Preparation of a novel (polymer/inorganic nanofiber) composite through surface modification of natural aluminosilicate nanofiber

Kazuya Yamamoto[a]; Hideyuki Otsuka[a]; Atsushi Takahara[a]; Shin-Ichiro Wada[b]

[a] Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Fukuoka, Japan [b] Faculty of Agriculture, Kyushu University, Hakozaki, Fukuoka, Japan

Online publication date: 08 September 2010

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PREPARATION OF A NOVEL (POLYMER/INORGANIC NANOFIBER) COMPOSITE THROUGH SURFACE MODIFICATION OF NATURAL ALUMINOSILICATE NANOFIBER

Kazuya Yamamoto
Hideyuki Otsuka
Atsushi Takahara
Institute for Fundamental Research of Organic Chemistry,
Kyushu University, Hakozaki, Fukuoka, Japan

Shin-Ichiro Wada
Faculty of Agriculture, Kyushu University,
Hakozaki, Fukuoka, Japan

Imogolite is one of the aluminosilicates with a chemical formula of $Al_2O_3SiO_2$ $(H_2O)_n$, consisting of hollow nanotubes with an external diameter of about 2.5 nm and a length from several hundred nanometers to a micrometer. Atomic force microscopic (AFM) observation revealed that the imogolite molecules form a fibrous network at pH = 3.0. Since the outer surface of imogolite consists of the Al-OH group, a strong interaction can be expected between the Al-OH and the -$PO(OH)_2$ groups. Octadecylphosphonic acid (OPA) was chosen as a model amphiphilic molecule, and it chemisorbed onto the surface of imogolite. Surface coverage of imogolite with OPA was confirmed by infrared spectroscopy, thermogravimetric analysis, and adhesion force measurement by (AFM). The OPA-chemisorbed imogolite was dispersed in hexane whereas it forms precipitates in water. Since imogolite engages in a specific interaction with -$PO(OH)_2$ groups, it is expected that imogolite can be molecularly dispersed in -$PO(OH)_2$ group-modified poly(vinyl alcohol) (PVA). Temperature dependence of dynamic viscoelasticity exhibited a higher temperature shift of the

α_a-absorption of the matrix phosphorylated PVA for the (imogolite/phosphorylated PVA) hybrid compared with that for phosphorylated PVA.

INTRODUCTION

Imogolite, a hydrous aluminosilicate polymer, was discovered in the clay fraction of a glassy volcanic ash soil ("Imogolayer") of Kyushu, Japan in 1962 [1]. Figure 1 shows the schematic representation of the structure of imogolite. Imogolite forms hollow nanotubes with an external diameter of ca. 2.5 nm, an internal diameter of 1 nm [2, 3], and lengths from several hundred nanometers to a micrometer, and it has the general formula of $Al_2O_3SiO_2(H_2O)_n$. 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, isolated units can form nanofiber in acid dispersions (pH below 5). As can be expected from the large aspect ratio of imogolite rods, dispersions of imogolite rods can form space-filling gels with volume fractions as low as 0.2% [4].

Several studies have been reported on the preparation of an (imogolite/polymer) hybrid [5, 6]. However, effective reinforcement has not yet been achieved due to the lack of control of interfacial structure between imogolite and the matrix polymer. In order to achieve effective reinforcement, the interaction between organic polymer and imogolite must be enhanced. As imogolite is a natural clay that exists as a water swollen gel in the soil, it can be used as an environmentally benign reinforcing material for polymer composites. If one employs a biodegradable polymer as a matrix phase, an
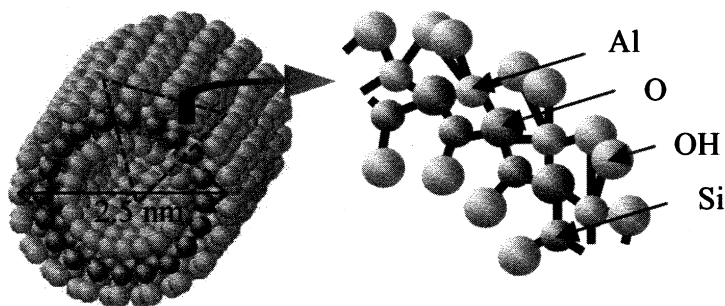

FIGURE 1 Schematic representation of the structure of imogolite.

environmentally friendly "green" nanohybrid can be prepared. The purpose of this study is to observe directly the imogolite nanofiber network formation and confirm the extent of interaction between the functional group on the organic amphiphile and the imogolite rod. Also, a novel green nanohybrid was prepared from phosphorylated poly (vinyl alcohol) and imogolite.

EXPERIMENTAL

Materials

Raw material of imogolite gel was collected from the pumice bed in the Kitakami area, Iwate, Japan. Figure 2 shows photographs of imogolite gel before and after purification. The raw material is a red-brown color due to contaminants such as metal oxides and metal hydroxides. Imogolite gel purified of contaminants was dispersed in a weak acidic solution (pH = 5.0−6.0) by applying a 42 kHz ultrasonic wave for a week. Freeze-drying this dispersion gives white fibrous imogolite. The details of the purification of imogolite can be found elsewhere [7]. Octadecylphosphonic acid (OPA, Johnson Matthey Co.) and stearic acid (SA, Nacalai Tasque, Inc., Japan) were used as amphiphilic molecules, the hydrophilic groups of which can be expected to interact

Purification

Raw imogolite   **Purified imogolite**

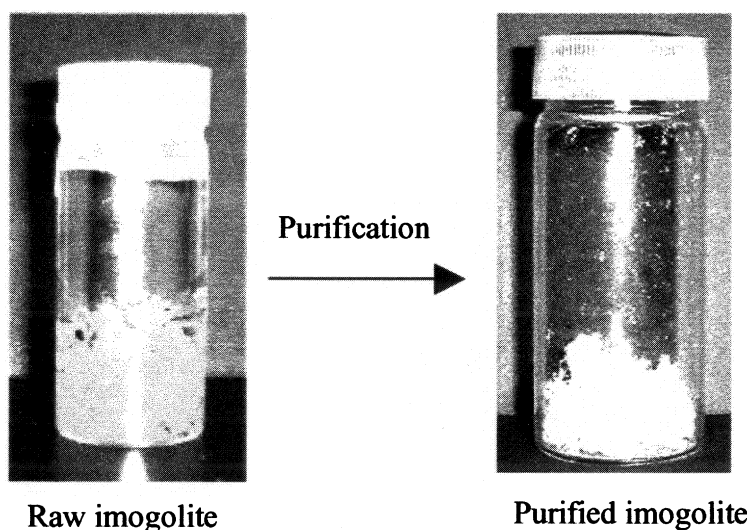FIGURE 2 Purification process of imogolite gel. Contaminants were removed from raw materials and dispersed in aqueous solution at pH = 3.0, then freeze-dried to give a purified imogolite.

with the Al-OH groups of imogolite. OPA and SA were used without further purification.

Poly (vinyl alcohol) (PVA) (Unitika Chemical Co., Ltd., Osaka, Japan) was chosen as a matrix polymer for the nanocomposite, since it shows biodegradation. PVA with degree of polymerization of 630 was used. Also, in order to improve the adhesion between imogolite and PVA, the phosphoric acid group was introduced into the side chains of PVA. The degree of phosphorylation of P-PVA was ca. 20%.

PVA/imogolite hybrid was prepared by mixing the solutions of imogolite and PVA. The weight fraction of imogolite was ca. 2.0 wt%. The mixed solution was placed on a flat petri dish and the water was evaporated at 353 K. The specimen was annealed at 353 K for 2 h in vacuo.

Atomic Force Microscopic (AFM) Observation

AFM study of imogolite was carried out by using the SPA300 AFM head with SPI3700 controller (Seiko Instruments Industries Co., Ltd., Chiba, Japan). The sample for AFM observation was prepared by spreading one drop of 0.05 wt% sonicated aqueous dispersion of imogolite at pH 3 on a polished silicon wafer. AFM observation was carried out at room temperature using constant force mode with a reference force of 0.1 nN. A Si_3N_4 triangular cantilever with a spring constant of $0.02 Nm^{-1}$ was used.

State of Interaction between Imogolite and Amphiphilic Molecules

Imogolite was immersed in an ethanol solution of OPA or SA $(1:3.5 = w/w)$ at 293 K for 5 days and the supernatant was removed. Imogolite chemisorbed with OPA or SA was recovered by centrifugation, repeated decantation, and rinsing with ethanol. Infrared spectroscopy was carried out with a Magna 860 (Nicolet, Co. Ltd., Madison, WI, USA) with a resolution of $1 cm^{-1}$ at room temperature. A sample of imogolite for IR measurement was prepared by forming a pellet under pressure with KBr powder.

Thermogravimetric analysis (TGA) was carried out in order to estimate the amount of adsorbed OPA on the surface of the imogolite. It was done with an SCC-5200 (Seiko Instrument Industries Co., Ltd., Chiba, Japan) in nitrogen atmosphere from 323 K to 1273 K at a heating rate of $10 K min^{-1}$.

Surface coverage of imogolite with alkyl groups was confirmed with an adhesion force measurement. A force-distance curve between the probe tip and modified or unmodified imogolite was measured in air using the Nanoscope IIIa (Digital Instruments Co., Ltd., Santa

Barbara, CA, USA). A rectangular Si_3N_4 cantilever with a spring constant of $0.09 \, N/m^{-1}$ was used for the force-curve measurements. The approaching and retraction speed of the cantilever was $2 \, nm/s^{-1}$. Force-distance curves were collected and the adhesion force was evaluated from the maximum attractive force.

Characterization of Nanohybrids

The temperature dependence of dynamic viscoelasticity of (imogolite/PVA) hybrid was measured with a Rheovibron DDV-IIFP (Orientec A&D Co., Ltd., Tokyo, Japan) from $123 \, K$ to $473 \, K$ at $11 \, Hz$ under nitrogen atmosphere.

RESULTS AND DISCUSSION

Characterization of Imogolite Nanofiber

Figure 3 shows the AFM images of imogolite, on a Si wafer, prepared from aqueous dispersions with a concentration of 0.05 wt% at pH = 3.0 and 7.0. At pH = 3.0, the nanofiber structure of imogolite was confirmed by AFM observation. However, the imogolite prepared from an aqueous dispersion at pH = 7.0 forms a solid aggregate. It can be inferred that the imogolite forms nanofiber under acidic conditions. Even though the concentration was below 0.2 wt%, a network structure was formed since the solution was evaporated onto a 2-dimensional plane. Line-profiling of AFM images of imogolite measured the rod height as ca. 2.6 nm and the width as 20−30 nm. However, the convolution effect of the AFM tip overestimates the molecular width. For a tip radius of 20 nm, the deconvolution of the observed diameter with the tip radius gives a molecular width of about 2−3 nm, which is in good agreement with electron diffraction [8] and computer simulation [3]. The dispersion of imogolite at low pH can be ascribed to the electrostatic repulsion among protonated outer surface Al-OH groups. Thus, the dispersion of imogolite in the polymer matrix at low pH can be expected to give nanofiber networks that are suitable for nanocomposite formation.

Modification of Imogolite Surface

In order to make imogolite soluble in an organic solvent and to achieve an effective reinforcement of the matrix polymer phase in a nanocomposite, it is necessary to modify the surface of imogolite or to introduce functional groups in polymers that have an attractive
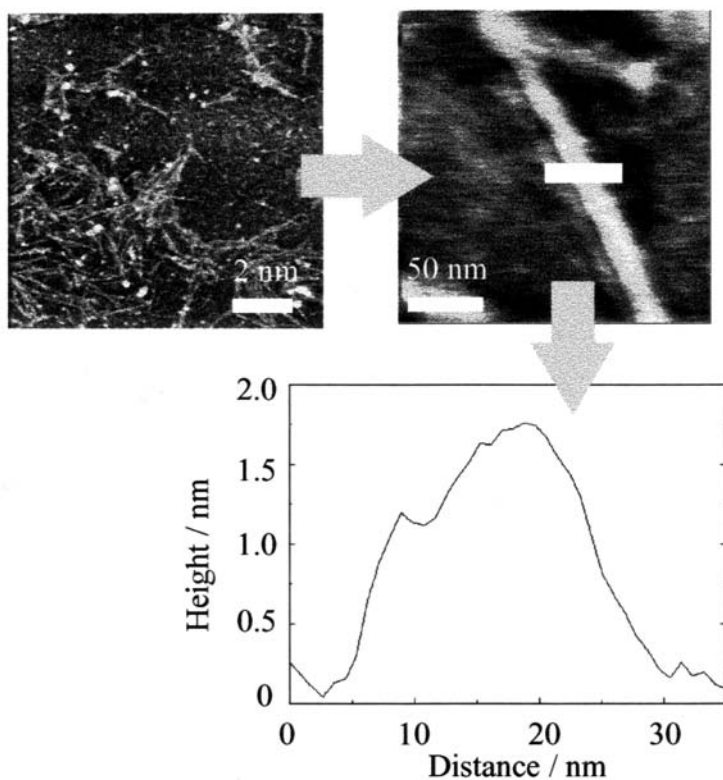
FIGURE 3 AFM images of the imogolite, on a Si wafer, prepared from an aqueous dispersion with concentration of 0.05 wt% at pH = 3.0.

interaction with imogolite. Since the surface of imogolite has Al-OH groups, amphiphilic molecules, R-X, with different hydrophilic functional groups, X, were employed in order to study the interaction between Al-OH and R-X. The interaction between imogolite and OPA or SA molecules was studied with transmission infrared (IR). Figure 4 shows the transmission IR spectra of imogolite chemisorbed with OPA (Figure 4a), SA (Figure 4b), and unmodified imogolite (Figure 4c) with the CH_2 stretching region enlarged. The absorptions at 995 and $935 \, cm^{-1}$ were attributed to the stretching vibration of Al-O and Si-O of imogolite. The absorption peaks at $2850-2853$, $2921-2925$, and $2956 \, cm^{-1}$ can be attributed to the symmetric stretching vibrations of CH_2, antisymmetric stretching of CH_2, and antisymmetric stretching of CH_3 of the alkyl chains of OPA and SA, respectively. The absorption peaks of the alkyl chains for OPA chemisorbed imogolite were stronger
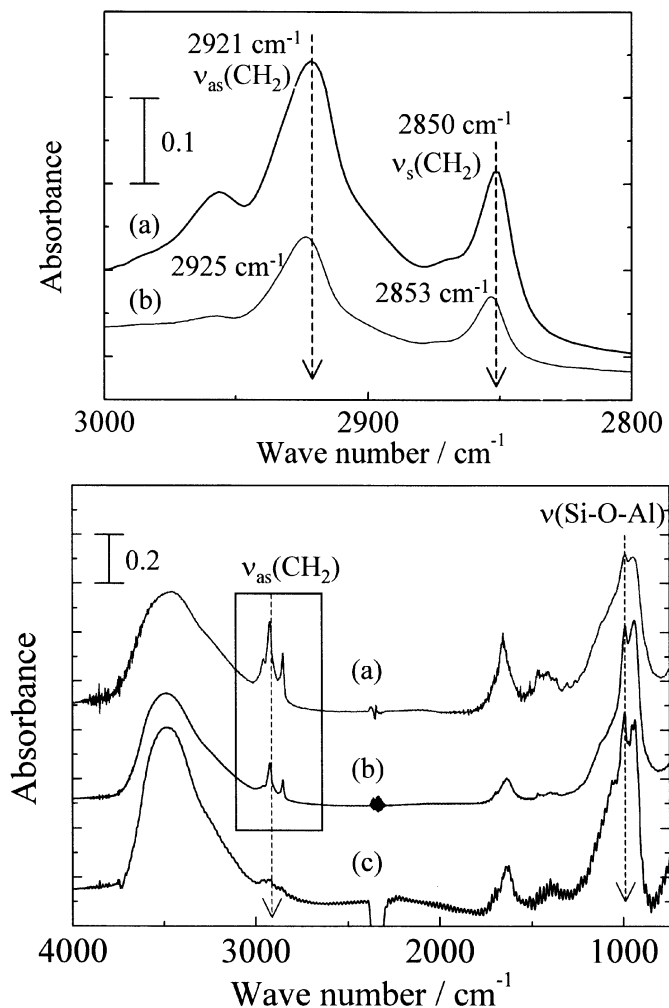
FIGURE 4 Transmission IR spectra of imogolite chemisorbed with OPA(a), SA(b), and unmodified imogolite(c).

and 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. The ν_{as} (CH$_2$) for OPA on imogolite was located at 2921 cm^{-1}, whereas that for SA was 2925 cm^{-1}. The lower wave-number of the alkyl stretching bands of OPA on the imogolite surface compared with that of SA suggest that the alkyl chains of OPA on

imogolite were more ordered than those of SA on imogolite. Thus, it can be concluded that the alkyl chains of OPA on imogolite is more densely packed than SA on imogolite and that the phosphonic acid group has a stronger interaction with Al-OH groups than do the carboxylate groups [9].

It is necessary to estimate the amount of adsorbed OPA on the imogolite surface. Figure 5 shows TGA curves of imogolite chemisorbed with OPA from a water-ethanol mixture (water:ethanol = 2:3). The ethanol was used to increase the solubility of OPA in the solvent mixture. There is a weight loss of $5-10\%$ up to 523 K and $40-65\%$ up to 832 K. The weight loss in the low temperature region is attributed to the desorption of weakly adsorbed water and the later weight loss to the bound water and the desorption/decomposition of OPA. In order to confirm the desorption and decomposition of adsorbed OPA, an IR measurement was carried out for the imogolite chemisorbed OPA after heating at 1273 K. Absorption peaks attributed to the stretching vibration of the alkyl chains of OPA disappeared after heating above 1273 K. Also, the absorption peaks at 995 and 935 cm^{-1} assigned to the stretching vibration of Al-O and Si-O of imogolite $(Al_2O_3SiO_2(H_2O)_n)$ shifted to a higher wavenumber due to the formation of mullite $(3Al_2O_3,2SiO_2)$ [10]. Therefore, from the weight loss at ca. 732 K, it is inferred that the amount of adsorbed OPA increased with an increase in the (OPA/imogolite) ratio. Also, the desorption of adsorbed OPA at a higher temperature than either vaporization or decomposition of solid OPA suggests a strong interaction between the imogolite surface and phosphonic acid groups of OPA. An equilibrium was attained at the composition imogolite:OPA = 1:5 (weight/weight). The amount of
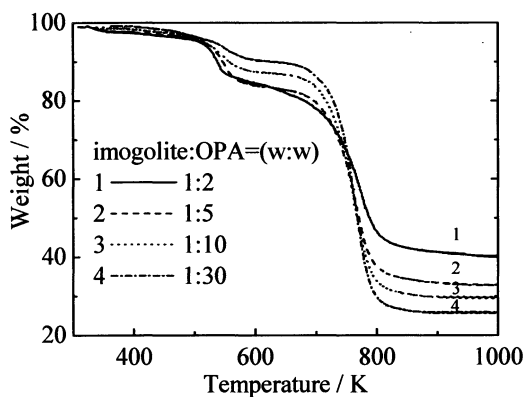
FIGURE 5 TGA curves of imogolite chemisorbed with OPA from a water-ethanol mixture (water:ethanol = 2:3).

adsorbed OPA estimated at equilibrium corresponded to complete surface coverage of imogolite with an OPA monolayer. This result was confirmed by the elemental analysis.

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 relationship between the cantilever tip and the imogolite surface was measured before and after adsorption of OPA. Figure 6a shows the force-distance curve between the cantilever tip and the imogolite surface before and after adsorption of OPA. The adhesion force was estimated from the maximum attractive force observed as a minimum in the force-distance curve. Figure 6b shows histograms of adhesion force observed between the cantilever tip and the surface of imogolite before and after OPA adsorption. The measurement was carried out in air at 293 K. The adhesion force between imogolite and the cantilever tip is larger than that between the OPA-chemisorbed imogolite and the tip. Since the surface of the Si_3N_4 cantilever tip is covered with SiO_2, a strong adhesion force is present between Al-OH and the SiO_2 of the cantilever tip. On the other hand, in the case of OPA-chemisorbed imogolite, the adhesion force is weak because of the presence of a hydrophobic alkyl group on the surface of OPA-chemisorbed imogolite. The hydrophobized imogolite thus prepared was dispersed in hexane and chloroform; however, in water the modified imogolite precipitated or floated. On the other hand, the unmodified imogolite was observed as a macroscopic aggregation in hexane.

Characterization of (Imogolite/PVA) Nanohybrid

A novel nanohybrid was prepared from environmentally-benign PVA and imogolite. PVA was chosen as a matrix polymer since relatively strong interaction has been reported between aluminum oxide and PVA [11]. The state of interaction between imogolite and the matrix PVA was confirmed based on the temperature dependence of the dynamic viscoelasticity of the nanohybrid. Figure 7 shows the temperature dependences of tan δ for PVA and (imogolite/PVA) nanohybrid with 2.0 wt% imogolite. Temperature dependence of tan δ shows a large absorption peak at ca. 352 K that can be ascribed to the micro-Brownian motion of the amorphous phase of PVA [12]. The peak temperature of α_a-absorption for the hybrids was ca. 11 K higher than that for the matrix PVA phase. This suggests a strong interaction between amorphous PVA chains and Al-OH groups on the surface of imogolite. Thus, effective reinforcement by imogolite nanofiber can be
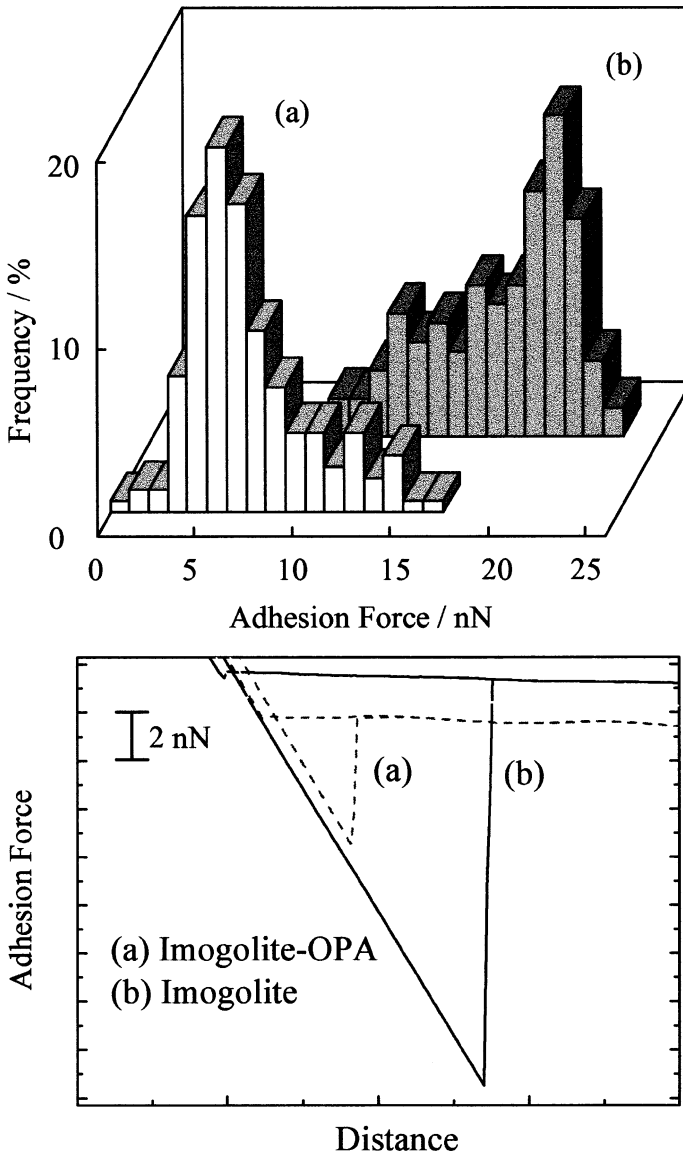
FIGURE 6 Typical force-distance curves and histograms of adhesion force observed on the surface of imogolite chemisorbed with OPA(a) and imogolite(b).
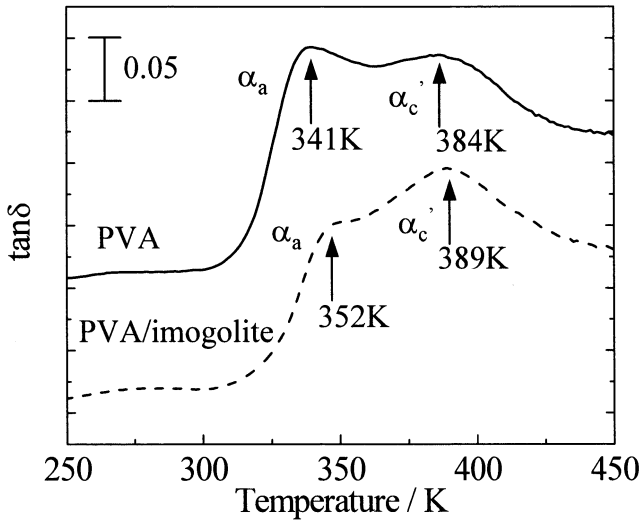
FIGURE 7 Temperature dependences of tan δ for PVA and (imogolite/PVA) nanohybrid with 2.0 wt% imogolite at 11 Hz.
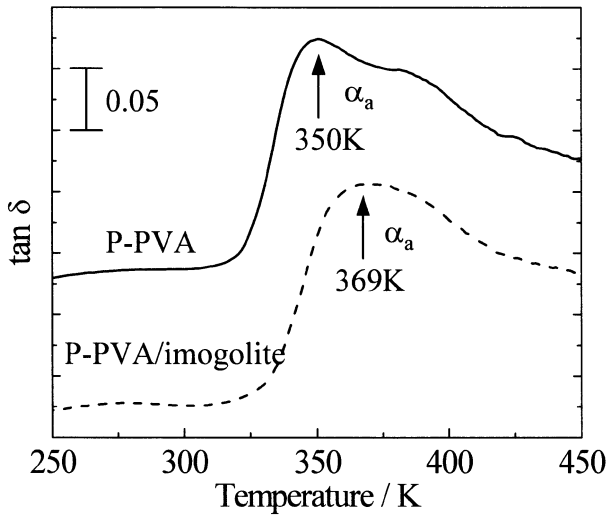

FIGURE 8 Temperature dependences of tan δ for P-PVA and (imogolite/ P-PVA) nanohybrid with 2.0 wt% imogolite at 11 Hz.

expected for this novel nanohybrid system by uniform dispersion of imogolite in the matrix polymer.

In order to increase the interaction between the matrix polymer and the surface of imogolite, the phosphoric acid groups were introduced into the side chains of the PVA. The reaction seems to be accompanied by the scission of the PVA main chain. Figure 8 shows the temperature dependences of tan δ for phosphorylated PVA (P-PVA) and (imogolite/P-PVA) composites. The α_a-absorption peak for P-PVA appeared at higher temperature than for unmodified PVA because of restricted thermal molecular motion due to the inter- and intramolecular interactions of the phosphoric acid groups. The α_a-absorption temperature of P-PVA in the hybrid was observed to be ca. 19 K higher than for P-PVA. This also suggests a strong interaction between P-PVA and the surface of imogolite. Thus, a strong interface between imogolite and matrix polymer can be realized by the introduction of phosphoric acid groups into the matrix polymer.

CONCLUSION

A method to modify the surface of the natural aluminosilicate nanofiber imogolite was proposed. It was revealed that phosphonic acid groups have strong interactions with the Al-OH groups on the surface of imogolite. A strong interaction between imogolite and modified PVA was confirmed by the higher temperature of the α_a-absorption of the (imogolite/modified PVA) hybrid as compared to the modified PVA.

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