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Preparation of Polymer Nanohybrid via *in situ* Synthesis of Inorganic Nanofiber in Polymer Solution

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Imogolite is a hydrous aluminosilicate with a unique nanofiber structure. A novel polymer nanohybrid consisting of poly(vinyl alcohol) [PVA] and nanofiber imogolite was prepared via *in situ* synthesis of imogolite in order to achieve the molecular dispersion of imogolite in a PVA matrix. The imogolite/PVA hybrid thus obtained was characterized by infrared spectroscopy and X-ray diffraction. The morphology of the synthetic imogolite nanofiber in hybrid materials was observed by atomic force microscopy. In addition, the synthetic imogolite/PVA hybrid film formed via *in situ* method exhibited high optical transparency in the visible light regions, owing to the fine dispersion of synthetic imogolite in the PVA matrix.

Key Words: Nanohybrid, Nanofiber, Synthetic imogolite, Poly (vinyl alcohol)

1. INTRODUCTION

Imogolite, a hydrous aluminosilicate polymer, was discovered in the clay fraction of a glassy volcanic ash soil ("Imogolayer") in Kyushu, Japan, in 1962 [1]. Fig. 1 shows the schematic representation of the structure of imogolite. Imogolite forms a hollow nanotube with an external diameter of ca. 2.5 nm, an internal diameter of 1 nm, and lengths ranging from several hundred nanometers to a micrometer, and has the general formula of $Al_2O_3 \cdot SiO_2 \cdot 2H_2O$ [2]. The outer surface of imogolite is composed of Al-OH groups; therefore, the outer surface wall can be charged depending on the pH of the solution. Owing to the electrostatic repulsion, the isolated units can form nanofiber in acidic dispersions (pH below 5). Due to its extremely high aspect ratio and large specific surface area, a polymer nanocomposite with imogolite can be expected to have improved mechanical and thermal properties. In addition, since imogolite has a refractive index which is almost similar to that of a conventional polymer, it offers application as a transparent polymer additives.

However, there is little imogolite found in the soil, and it is difficult to purify, so establishing a synthetic method of imogolite may give rise to various potential commercial applications. A synthetic pathway of imogolite was first described in 1977 from dilute solutions of aluminum chloride and monosilicic acid [3], and several investigations concerning the method of synthetic imogolite have been reported [4]. However, the preparation of a polymer/nanofiber hybrid utilizing *in situ* synthesized imogolite has not been achieved. In the present work, the authors synthesized an aluminosilicate nanofiber for the preparation of a polymer nanohybrid, and characterized the imogolite/polymer hybrid prepared by *in situ* synthesis.

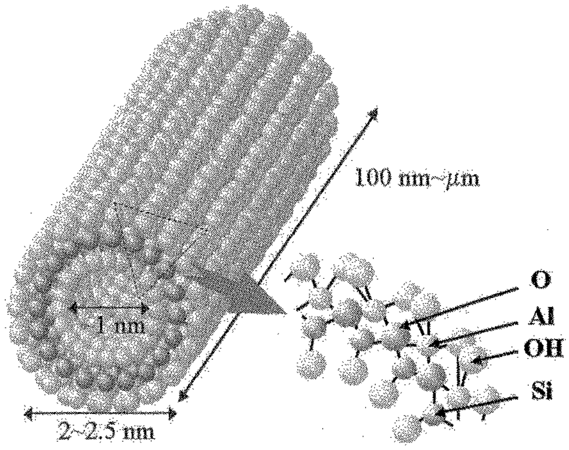


Fig. 1 Schematic representation of structure of imogolite.

2. EXPERIMENTAL

2.1 Synthesis of imogolite

Imogolite was synthesized by the method of Farmer et al [3]. An aqueous solution of aluminum chloride [$AlCl_3 \cdot 6H_2O$] was mixed with an aqueous solution of tetraethoxysilane [$Si(OEt)_4$]. The final concentration of the solution was 2.4 mmol/L with respect to Al and 1.4 mmol/L with Si. Aqueous sodium hydroxide (0.1 mol/L) was then added slowly until the aqueous solution reached pH 5, and the solution was next reacidified by addition of 1 mmol of hydrochloric acid and 2 mmol of acetic acid per liter of the solution. The solution was then refluxed at 369 K for various periods (24-120 hours). After being cooled to room temperature, the suspended material was gelated by sodium chloride solution and rinsed with distilled water using a 100 nm Millipore filter. The rinsed imogolite gel in the low acidic aqueous solution was dispersed by sonication. The cotton-like white solids were obtained by freeze-drying the dispersed solution of imogolite.

2.2 Synthesis of imogolite/PVA hybrid by *in situ* method

A polymer nanohybrid with imogolite was prepared utilizing a new method of synthesizing imogolite, which can be expected to improve the dispersibility of imogolite into the polymer matrix, compared with the hybrid prepared by the blending method [5]. The polymer nanohybrid was prepared by *in situ* synthesis of imogolite in the presence of poly(vinyl alcohol)[PVA] in solution. PVA with a degree of polymerization of 630 was used. The solution prepared by using the conventional method of synthesizing imogolite was mixed with PVA aqueous solution, and refluxed at 369 K for 96 h. The mixed solution of imogolite and PVA was reprecipitated with ethanol, and the precipitate was filtered using a 450 nm Millipore filter and then rinsed by water and ethanol. The white product of (imogolite/PVA) hybrid was then obtained.

2.3 Infrared spectroscopy

The infrared (IR) spectroscopy measurement was carried out with Spectrum One (Perkin Elmer Japan Co., Ltd.) with a resolution of 0.5 cm^{-1} at room temperature. IR data was collected by averaging 64 scans between 4000 and 500 cm^{-1}. A specimen of the synthetic products for IR measurement was prepared by forming under pressure with KBr powder.

2.4 X-ray diffraction

The X-ray diffraction (XRD) measurement was carried out at the BL02B2 beam line of SPring-8 using white powder products packed in a quartz glass capillary. The diameter of the quartz glass capillary was 0.3 mm. The main optics is the bending magnet system, which contains a fixed-exit double-crystal monochromator and a mirror coated with two elements of Pt and Ni on a Si substrate. Diffraction from a sample was detected with imaging plates of a Debye-Scherrer camera in the BL02B2 beamline. XRD was carried out at room temperature using incident X-rays with a wavelength, λ, of 0.10 nm.

2.5 Atomic force microscopy

The tapping mode atomic force microscopic (AFM) observation of imogolite was carried out by using an SPA400 AFM head with a SPI3800 controller (Seiko Instruments Industries Co., Ltd.). The sample for AFM observation was prepared by the spin-coating of a 1% PVA/imogolite mixture solution at 3000 rpm for 1 min on a silicon wafer. The obtained film was then vacuum dried for 12 h. A tapping mode AFM observation was carried out at room temperature using a Si_3N_4 rectangular cantilever with a spring constant of 15 N m^{-1}, and the resonant frequency of the cantilever was around 160 kHz. The setpoint amplitude was –30 %.

2.6 Light transmission measurement

Light transmission measurement was measured with a UV-Vis spectrometer, Lamda 35 (Perkin Elmer Japan Co., Ltd.) at the region of the visible light wavelength. The hybrid films used in this method were prepared by the cast method from imogolite/PVA solution. The concentration of imogolite/PVA aqueous solution was 5 wt%. This solution was kept in a glass petri dish at 323 K for 24 h. After drying, the film was peeled off from the glass petri dish, and dried in vacuum for 12 h. The thickness of the imogolite/PVA hybrid films was ca. 100 μm.

3.RESULTS AND DISSCUSSION

3.1 Characterization of synthetic imogolite

Fig. 2 shows the IR spectra of the freeze-dried synthetic imogolite sample after various reaction times. The two sharp absorptions at 995 and 935 cm^{-1}, which were assigned to the Si-O-Al stretching vibration, are characteristic of imogolite. The IR spectra in this region was not sufficiently distinctive to allow for the presence of other aluminosilicates such as allophane (spherical structure). The previous paper on the synthesis of imogolite [6] revealed that the appropriate reaction time for the formation of imogolite is 4-5 days. Consequently, the reaction time of the *in situ* synthesis in the polymer solution was set to be 96 h.

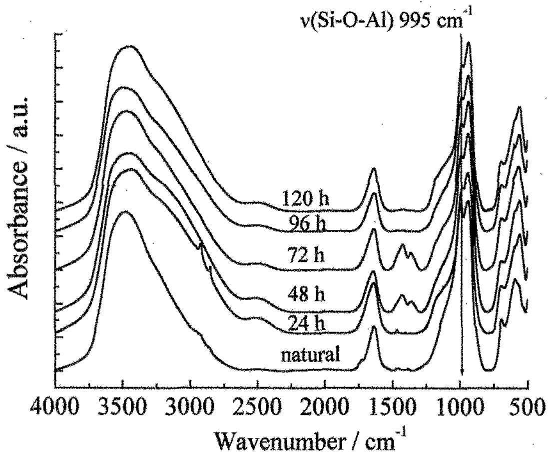


Fig. 2 IR spectra of natural and synthetic imogolite after various reaction times.

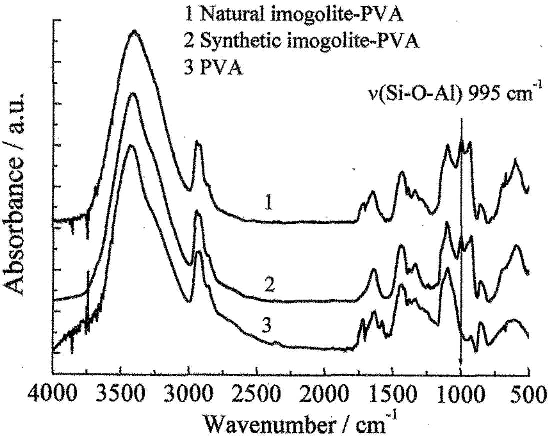


Fig. 3 IR spectra of natural and synthetic imogolite / PVA mixture and PVA.

3.2 Recognition of synthetic imogolite structure from *in situ* method

Fig. 3 shows the IR spectra of PVA and the imogolite/PVA hybrid prepared by two different methods. One was prepared by the *in situ* method, and the other consists of the blending of PVA powder and freeze-dried natural imogolite. The weight ratio of the imogolite and PVA was 1:1. The IR spectra of the hybrid with imogolite showed two sharp peaks corresponding to the Si-O-Al stretching vibration, which is characteristic of imogolite. The IR spectra of the natural imogolite/PVA and synthetic imogolite/PVA hybrid materials are quite similar to that of the PVA powder, except for the characteristic imogolite absorptions at 995 and 935 cm^{-1}. It is suggested that imogolite was successfully formed in the polymer solution.

3.3 Aggregation structure of synthetic imogolite/PVA hybrid prepared by *in situ* method

Fig. 4 shows the wide-angle X-ray diffraction profiles of natural and synthetic imogolite and the imogolite/PVA hybrid samples. Imogolite:PVA weight ratio was 1:1 for the hybrid. Scattering vector q [nm^{-1}] is defined as $q=(4\pi/\lambda)\sin\theta$ where λ and θ are the wavelengths of the X-ray and scattering angle respectively. The XRD patterns of imogolite consist of a number of broad reflections. The reflections at 1.77-1.27 and 0.79 nm for natural imogolite [2], and at 2.30-1.50 and 0.98 nm for synthetic imogolite [6], are associated with the hexagonally packed nanotube [7]. The peak for the synthetic imogolite was observed at a lower q value than that for natural imogolite. This indicated that the diameter of the synthetic imogolite is slightly larger than that of the natural imogolite [8]. The sharp peak at 2.0 nm for the imogolite/PVA hybrid was ascribed to the rearrangement of parallel imogolite nanotube bundles. The absence of peaks except for imogolite and PVA in the XRD pattern, suggested that there were no by-products in the *in situ* synthesized hybrid. Even though the synthesis of imogolite was carried out in a polymer solution, imogolite fiber of high quality was obtained.

3.4 Morphology of synthetic imogolite nanofiber in hybrid materials

The inorganic nanofiber in the polymer matrix was imaged by tapping mode AFM. Fig. 5 shows the tapping mode AFM images of the PVA/imogolite hybrid prepared with various weight ratios of the imogolite/PVA. The brighter areas in the tapping mode AFM image correspond to the height region. The AFM images,

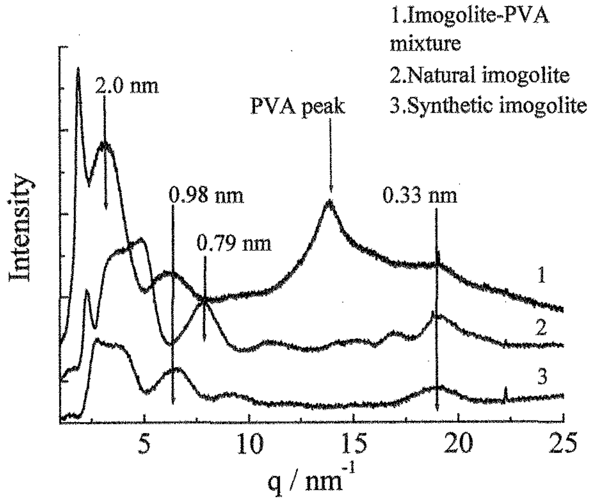
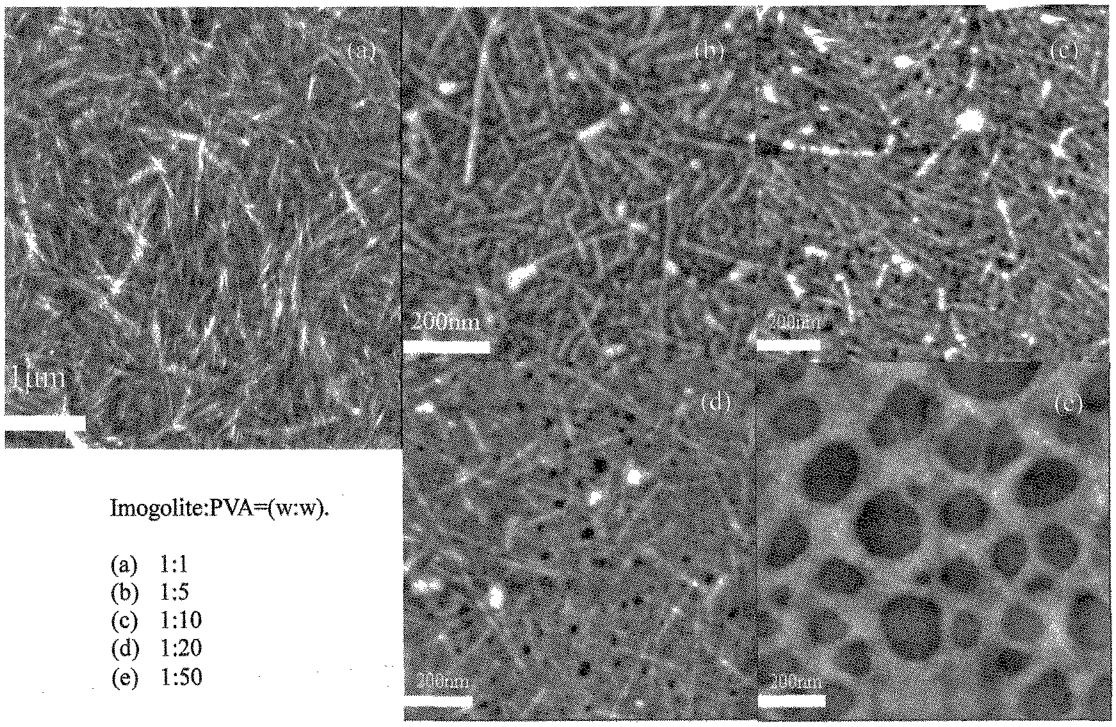


Fig. 4 XRD profiles of natural and synthetic imogolite and PVA/synthetic imogolite mixture.



Imogolite:PVA=(w:w).

- (a) 1:1
- (b) 1:5
- (c) 1:10
- (d) 1:20
- (e) 1:50

Fig. 5 Tapping mode AFM height images of synthetic PVA/imogolite mixture.

except for the weight ratio of 1:50 for imogolite/PVA, showed the fiber morphology on the substrate. This morphology revealed the formation of the bundle of imogolite nanofiber. The average length of the synthetic imogolite fiber observed for the films prepared by *in situ* method was ca. several hundred nanometers. This value is smaller than that of typical natural and synthetic imogolite fibers. Furthermore, the AFM image of the imogolite/PVA weight ratio of 1:50 (Fig. 5e) showed no evidence of imogolite fiber formation. The reason for the inhibition of the formation of the imogolite structure in the PVA matrix is the influence of the PVA concentration in the solution. Previous papers described how the important factors governing the formation of imogolite are the pH, OH/Al molar ratio, Si/Al ratio, temperature, and additives in the solution [6,9]. In particular, additives such as organic ligands, which can interact with the Al ion, are very important in determining the formation and nature of short-range ordered aluminosilicate [9]. The data obtained from the AFM images revealed that the growth of the imogolite nanofiber to the axial direction might be impeded by the presence of PVA. The intermolecular interaction between PVA and imogolite was maintained by the formation of mesophase of two contents [10]. It is suggested that the higher PVA concentration inhibited the formation of the synthetic imogolite nanofiber. Thus, it seems that there is a critical concentration of PVA for synthetic imogolite.

3.5 Optical properties of synthetic imogolite/PVA hybrid film prepared by *in situ* method

Fig. 6 shows the light transmittance through the imogolite/PVA hybrid and PVA films. Two kinds of imogolite/PVA hybrids prepared by different procedures were used for the measurement. One was prepared by the *in situ* method with various weight ratios of imogolite/PVA, and the other was prepared by blending of PVA and freeze-dried imogolite powder. Imogolite/PVA hybrid film from *in situ* method was optically transparent, and thus comparable to imogolite/PVA blend film with the same quantity of freeze-dried imogolite powder at a high fraction of imogolite. It was difficult to re-disperse the freeze-dried imogolite powder, since imogolite fiber aggregates during the process of air-drying or freeze-drying. However, imogolite formed via *in situ* synthesis in a polymer solution could inhibit aggregating, because all the reaction is preceded in the polymer solution. In addition, the PVA hybrid film that contained large amounts of imogolite, up to the weight ratio of 1:5 (imogolite/PVA), could keep high optical clarity, not only because of the dispersibility of synthetic imogolite in the PVA matrix, but also because of the change of the degree of crystallinity and crystal size of PVA influenced by the dispersion of imogolite in the polymer matrix. It was revealed that synthetic imogolite prepared by *in situ* synthesis was finely dispersed in the PVA matrix, compared with the hybrids prepared by the blend of freeze-dried imogolite and PVA from the UV-Vis spectroscopic measurements.

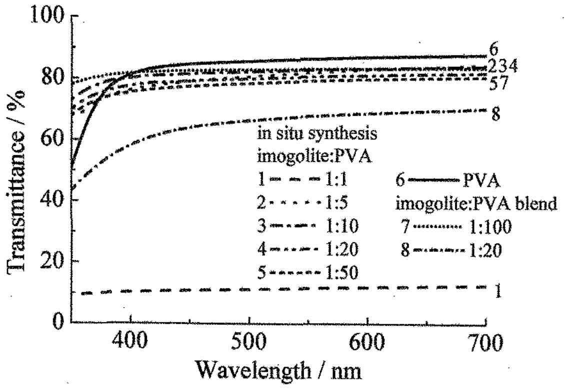


Fig. 6 Light transmittance through synthetic (imogolite/PVA) hybrid and PVA films.

4. CONCLUSION

The aluminosilicate nanofiber "imogolite" was successfully synthesized in PVA aqueous solution through the novel "*in situ* method". The growth of the nanofiber structure in the polymer solution was confirmed by AFM observation. From the viewpoint of dispersibility, the preparation of synthetic imogolite by *in situ* method could be more effective for constructing of polymer nanohybrid than the conventional blending method.

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