

Surface Modification of "Imogolite" Nanofiber for Nanocomposite Applications

Kazuya Yamamoto¹, Hideyuki Otsuka¹, Shin-Ichiro Wada², and Atsushi Takahara¹

¹Institute for Fundamental Research of Organic Chemistry, Kyushu University, Higashi-ku, Fukuoka 812-8581, JAPAN

FAX:81-92-642-2715, e-mail:takahara@cstf.kyushu-u.ac.jp

²Graduate School of Bioresource and Bioenvironmental Sciences,

Kyushu University, Higashi-ku, Fukuoka 812-8581, JAPAN

Imogolite is one of aluminosilicates with a net composition $\text{Al}_2\text{O}_3\text{SiO}_2(\text{H}_2\text{O})_n$ consisting of hollow nanotube with an external diameter of about 2.5 nm and a length in the range of 400-1000 nm. Atomic force microscopic observation revealed that the imogolite molecules form fibrous network at pH=3.0. Since the outermost surface of imogolite is Al-OH groups, a strong interaction can be expected between Al-OH and phosphonic acid groups. Octadecylphosphonic acid (OPA) was chemisorbed onto the surface of imogolite. Adsorption of imogolite with OPA was confirmed by infrared spectroscopy. The hydrophobization of imogolite surface by OPA owing to the coverage with long alkyl groups was studied with adhesion force measurement. (Poly(vinyl alcohol)(PVA)/imogolite) hybrid was prepared and characterized based on dynamic viscoelastic measurement. It was revealed that the presence of imogolite restricts the micro-Brownian motion of PVA.

Key words: imogolite, nanofiber network, interaction, hydrophobization, nanocomposite

1. Introduction

Imogolite, a hydrous aluminosilicate polymer was discovered in the clay fraction of a glassy volcanic ash soil ("Imogolayer") of Kyushu, Japan in 1962¹⁾. Figure 1 shows the schematic representation of the structure of imogolite. Imogolite forms hollow nanotube with an external diameter of ca.2.5 nm, and an internal diameter of 1 nm^{2,3)} and lengths from several hundreds nanometer to micrometer, which has the general formula of $\text{Al}_2\text{O}_3\text{SiO}_2(\text{H}_2\text{O})_n$. Outer surface of imogolite is composed of Al-OH groups, therefore, the outer surface wall can be charged depending on the pH of the dispersions. Owing to the electrostatic repulsion, isolated units can form nanofiber in acidic solution (pH below 5). As can be expected from the large aspect ratio of imogolite rod, the dispersion of imogolite rods can form space filling gels with volume fractions as low as volume fraction of 0.2%⁴⁾. Several studies have been reported on the preparation of (imogolite/polymer) hybrids^{5,6)}, however, effective reinforcement has not

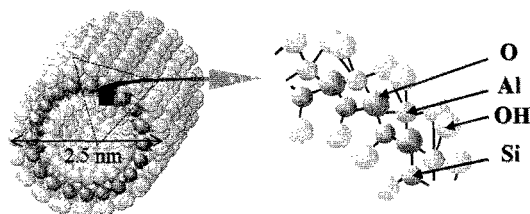


Figure 1 Schematic representation of structure of imogolite.

been achieved yet due to the lack of the control of interfacial structure between imogolite and matrix polymer. In order to achieve effective reinforcement, it is necessary to enhance the interaction between organic polymer and imogolite. The purpose of this study is to directly observe the imogolite nanofiber network formation and confirms the extent of interaction between functional group of organic amphiphile and imogolite rod. This will give a good insight on the design of imogolite/polymer interface. Also, a novel nanohybrid was prepared by blending water-soluble poly(vinyl alcohol) (PVA) with imogolite nanofiber.

2. Experimental

Materials

Raw material of imogolite gel was collected from the weathered pumice bed in Kitakami area, Iwate, Japan. Imogolite gel purified from contamination in the raw materials was dispersed in weak acidic solution (pH=5.0-6.0) by applying 42 kHz ultrasonic wave for a week. Freeze-drying of this dispersion gave fibrous imogolite. Purification method of imogolite can be found in elsewhere⁷. Octadecylphosphonic acid (OPA, A Johnson Matthey Co.) and stearic acid (SA, Nacalai Tasque, Inc.) were used for amphiphilic molecule of which hydrophilic group can be expected to interact with Al-OH groups of imogolite. OPA and SA were used without further purification.

PVA was chosen as a matrix polymer for green nanocomposite, since it shows biodegradation. PVA (Unichika. Co.) with degree of polymerization of 630 was used. (PVA/imogolite) hybrid was prepared by mixing the solutions of imogolite and PVA. Weight fraction of imogolite was ca. 2wt%. The mixture solution was placed on the flat petri dish and the water was removed at 353K. The specimen was annealed at 353K for 2hr in vacuo.

Atomic force microscopic (AFM) observation

AFM observation of imogolite was carried out by using SPA300 with SPI3700 controller (Seiko Instruments Industries Co., Ltd.). The sample for AFM observation was prepared by spreading one drop of dispersed solution of imogolite on the silicone wafer. AFM observation was carried out at room temperature under constant force mode with a reference force of 0.1 nN. Si_3N_4 triangular cantilever with a spring constant of 0.02 N m^{-1} was used.

State of interaction between imogolite and amphiphilic molecules

Imogolite was immersed in ethanol solution of OPA or SA (1:3.5=w/w) at 293K for 5 days and supernatant was removed. Imogolite chemisorbed with OPA or SA was recovered by centrifugation and repeated decantation. Infrared spectroscopy was carried out with Magna 860 (Nicolet, Madison, WI) with a resolution of

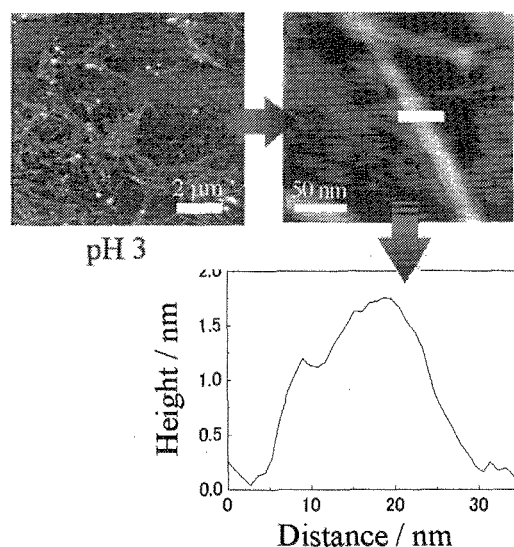


Figure 2 AFM image of the imogolite on Si wafer prepared from the aqueous dispersion with concentration of 0.05 wt% at pH 3.0.

1 cm^{-1} . Sample pellet of imogolite for IR measurement was prepared by forming a pellet under pressure with KBr powder.

Surface coverage of imogolite with alkyl group was confirmed on the basis of adhesion force measurement. Force-distance curve was measured in air by using SPA300 with SPI3700 controller. Rectangular Si_3N_4 cantilever with a spring constant of 0.09 N m^{-1} was used for the force-distance curve measurements. The approaching and retraction speed of cantilever was 2 nm s^{-1} . Force-distance curves were collected and the adhesion force was evaluated from the maximum attractive force in the retraction process.

Characterization of nanohybrids

The temperature dependence of dynamic viscoelasticity of (PVA/imogolite) hybrid was measured with Rehovibron DDV-01FP (Orientec Co., Ltd.) at 11 Hz under nitrogen atmosphere.

3. Results and Discussion

Characterization of imogolite nanofiber

Figure 2 shows the AFM image of the imogolite on Si wafer prepared from the aqueous dispersion with concentration of 0.05 wt% at pH=3.0. The nanofiber structure of imogolite was confirmed by AFM observation. However, the imogolite prepared from the

aqueous dispersion at pH=7.0 formed solid aggregates. It can be inferred that the imogolite formed the nanofiber under acidic condition. Also, a network structure was formed since the solution was evaporated onto the two dimensional plane. Line-profile of AFM image of imogolite revealed a size of rod of imogolite with a height of 1.5-2.5 nm and width of 20-30 nm. However, convolution effect of the AFM tip overestimates the molecular width. In the case of tip radius of 20 nm, the deconvolution of the observed diameter with the tip radius gives the molecular width of about 2-3 nm, which is in good agreement with the molecular diameter of imogolite evaluated from X-ray diffraction⁸⁾ and molecular dynamics simulation³⁾. The dispersion of imogolite at low pH can be ascribed to the electrostatic repulsion among protonated Al-OH groups at the outer surface. Thus, the dispersion of imogolite in polymer matrix at low pH can be expected to give nanofiber networks, which are suitable for the nanocomposite formation.

Modification of imogolite surface

In order to make imogolite dispersible in organic solvent and to achieve an effective reinforcement of matrix polymer phase in nanocomposite, it is necessary to modify the surface of imogolite or to introduce functional groups into polymers which have an attractive interaction with imogolite. Since the surface of imogolite has Al-OH groups, the amphiphilic molecules, R-X with different hydrophilic functional group, X was employed in order to study the interaction between Al-OH and R-X. At first the interaction between imogolite and OPA or SA molecules was studied on the basis of transmission IR. Figure 3 shows IR spectra of unmodified imogolite (a) and imogolite chemisorbed with OPA (b) and SA (c). The absorptions at 995 and 935 cm⁻¹ were attributed to the stretching vibration of Si-O-Al in imogolite. The absorption peaks at 2850-53, 2921-25, and 2956 cm⁻¹ can be attributed to the symmetric stretching vibrations of CH₂, antisymmetric stretching one of CH₂, and antisymmetric stretching one of CH₃ of alkyl chain in OPA and SA, respectively. The absorption peaks of the alkyl chains for OPA chemisorbed imogolite were stronger and

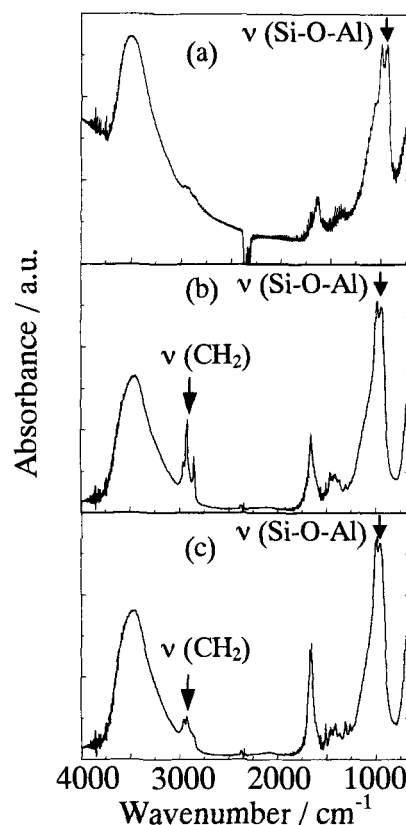


Figure 3 IR spectra of unmodified imogolite(a) and imogolite chemisorbed with OPA(b) and SA(c) from ethanol solution.

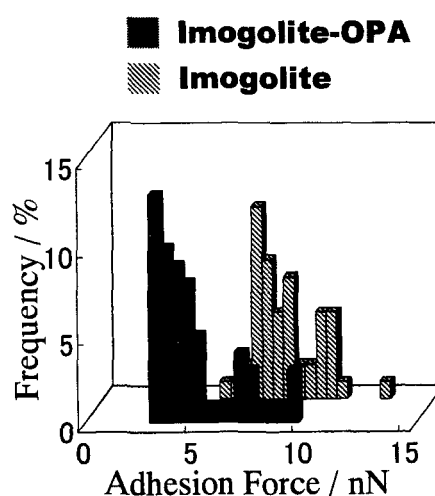


Figure 4 Histograms of adhesion force observed on the surface of imogolite and imogolite adsorbed OPA from ethanol solution.

sharper than that chemisorbed with SA. This suggests that the amount of adsorption of OPA onto imogolite was greater than that of SA onto imogolite. Also, the lower wavenumber of alkyl stretching bands of OPA on imogolite surface compared with that of SA suggested that the fraction of *trans* conformation of alkyl chain in

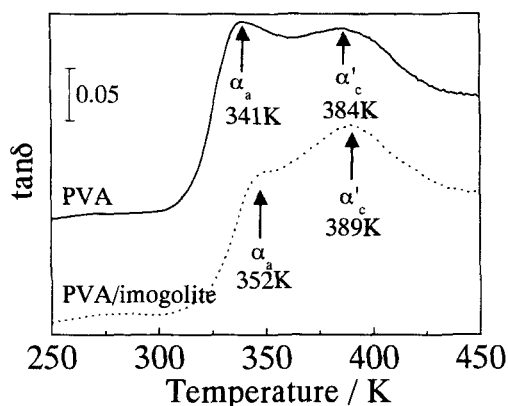


Figure 5 Temperature dependence of dynamic viscoelasticity for (PVA/imogolite) hybrid.

OPA on imogolite were greater than those of SA on imogolite. Thus, it can be concluded that phosphonic acid group has stronger interaction with Al-OH groups compared with carboxylic acid groups⁹).

The adsorption of OPA onto imogolite would be expected to change the surface hydrophilicity since the hydrophobic alkyl groups cover the imogolite surface. The force-distance curve measurement between cantilever tip and imogolite surface was measured before and after adsorption of OPA. The adhesion force was estimated from the maximum attractive force observed as a minimum in force-distance curve. Figure 4 is the histograms of adhesion force observed on the surface of imogolite and OPA-adsorbed imogolite. The adhesion force between imogolite and cantilever is larger than that between OPA-chemisorbed imogolite and cantilever tip. Since the surface of cantilever tip is covered with SiO₂, there is the strong adhesion force between Al-OH and SiO₂ of cantilever tip. On the other hand, in the case of OPA-chemisorbed imogolite, the adhesion force is weak because of the presence of hydrophobic alkyl group on the surface of OPA-chemisorbed imogolite. The hydrophobized imogolite thus prepared can be dispersed in organic solvent.

Characterization of (imogolite/PVA) nanohybrid

A novel "green nanohybrid" was prepared from biodegradable PVA and natural inorganic nanofiber "imogolite". The state of interaction between imogolite and the matrix PVA was confirmed based on dynamic

viscoelastic measurement. Figure 5 shows temperature dependence of mechanical loss tangent, $\tan\delta$ for PVA and (PVA/imogolite) hybrid annealed at 353 K for 2 hr. Temperature dependence of $\tan\delta$ shows a large absorption peak at ca. 352K which can be ascribed to the micro-Brownian motion of the amorphous phase of PVA¹⁰. The peak temperature of α_a -absorption for hybrids was higher than that for matrix phase. This suggests the presence of strong interaction between amorphous PVA chain and imogolite surface. Also, the peak of α'_c -absorption corresponded to the crystalline relaxation, was higher than that of matrix PVA. Thus, an effective reinforcement by imogolite nanofiber can be expected for this novel nanohybrid system.

Acknowledgment

This research was partially supported by a research grant from Iketani Science and Technology Foundation (Tokyo, Japan).

References

- [1] S.-I. Wada, K. Wada, *Clays Clay Miner.*, **30**, 123 (1982).
- [2] P. D. G. Cradwick, V. C. Farmer, J. D. Russell, C. R. Masson, K. Wada, N. Yoshinaga, *Nature*, **240**, 187 (1972).
- [3] P. I. Pohl, J.-L. Faulon, D. M. Smith, *Langmuir*, **12**, 4463 (1996).
- [4] A. P. Philipse, A. M. Wierengs, *Langmuir*, **14**, 49 (1998).
- [5] H. Hoshino, T. Ito, N. Donkai, H. Urakawa, K. Kajiwara, *Polym. Bull.*, **29**, 453 (1992).
- [6] H. Choi, Y.-W. Cho, W.-S. Ha, W.-S. Lyoo, C.-J. Lee, B.-C. Ji, S.-S. Han, W.-S. Yoon, *Polym. Intern.*, **47**, 237 (1998).
- [7] S.-I. Wada, Y. Kakuto, *Soil Sci. Plant Nutr.*, **45**, 947 (1999).
- [8] K. Wada, N. Yoshiinaga, *Am. Mineral.*, **54**, 50 (1969).
- [9] M. Rohwerder, M. Stratmann, *MRS Bull.*, **24**(7), 43 (1999).
- [10] M. Takayanagi, *Mem. Fac. Eng. Kyushu Univ.*, **23**(1), 1 (1963).