 9.9 Å (Figure 2d). Because the kaolinite-ammonium acetate intercalate completely collapsed by the same treatment, the carbonaceous material between the layers must have originated from PAN. Therefore, the differences in the thermal decomposition strongly suggest the successful polymerization of acrylonitrile between the layers of kaolinite.

Infrared spectroscopy

The principal bands due to ammonium acetate and PAN, as well as those of their intercalation complexes, are listed in Table 1. The characteristic bands for ammonium acetate and PAN are as follows: ammonium acetate—3120, 1574, 1400 cm^{-1}; PAN—2939, 2245, 1454 cm^{-1}.

The kaolinite-ammonium acetate intercalate showed the principal bands of ammonium acetate. All three bands were observed; however, the positions of the former two were shifted compared with the spectrum of ammonium acetate itself.

The spectrum of the suspected kaolinite-PAN intercalation complex indicated that ammonium acetate was still present between the layers. As characteristic bands due to PAN, a C≡N stretching band was observed at 2253 cm^{-1}. Also, bands that can be ascribed to ammonium acetate were detected at 3190, 1690–1640, and 1405 cm^{-1}. Other vibrational modes possibly contributed to the 1690–1640-cm^{-1} band. In addition, bands due to benzoyl peroxide and unidentified bands were detected, indicating that more complicated reactions had also taken place.

The heat treatment of the suspected kaolinite-PAN intercalation complex at 220°C did not significantly affect the profile of the spectrum. After the treatment at 220°C, the C≡N stretching band was still detected. A band due to a C=C or a C=N stretching mode was not detected. Therefore, no evidence for the cyclization of PAN was obtained. Also, most of the other bands did not disappear as a result of the treatment. On the contrary, the profile of the spectrum drastically changed on heating the sample at 400°C; only a band at 1620 cm^{-1}, which was possibly due to a C=O group, was present, in addition to those of kaolinite.

Table 1. Principal infrared bands due to organic materials.

Wavenumbers (cm^{-1})				
AA[1]	Kaolinite-AA complex	PAN[1]	Suspected kaolinite-PAN complex	Assignment
3120	3136 3024		3190	N–H stretching
		2939		C–H stretching
		2245	2253	C≡N stretching
1574	1599		1690–1640	COO^-
		1454		C–H bending
1400	1415		1405	COO^-

[1] Samples were solid so that KBr method was applied. AA = ammonium acetate; PAN = polyacrylonitrile.

The thermal behavior of the kaolinite-ammonium acetate intercalate was different. On heating the sample at 220°C, the N–H stretching band and those of the COO^- group disappeared. Correspondingly, new bands appeared at about 1650, 1420, and 1300 cm^{-1}. Hence, ammonium acetate seemed to degrade by the treatment, and carbonaceous materials having a C=O group seemed to form. After the treatment at 400°C no peaks due to organics were detected.

The vibrational modes of kaolinite were generally influenced by intercalation. Although its framework modes (an Si–O and an Al–OH stretching) were essentially the same as those of the raw kaolinite, the profile of its OH-stretching modes was drastically affected by intercalation. Therefore, the intercalation of kaolinite and the intercalated species can be discussed on the basis of the variations in the IR spectra in the OH-stretching region of both the suspected kaolinite-PAN intercalation complex and the kaolinite-ammonium acetate intercalation complex due to the heat treatment.

The profile of the OH-stretching bands suggests the formation of hydrogen bonds. That the OH-stretching modes of kaolinite show four different bands is well known. Whereas the 3621-cm^{-1} band has been assigned to "inner" hydroxyls, the other three bands at 3693, 3670, and 3653 cm^{-1} have been ascribed to "inner-surface" hydroxyls. Only the latter three bands can be perturbed by intercalated molecules. The resulting hydrogen-bonded hydroxyls show new bands at lower frequencies. Thus, the kind of the perturbed bands and the position of the shifted bands depend on the conditions between the layers (Theng, 1974).

Figure 3 shows the IR spectra in the OH-stretching region of the kaolinite-ammonium acetate intercalation complex and its heat-treated products. The hydrogen bonds in the complex were easily broken by the heat treatment. The intensities of the bands at 3693, 3670, and 3653 cm^{-1} in the IR spectrum of the kaolinite-ammonium acetate intercalate decreased com-

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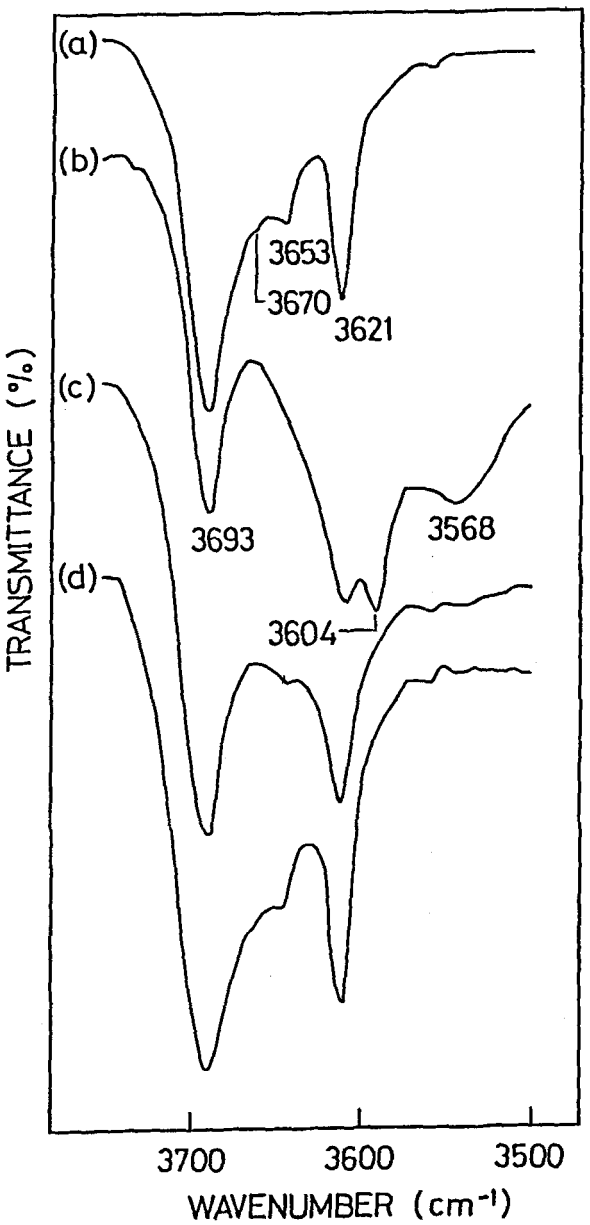


Figure 3. Infrared spectra in the OH-stretching region of (a) untreated kaolinite, (b) kaolinite-ammonium acetate intercalation complex, (c) kaolinite-ammonium acetate intercalation complex heated at 220°C for 1 hr, and (d) kaolinite-ammonium acetate intercalation complex heated at 400°C for 1 hr.

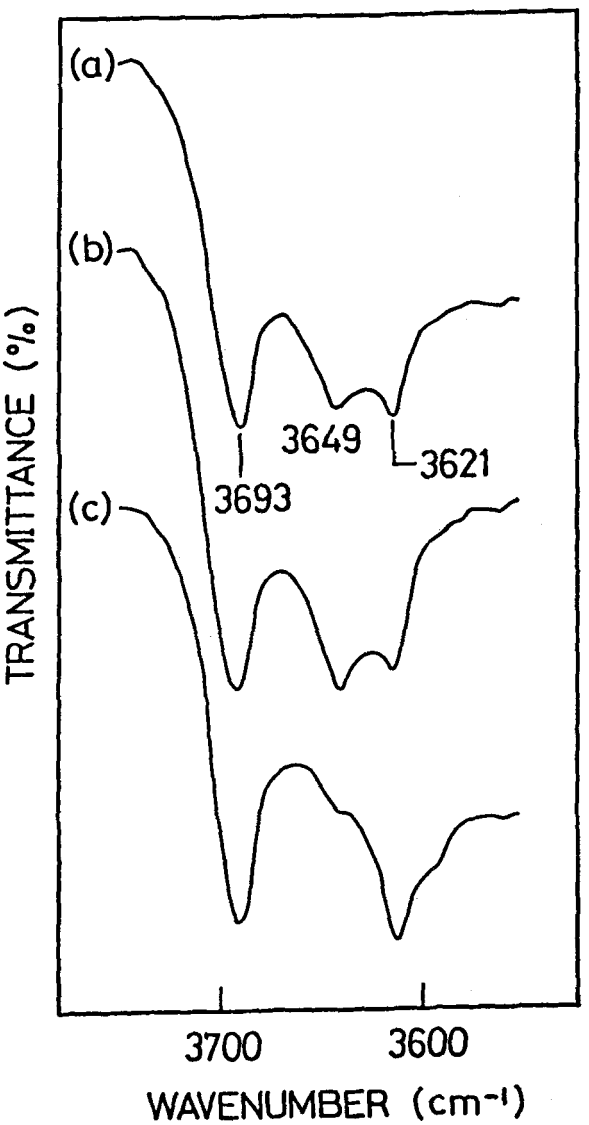


Figure 4. Infrared spectra in the OH-stretching region of (a) kaolinite-polyacrylonitrile intercalation complex, (b) kaolinite-polyacrylonitrile intercalation complex heated at 220°C for 1 hr, and (c) kaolinite-polyacrylonitrile intercalation complex heated at 400°C for 1 hr.

pared with those of the raw kaolinite (Figures 3a and 3b). Correspondingly, additional bands appeared at 3604 and 3568 cm^{-1}. On heating the sample at 220°C, the shifted bands disappeared and the intensities of the perturbed bands increased (Figure 3c); however, the profile was still different from that of the raw kaolinite. Because the layers were still expanded (Figure 2a) and the ammonium acetate had been degraded, these observations suggest that the carbonaceous material having C=O group formed from ammonium acetate interacted with the hydroxyls in a different way. On heating the sample at 400°C, the profile of the spectrum was similar to that of the raw kaolinite, in line with complete collapse, as shown by the XRD results.

On the other hand, the hydrogen bond in the suspected kaolinite-PAN intercalation complex was more resistant to the heat treatment (Figure 4). In the spectrum of the suspected kaolinite-PAN intercalate, the intensity of the 3693-cm^{-1} band decreased and a new band appeared at 3649 cm^{-1} (Figure 4a). Surprisingly, the profile of the OH-stretching bands, as well as those of the bands due to organics, was preserved after the

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treatment at 220°C (Figure 4b). Therefore, thermally stable PAN was probably involved in hydrogen bonding to the surface hydroxyls of kaolinite in the complex via the C≡N group, although part of the ammonium acetate may also have been present between the layers before the heat treatment. Because the shift for the hydrogen-bonded OH-stretching band in the suspected kaolinite-PAN intercalation complex was smaller than those of the kaolinite-ammonium acetate intercalate, the interaction in the suspected kaolinite-PAN intercalate was weaker (Cruz *et al.,* 1969). On heating the sample at 400°C, the intensity of the 3649-cm^{-1} band decreased; however, the profile still showed a slight perturbation of the hydroxyls. These results support the presence of the polymeric species between the layers after the treatment.

SUMMARY AND CONCLUSION

A kaolinite-polyacrylonitrile intercalation complex was apparently prepared by using a kaolinite-ammonium acetate intercalation complex as an intermediate. The monomer was introduced between the layers by displacing ammonium acetate and subsequently polymerized by heat treatment. The presence of PAN between the layers was indicated by the fact that the expansion of the layers and the perturbation of the hydroxyls in the suspected kaolinite-PAN intercalation complex were thermally more stable than those of the kaolinite-ammonium acetate intercalation complex. Thus, various organic monomers may be polymerized between the layers of kaolinite by using appropriate pre-formed intercalation complexes as intermediates.

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