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–Paper–

NARROWING OF X-RAY DIFFRACTION PEAK OF CLAY-ORGANIC HYBRID FILMS BY SWELLING AND DRYING PROCEDURE

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ABSTRACT

We have found that X-ray diffraction peaks of clay-organic hybrid films were narrowed after swelling followed by removing of solvent. We fabricated hybrid films consisting of natural montmorillonite (Mont), synthetic saponite (SSA) or synthetic stevensite (SST) and a cationic organic molecule. Full width at half maximum (FWHM) of 001 reflection of as-prepared Mont hybrid was 1.58 2θ degree whereas that after swelling and solvent removing procedure was 0.84 2θ degree. This decreasing of FWHM indicated that the improvement of packing order of clay particles in clay-organic hybrid was occurred during swelling and solvent removing procedure. Similar decreasing of FWHM was also found in hybrids consisting of SSA or SST. Improvement of packing order of hybrid was found to accompany suppression of light scattering of hybrid at the same time.

Key words: Clay-organic hybrid, Smectite, Swelling

INTRODUCTION

Organic molecules in clay mineral-organic hybrid materials exhibit prominent optical functionalities compared to those in solution or solid state (Ishida et al., 2014; Schoonheydt et al., 2014; Sasai et al., 2011). However, significant light scattering often hinder the advantage of such hybrid materials. Light scattering of hybrid material occurs at the gaps between each particles of hybrid, when sizes of gaps are larger than the wavelength of the light. These gaps are formed by the packing fluctuation of the clay particles stacked in hybrid. To suppress the light scattering, gaps should be sufficiently smaller than the wavelength of light. One way how to achieve gaps with smaller dimensions is to control the packing order of clay particles.

Filtration based technique is known to obtain a low light scattering hybrid film (Suzuki et al., 2012; Kawamata et al., 2010). In this technique, hybrid materials with small gaps can be obtained by slow deposition of small sized hybrid dispersed in water by filtration. In this study, we attempted to improve the particle packing of hybrid fabricated by the filtration based technique followed by re-packing procedure of the clay particles. In swollen states, the gallery height of a clay mineral expanded. Removing of the solvent from the interlayer space induces shrinking of the gallery height. This change of gallery height is a reversible process. The hybrid particles are thought to be re-packed throughout the swelling and solvent removing procedure. This re-packing process should result in the decreasing the defect of stacking structure of the hybrid material and hence low light scattering characteristic thought to be obtained.

Thus, we investigated the change in stacking structure and light scattering characteristic of hybrid through swelling and solvent removing procedure by a powder X-ray diffraction (XRD) and light transmittance measurements. We fabricated hybrid films consisting of natural montmorillonite (Mont; Kunipia-F, Kunimine Industries co. ltd.), synthetic saponite (SSA; Sumecton SA, Kunimine Industries co. ltd.) or synthetic stevensite (SST; Sumecton ST, Kunimine Industries co. ltd.) and *4,4'-[4,1-phenylenedi-(1E)-2,1-ethenediyl]bis- (1-methyl-pyridinium) dichrolide* (Bis-Bz; Fig. 1). Aggregation manner of confined organic molecule is thought to be perturbed through the swelling and solvent removing procedure. In order

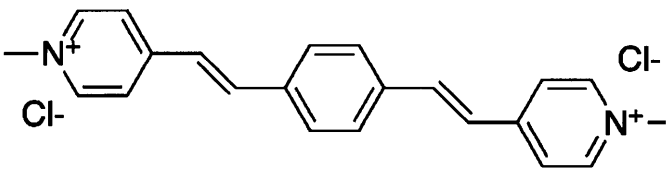

FIG. 1. Chemical structure of Bis-Bz.

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to investigate the change, we employed the Bis-Bz which exhibits suitable absorption band for monitoring aggregation manner by means of UV-Vis absorption spectrum.

After swelling and solvent removing procedure, full width at half maximum (FWHM) of 001 reflection was reduced from 1.58 to 0.84 2θ degree for Mont hybrid films. This observation indicated that the stacking structure of hybrid was improved by swelling and solvent removing procedure. Furthermore, suppression of light scattering was also observed after applied procedure.

EXPERIMENTS

Clay minerals

Ordering of clay platelets in a hybrid is thought to be improved by employing larger sized clay particles. On the other hand, enhancing the light scattering of hybrid material is expected by employing larger sized clay particles due to formation of larger sized gaps. Thus, three types of clay minerals with different particle size were employed to compare the effects of lateral size onto order of the stacking structure and light scattering properties. Average diameter of Mont, SSA and SST were 1000 (Miyawaki et al., 2010), 50 (Miyawaki et al., 2010) and 40 nm (provided for supplier), respectively. Employed cation exchange capacities (CEC) of Mont, SSA and SST, were 1.15, 0.997 (Takagi et al., 2002) and 0.57 meq g^{-1}, respectively. CEC values of Mont and SST were received from supplier.

Synthesis of 4,4'-[4,1-phenylenedi-(1E)-2,1-ethenediyl]bis (1-methylpyridinium) dichrolide (Bis-Bz)

A mixture of 1,4-dimethyl pyridinium iodide (1.18 g, 5.00 mmol), terephthalaldehyde (0.34 g, 2.50 mmol) and piperidine (10 drops) in ethanol (20 mL) was refluxed for 7 hours at 80°C. After cooling to room temperature, the reaction mixture was filtered. The residual yellow solid was recrystallized from deionized water to obtain 4,4'-[4,1-phenylenedi-(1*E*)-2,1-ethenediyl]bis-(1-methylpyridinium) diiodide (54% yeild).

4,4'-[4,1-phenylenedi-(1*E*)-2,1-ethenediyl]-bis(1-methylpyridinium) diiodide (0.57g, 1.00 mmol) was dissolved in deionized water (40 mL). Sodium hexafluorophosphonate (0.90 g, 5.36 mmol) dissolved in deionized water (40 mL) was dropped into the solution of reactant. The yellow precipitate was filtered to obtain 4,4'-[4,1-phenylenedi-(1*E*)-2,1-ethenediyl]bis-(1-methylpyridinium) dihexafluorophosphate (99% yeild).

4,4'-[4,1-phenylenedi-(1*E*)-2,1-ethenediyl]-bis(1-methylpyridinium) dihexafluoro- phosphate was dissolved in deionized water (40 mL). Anionic exchange resin (DOWEX^{TM} 1x8 50-100 Mesh, 20.8 g) was added to the solution and stirred for 24 hours. After filtrate evaporation, the resultant solid was recrystallized from methanol to obtain 4,4'-[4,1-phenylenedi-(*1E*)-2,1-ethenediyl]bis-(1-methylpyridinium) dichrolide as a yellow solid (25% yeild). 1H NMR (500 MHz, DMSO), d(ppm): 8.90 (d, J = 6.5 Hz, 4H), 8.25 (d, J = 6.5 Hz, 4H), 8.05 (d, J = 16.5 Hz, 2H), 7.88 (s, 4H), 7.64 (d, J = 16.5 Hz, 2H), 4.28 (s, 6H)

Fabrication of hybrid films

Hybrid films were fabricated by using a simple protocol reported in our previous paper (Kawamata et al., 2010). This protocol involves mixing of an aqueous dispersion of an exfoliated clay mineral with a dye solution, followed by filtration. Film thicknesses of obtained films were unified to 1.5 μm.

Swelling and drying

In order to investigate the interlayer distance in swollen state, the use of a solvent with a negligible vapor pressure is preferable. Additionally, to swell the clay mineral, a polar character of used solvent is required, and therefore dimethylsulfoxide (DMSO) was employed as a solvent. The vapor pressure of DMSO is too low, so the prepared hybrid material cannot be dried in a direct manner. Therefore the drying procedure was followed after the DMSO was washed out with ethanol. Hereafter we called this state as "drying".

X-ray diffraction measurement

The change in gallery height of film samples of hybrid associated with swelling and drying was observed by powder X-ray diffraction (XRD) measurement. The data were collected using a Rigaku Ultima-IV diffractometer with monochromatized Cu Kα radiation (λ = 0.154 nm). Sampling step, Scan speed and Slit width were 0.05 degree, 1 degree/min and 5 mm, respectively.

Measurement of UV-Vis spectra

Absorption spectra of hybrid films were measured using a JASCO Model U-670 spectrometer equipped with a film holder (JASCO, VTA-752).

Evaluation of light scattering

Light scattering of hybrids were evaluated by using a semiconductor laser irradiating at 635 nm (Sigmakoki, LDU-33-635-4.5). The optical setup is illustrated in Figure 2. Laser beam with a diameter of 2 mm was irradiated to the hybrid deposited on a glass substrate without focusing. The 2 mm

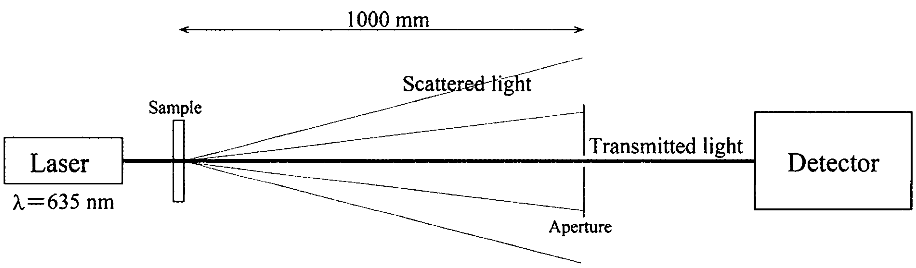

FIG. 2. Schematic representation of optical setup for measurement of transmittance.

aperture was placed at 1 m distance from the sample. At this setup, the intensity of laser beam was monitored behind the aperture. The majority of the scattered light should be blocked by used aperture. We compared the light intensity observed for the sample and blank (substrate without hybrid). The transmittances determined in this study were the averaged value from 5 samples fabricated at the same condition. Errors were estimated by the differences of measured transmittances.

RESULTS & DISCUSSION

Absorption spectra of Mont, SSA and SST hybrid films fabricated at 5, 10, 20 and 40% loading levels versus CEC (%CEC) were shown in Figure 3. The shape of absorption bands of Mont, SSA and SST hybrid film at 5 and 10%CEC were found to be essentially the same. This fact indicates the electronic state of Bis-Bz in Mont, SSA and SSA hybrid at these %CEC is thought to be the same. In such low dye loading condition, the intercalated molecule tends to lie in the clay layer without forming aggregated state (Suzuki et al., 2011). Therefore, at this dye loading level, Bis-Bz was thought to be present in monomer state. On the other hand, at %CEC higher than 20%, component of absorption of which maximum is located at around 420 nm increased. This change was remarkable in SST. Such change in the absorption characteristics is often seen in hybrids fabricated at a high %CEC (Martínez et al., 2004). The change has typically been attributed to formation of aggregated state (Martínez et al., 2004). Thus the spectrum change found in this study strongly suggests the formation of some kind of aggregation at a %CEC higher than 20%. Thus, we employed the 10%CEC hybrid film that possesses monomeric Bis-Bz in the following studies.

The XRD peaks of 001 reflection of Mont, SSA and SST hybrids fabricated at 10%CEC are shown in Figure 4. Values of 2θ, interlayer spacing (d) and FWHM of 001 reflection of hybrids are summarized in Table 1.

Interlayer spacing of Mont hybrid of as-prepared and in swollen and dried states were 1.48, 1.67 and 1.47 nm, respectively. Interlayer spacing of Mont hybrid of as-prepared and in dried state corresponded to the sum of thickness of monolayer of Mont and π-electoron system of Bis-Bz. This result indicated that Bis-Bz is accommodated in the interlayer space of Mont without stacking. On the one hand, after swelling, interlayer space was expanded as expected. In drying state, the spacing was almost same as as-prepared sample. Similar changes of interlayer spacing by swelling and drying proce-

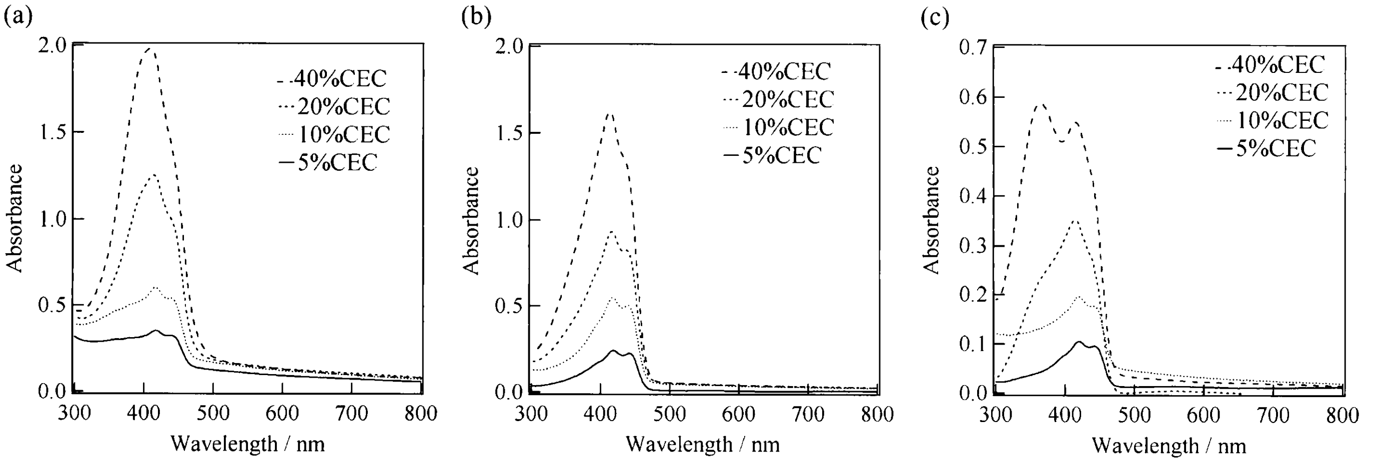

FIG. 3. Absorption spectra of Mont (a), SSA (b), SST (c) hybrid film fabricated at 5, 10, 20, 40%CEC.

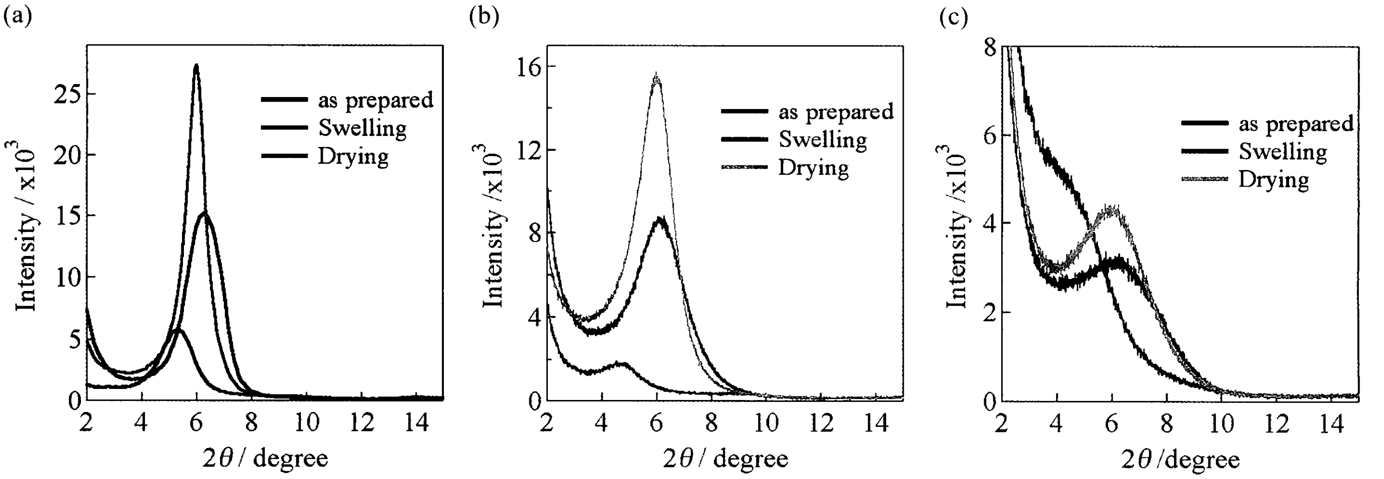

FIG. 4. XRD pattern of Mont (a), SSA (b), SST (c) hybrid film fabricated at 10%CEC of as prepared, swelling and drying state.

TABLE 1. XRD data, transmittance estimated using a laser beam and wavelength of absorption maximum of Bis-Bz of Mont, SSA and SST hybrid fabricated at 10%CEC

Clay mineral		2θ (degree)	d (nm)	Full width half maximum (degree)	Transmittance (%)	Wavelength of absorption maximum (nm)
Mont	as prepared	6.30	1.48	1.58	51±2	419
	Swelling	5.31	1.67	1.40	–	
	Drying	5.99	1.47	0.84	56±2	418
SSA	as prepared	6.03	1.46	1.91	73±1	418
	Swelling	4.82	2.03	2.03	–	
	Drying	6.04	1.46	1.61	75±1	416
SST	as prepared	6.11	1.44	2.99	89±1	420
	Swelling	–	–	–	–	
	Drying	6.05	1.47	2.58	90±1	417

dures were also found from both of SSA and SST hybrid films, though not a clear peak but only a shoulder was observed in the case of swollen state of SST hybrid. When the packing order is high, the FWHM of corresponding reflection is decreasing (Patterson, 1939). FWHM of as-prepared hybrids consisting of Mont, SSA and SST were 1.58, 1.91 and 2.99 2θ degrees, respectively. The stacking structure tended to improve when the clay with a larger sized platelet was employed. Due to this less ordered stacking structured SST hybrid, no clear peak of 001 reflection in swollen state was thought to be observed.

FWHM of Mont hybrid decreased to 0.84 2θ degree after swelling and drying procedure. Therefore, observed decrease of FWHM, and also decreasing the defect of stacking structure, was achieved by swelling and drying procedure. Decreases of the FWHM by swelling and drying procedure were also observed even for other clay minerals, SSA and SST. FWHM of Mont, SSA and SST hybrids after swelling and drying procedure were 53, 84 and 86% smaller than those of as-prepared state, respectively. Thus, decreasing the defect of stacking structure by swelling and drying procedure should be effective for the hybrids consisting of larger clay platelets.

Transmittances of hybrids measured using a laser beam are summarized in Table 1. Those of Mont, SSA and SST hybrid of as-prepared sample were 51, 73 and 89%, respectively. Higher transmittance values were observed for smaller sized clay mineral particles. From the light scattering point of view, the larger sized clay was unfavorable, though the order of stacking structure was high. Transmittances of Mont, SSA and SST hybrid after swelling and drying procedure were 56, 75, and 90%, respectively. Improvements of the transmittances were thought to be obtained by decreasing the defect of stacking structure. The extent of improved transmittance of Mont, SSA and SST hybrid were 5, 2 and 1%. Larger improvement of transmittance was observed for lower transmittance sample in as-prepared state.

As shown in Table 1, subtle blue-shifts of absorption maxima were observed for all hybrids by swelling and drying procedure. The π-conjugated molecules confined in interlayer space are typically forming clusters (Bujdak et al., 2006; Suzuki et al., 2014; Takagi et al., 2013). In our previous study (Suzuki et al., 2014), increasing of the size of cluster induced subtle blue-shift of absorption maxima. Thus, the subtle blue-shifts accompanying by swelling and drying process were likely to be attributed to small increase of the cluster size.

CONCLUSION

We found decreasing the defect of stacking structure of hybrid can be achieved by using swelling properties of smectites. The extent was significant for a smectite with a larger sized platelet. By decreasing the defect of stacking structure, the light scatterings of hybrids were surpressed. Utilization of this simple procedure should be effective means for obtaining hybrids with high packing order and thus low-light scattering characteristic.

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