

Preparation and properties of [poly(methyl methacrylate)/imogolite] hybrid via surface modification using phosphoric acid ester

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Abstract

Novel polymer nanohybrid was prepared by free radical polymerization of methyl methacrylate in the presence of inorganic nanofiber ‘imogolite’ as reinforcing nanofiller. Imogolite is a hydrous aluminosilicate with a unique nanofiber structure. The surface of imogolite was modified with 2-acidphosphoxyethyl methacrylate, which has a polymerizable methacrylate group and a phosphoric acid moiety, before preparation of polymer hybrid. The polymer nanohybrid was prepared by free radical polymerization in the presence of surface modified imogolite. The mechanical properties of (PMMA/modified imogolite) hybrid with the modified imogolite were improved in comparison with those of PMMA and (PMMA/unmodified imogolite) blend. Furthermore, the hybrid film prepared from the surface modified imogolite kept the transparency similar to PMMA film. These results indicate the usefulness of the surface modification method with phosphoric acid groups and imogolite nanofibers as a reinforcing material.

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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 below 1 nm, and lengths ranging from several hundred nanometers to a micrometer, and has the general formula of $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ [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 the unique nanostructure of imogolite, its various

potential applications as membranes, catalysts, and adsorbents have been discussed in the field of materials science [3–5]. Furthermore, our group has suggested that a polymer nanocomposite with imogolite could be expected to have improved mechanical properties and thermal stability due to its extremely high aspect ratio and large specific surface area [6]. In the case of a nanofiber such as carbon nanotube (CNT), which is used for reinforcement of polymer nanocomposites, the improvement of mechanical properties of the nanocomposites including CNT have been reported [7,8]. However, CNT cannot be used for the transparent polymer materials because CNT is colored due to its conjugated π -system. In contrast, because imogolite is transparent and has a refractive index similar to those of common polymers [9], it can be used in applications involving transparent polymer additives.

As described above, imogolite has the outer surface of hydrophilic Al–OH groups and can be dispersed in water at low acidic condition, therefore, it is very difficult to disperse imogolite in hydrophobic polymer matrix. Previous papers have described that the hydroxylated surface of imogolite was tried to be converted to the hydrophobic surface by the surface

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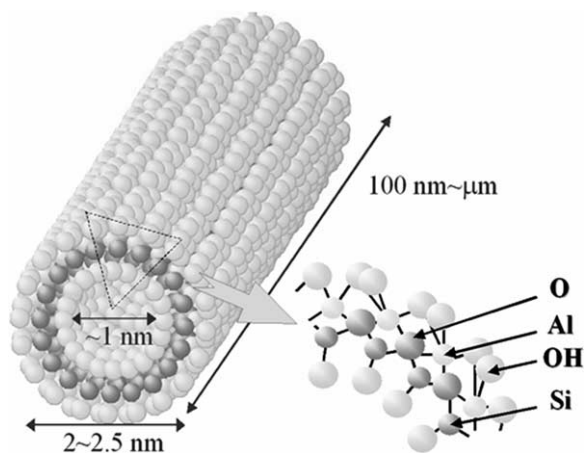


Fig. 1. Schematic representation of the structure of imogolite.

modification method using organosilane compounds [10]. Nevertheless, it has not been successful to change the surface properties of imogolite by surface treatment with organosilane due to the weak interaction of the outer Al–OH groups of imogolite and the silanol groups of organosilane [11]. Since, the phosphoric acid groups show strong interaction with Al–OH groups, the attempts have been made to modify the surface with alkyl phosphonic acid [12]. We have reported the modified imogolite nanofiber using alkylphosphonic acid could be dispersed into the hydrophobic solvents such as hexane and chloroform, in contrast, aggregated in water and ethanol. When we focus on the application of imogolite for the polymer composite, the surface modification of imogolite can be expected to improve its dispersibility into the hydrophobic polymer matrix. However, there is no report for preparation of hydrophobic polymer/imogolite composite through surface modification of imogolite. We and other researcher described polymer/imogolite composites without modifier [6,13]. Unfortunately, these approaches were limited to the hydrophilic polymer. Development of the preparation of polymer composite with surface modification of imogolite is important and is useful for application to hydrophobic commercial polymer, especially transparent polymers.

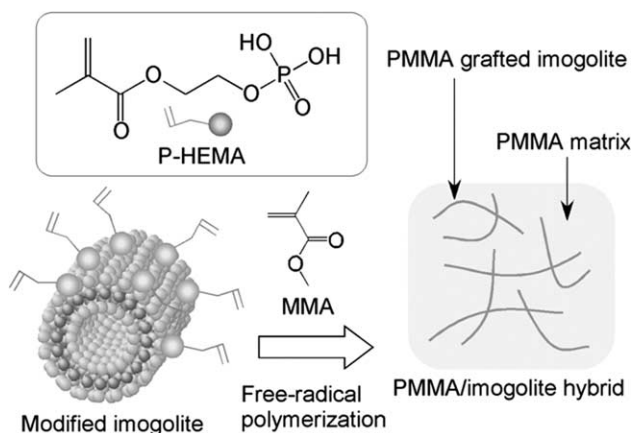


Fig. 2. Chemical structure of 2-acidphosphoxyethyl methacrylate (P-HEMA) and illustration of the preparation of polymer hybrid using imogolite modified with P-HEMA.

In this study, novel (polymer/imogolite) nanohybrid was prepared by free radical polymerization of methyl methacrylate in the presence of imogolite modified by phosphoric acid ester with a polymerizable methacrylate group which has a role of grafting PMMA chain from imogolite surface. To improve the dispersibility of imogolite in the polymer matrix is anticipated via the surface PMMA-grafting of imogolite. Fig. 2 shows the schematic illustration of preparation of (PMMA/imogolite) nanohybrid in this study.

2. Experimental

2.1. Materials

Raw material of imogolite gel was collected from the pumice bed in Kitakami area, Iwate, Japan. The raw material shows a red–brown color due to the contaminants such as metal oxides and metal hydroxides. The details of the purification method of imogolite can be found in elsewhere [14]. Purified imogolite gel was dispersed in a weak acidic solution (pH = 5.0) by applying a 42 kHz ultrasonic wave. Freeze-drying the suspension of imogolite gave white powder like cotton. 2-Acidphosphoxyethyl methacrylate (P-HEMA; Fig. 2) was used for the surface modifier of imogolite nanofiber. P-HEMA was provided by Unichemical Co., Ltd. Methyl methacrylate (MMA) was purchased from Wako Pure Chemical Industries, Ltd and purified by distillation under reduced pressure over calcium hydride. 2, 2'-Azo-bis-isobutyronitrile (AIBN) purchased from Tokyo Kasei Industry Co., Ltd was used as an initiator for free radical polymerization.

2.2. Surface modification of imogolite with P-HEMA

Imogolite nanofiber (freeze-dried powder: 46.6 mg) was dispersed into weak acidic water (10 mL, pH = 5.0) using sonication. P-HEMA (9.32, 27.96, or 46.6 mg) was dissolved into water (20 mL) and the solution was added into the imogolite aqueous suspension under stirring to yield cloudy solution. The weight ratio of imogolite/P-HEMA was 1:0.2, 1:0.6, and 1:1 in the mixed solution. After stirring for 24 h, the solution was centrifuged to collect the white precipitate of imogolite modified with P-HEMA. The precipitate was washed with water three times in centrifugation and decantation to remove the unreacted P-HEMA, and freeze-dried to give a white powder of imogolite/P-HEMA.

2.3. Preparation of PMMA/imogolite hybrid

The white powder of imogolite modified with P-HEMA (10 mg: the imogolite content was 1 wt) and AIBN (33 mg) as an initiator were mixed with MMA (1.0 g) as a monomer in a glass reactor. The molar ratio of the added monomer and initiator was 50:1. The mixture became cloudy due to the suspended imogolite nanofibers. The preparation of PMMA/imogolite hybrid was carried out by heating of the mixture at 343 K after degassing by freeze-pump-thaw cycle. After heating for 3 h, the obtained solid polymer was dissolved

in chloroform and reprecipitated by the large amount of methanol to afford white powder of PMMA/imogolite hybrid. The yield of PMMA/imogolite hybrid was 89.6%. Furthermore, the hybrid films were prepared by the solvent cast method from PMMA/imogolite solution in order to measure its optical and mechanical properties. The 5 wt% concentration of PMMA/imogolite chloroform solution was kept in a glass petri dish at room temperature for 12 h. After evaporating the solvent, the film was peeled off from the glass petri dish, and dried in vacuum for 12 h.

2.4. Measurement

Infrared (IR) spectroscopic 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 were collected by averaging 64 scans between 4000 and 500 cm^{-1} . A specimen of the products for IR measurement was prepared by forming under pressure with KBr powder. Thermal gravimetric analysis (TGA) using TG8120 (Rigaku Co., Ltd) was conducted from 323 to 1273 K at heating rate of 10 K/min . Each sample was put on the platinum pan with ca. 1 mg . Transmission electron microscopic (TEM) observations were performed by HITACHI H-7500 TEM using an acceleration voltage of 100 kV . Gel permeation chromatographic (GPC) analysis was carried out at 313 K on a Tosoh HLC-8120GPC with a differential refractometer RI-8020. Tetrahydrofuran (THF) was used as an eluent. GPC analysis was measured using only the soluble part of the polymer hybrid through $0.5\text{ }\mu\text{m}$ size filter before analysis.

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 from 350 to 700 nm . Furthermore, haze measurement was carried out with Haze Turbidimeter NDH 2000 (Nippon Denshoku Industries Co., Ltd) using D_{65} light source. The temperature dependence of dynamic viscoelasticity of each film was collected on Rheovibron DDV-IIIFP (Orientec A&D Co., Ltd). The storage modulus and loss tangent were obtained by sinusoidal vibration the samples in the tensile mode at 11 Hz under nitrogen atmosphere. The temperature range was between 123 and 473 K . The heating rate was 1 K/min . The tensile test was carried out with Ez-Graph (Shimazu Shikenki Engineering Co., Ltd). The head speed was 1 mm/min . The tensile test was done in five and more replicates and the values averaged.

3. Results and discussion

3.1. Preparation and characterization of surface modified imogolite with P-HEMA

P-HEMA can be expected to be adsorbed onto the surface of imogolite due to its phosphoric acid moiety, which can interact with Al–OH groups of imogolite surface. The chemisorption of P-HEMA onto the surface of imogolite was confirmed by IR measurement. Fig. 3 shows IR spectra of purified imogolite, P-HEMA, and imogolite adsorbed with P-HEMA.

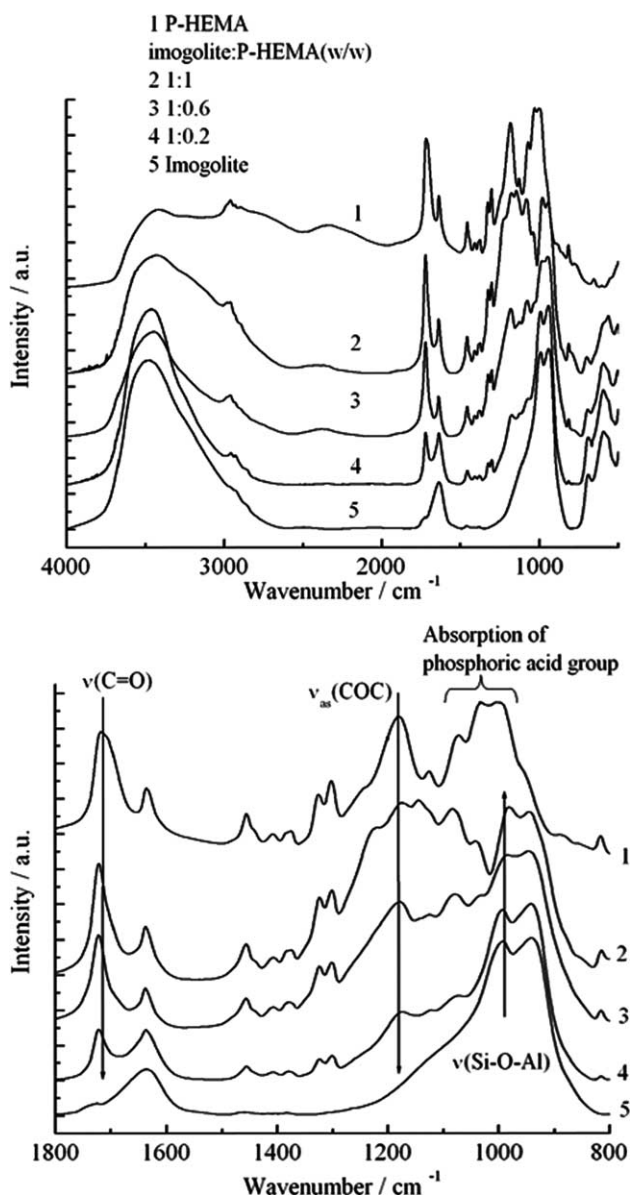


Fig. 3. IR spectra of imogolite, P-HEMA, and imogolite adsorbed with P-HEMA at various P-HEMA contents in the full scale (upper) and the region from 1800 to 800 cm^{-1} (lower).

The spectrum (Fig. 3, No. 5) of imogolite indicated the characteristic absorption of stretching vibration band ($\nu(\text{Si-O-Al})$) at 995 and 935 cm^{-1} , and large broad peak of $\nu(\text{OH})$ around 3450 cm^{-1} [15]. The spectrum of P-HEMA (Fig. 3, No. 1) showed also a few characteristics absorption peaks, which are ascribed to the stretching vibration of carbonyl groups ($\nu(\text{C=O})$) at 1714 cm^{-1} , the asymmetric stretching vibration ($\nu_{\text{as}}(\text{COC})$) of the methacryloyloxy group at 1179 cm^{-1} , and several peaks for coupled vibration of P–O stretching vibration at 1070 , 1030 , and 1000 cm^{-1} [16,17]. In contrast, P-HEMA chemisorbed imogolite with weight ratio of $1:0.2$ (Fig. 3, No. 4), showed the adsorption peak at 992 and 935 cm^{-1} , corresponding to the absorption imogolite and 1722 and 1180 cm^{-1} corresponding to ($\nu(\text{C=O})$, $\nu_{\text{as}}(\text{COC})$) of P-HEMA. These results indicated the evidence of P-HEMA

adsorption onto imogolite. Furthermore, the content of P-HEMA in imogolite/P-HEMA system (Fig. 3, No. 2 and No. 3) increased with the intensity of absorption peaks at 1080 cm^{-1} corresponding to the $\nu_{\text{as}}(\text{PO}_3^{2-})$ band. Also, the $\nu_{\text{s}}(\text{PO}_3^{2-})$ absorption peak will appear around 980 cm^{-1} , when a phosphoric acid group interacts with the substrate surface [16]. In consequence, the absorption around 995 cm^{-1} concerned the modified imogolite with P-HEMA broadened and the peak shifted to 987 cm^{-1} for 1:0.6 and 982 cm^{-1} for 1:1, because of the extent of interaction between the phosphoric acid groups of P-HEMA and Al–OH groups of imogolite.

The fraction of imogolite and P-HEMA was estimated by TGA and elemental analysis. Fig. 4 shows the TGA curves of imogolite and surface modified imogolite by P-HEMA with various weight contents. Two steps of weight loss were observed in TGA curve of imogolite, which is similar to the results reported by other investigators [1,18]. These weight losses indicated the release of adsorbed water and structural water. On the other hand, the TGA curves of the modified imogolite showed the rapid weight loss from 430 K in the modified imogolite including the high P-HEMA contents. This weight loss from 430 K means desorption and degradation of P-HEMA. The amounts of adsorbed P-HEMA on the surface of imogolite estimated from elemental analysis was 0.15 mg per 1 mg of imogolite (imogolite:P-HEMA = 1:0.2), 0.36 mg (1:0.6), and 0.51 mg (1:1), respectively. Furthermore, the coverage of the surface of imogolite with P-HEMA was estimated to be 13.8, 33.5, and 47.5%. The coverage value of surface imogolite was evaluated by the assumption of the complete monolayer coverage of imogolite nanofiber with P-HEMA.

Fig. 5 shows the TEM image of imogolite nanofiber adsorbed with P-HEMA. TEM image defines imogolite modified with P-HEMA can form the nanofiber structure with the diameter of nanometer order. The dispersibility of these nanofibers were similar to the morphology of unmodified imogolite nanofibers dispersed into low acidic water, because the diameter of nanofibers is around several nanometers or over

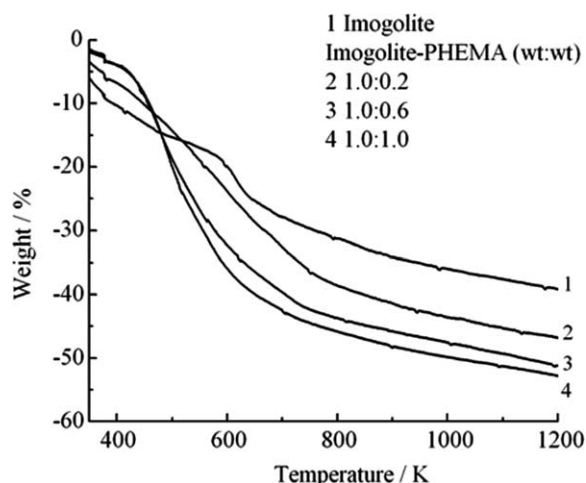


Fig. 4. TGA curves of imogolite and imogolite adsorbed with P-HEMA at various P-HEMA contents.

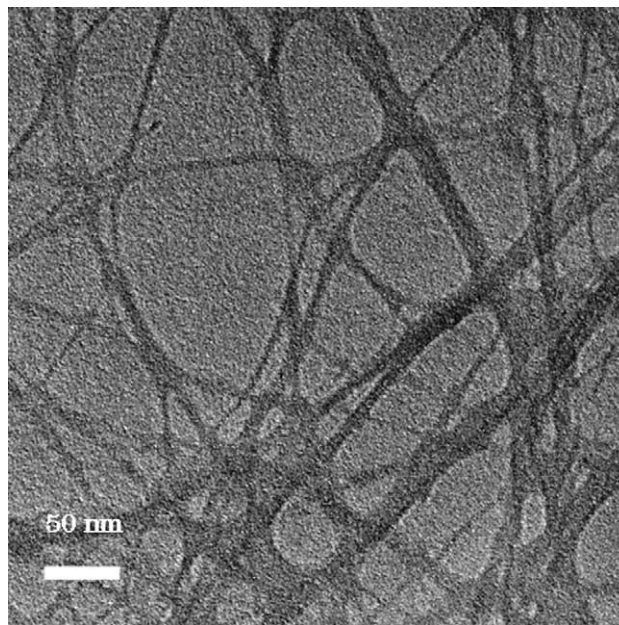


Fig. 5. TEM image of surface modified imogolite nanofibers adsorbed with P-HEMA. The sample was prepared from dispersed chloroform solution.

ten nanometers in both cases. The dispersibility of nanofibers also supported the successful surface modification of imogolite with P-HEMA.

3.2. Preparation of polymer hybrid including imogolite nanofiber

The modified imogolite with high amount of P-HEMA adsorption (imogolite:P-HEMA = 1:1) was employed for in situ MMA polymerization to prepare the PMMA/imogolite nanohybrid. The polymerization of MMA was confirmed by IR and NMR measurements (spectra not shown). The conversion of MMA in this condition was 95–98% estimated by NMR measurement. The number average molecular weight (M_n) and polydispersity index (M_w/M_n) of soluble polymer contents were estimated by GPC and summarized in Table 1. In order to confirm the formation of PMMA in the presence of imogolite nanofiber, both modified and unmodified imogolite were used. GPC results indicated the less influences for MMA polymerization in the presence of 1.0 wt% imogolite. In this study, we used mainly PMMA and PMMA/modified imogolite hybrid prepared through in situ polymerization with the aim to characterize mechanical and optical properties of hybrid

Table 1
Molecular weight and polydispersity index of soluble polymer contents in PMMA/imogolite hybrid

Run no.	Content of imogolite (wt%)	M_n	M_w/M_n	State of imogolite
1	0	58,800	2.50	–
2	1.0	65,100	2.55	Modified
3	1.0	65,600	2.54	Unmodified

Only soluble part through 0.5 μm size filter was measured.

materials. PMMA polymerized without imogolite was utilized for PMMA/imogolite blend film by simple solution blending.

After polymerization of MMA in the presence of the modified imogolite nanofibers, the surface grafting of imogolite nanofibers by PMMA chains was confirmed by IR measurement and the state of dispersion in contrastive solvent. To recover the PMMA-grafted imogolite, the chloroform suspension of polymerized PMMA/imogolite hybrid was centrifuged. Precipitated powder was rinsed with chloroform a few times to remove free PMMA homopolymers.

Fig. 6 shows the IR spectra of PMMA, modified imogolite, and unmodified imogolite powder recovered from PMMA/imogolite hybrid chloroform solution. In the spectrum of PMMA, the stretching vibration bands of CH_2 and $\text{C}=\text{O}$ at 2996 , 2952 , and 1733 cm^{-1} were observed clearly. The spectrum of the modified imogolite after polymerization showed the evidence of PMMA chain attributed to the CH_2 and $\text{C}=\text{O}$ absorption peaks at 2996 , 2953 , and 1727 cm^{-1} and retained the coupled vibration of $\text{P}-\text{O}$ stretching vibration at 1080 cm^{-1} . The $\text{C}=\text{O}$ band peak at 1727 cm^{-1} from the modified imogolite slightly shifted to lower wavenumber side as against the spectrum of PMMA, due to the difference of the environment between the grafted PMMA chain and the bulk PMMA. These results revealed that MMA could be polymerized and grafted via methacryloyl group of adsorbed P-HEMA on the surface of imogolite. Also, the presence of the absorption peak at 3450 cm^{-1} and the two peaks around 995 – 935 cm^{-1} shows the retention of imogolite structure after free radical polymerization process. On the other hand, the unmodified imogolite indicated very weak absorption peaks corresponding to the polymer chain. Since, the unmodified imogolite without reactive methacrylate group cannot be grafted by PMMA, these weak peaks indicated the small amount of physical adsorption of PMMA chain onto the surface of unmodified imogolite.

Fig. 7 shows the dispersion states of PMMA grafted imogolite and unmodified imogolite powders in water and

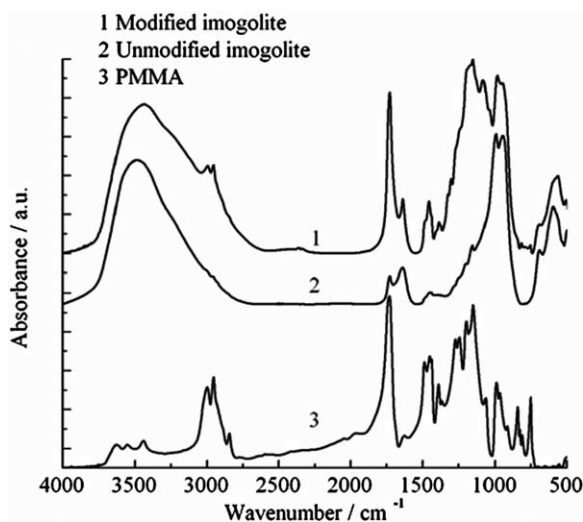


Fig. 6. IR spectra of PMMA, modified imogolite, and unmodified imogolite recovered from PMMA/imogolite hybrid chloroform solution.

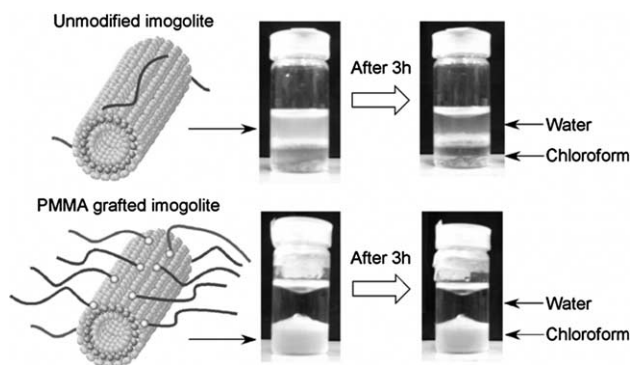


Fig. 7. Dispersion state of PMMA grafted imogolite and unmodified one in water/chloroform phase.

chloroform. These powders were added into the incompatible liquids such as water and chloroform mixed solution and dispersed by ultrasonic treatment for 10 min. After sonication, the unmodified imogolite did not disperse in the chloroform phase, but did in the aqueous phase. IR measurement revealed the physical adsorption of PMMA chains onto the surface of unmodified imogolite, however, unmodified imogolite could not disperse in chloroform, because the PMMA chain desorbed from imogolite surface and dissolved into chloroform phase. Furthermore, unmodified imogolite was precipitated onto the interface between water and chloroform after 3 h. On the other hand, PMMA grafted imogolite powder dispersed in the chloroform phase, and did not precipitate in the solution even after several days. The stable dispersion of PMMA grafted imogolite was due to the high affinity of graft PMMA for chloroform, which is good solvent of PMMA. IR measurement and the observation of dispersibility in solvent confirmed that the PMMA was successfully grafted from surface modified imogolite with P-HEMA.

3.3. Mechanical and optical properties of PMMA/imogolite hybrid film

PMMA is usually used as transparent materials, and it is important to retain the optical properties of PMMA, even after dispersion of reinforcing filler into polymer matrix. The grafted PMMA chains on the imogolite surface can be expected to give high affinity between imogolite nanofibers and PMMA matrix. To evaluate the optical properties of PMMA/imogolite hybrid film, the hybrid film including 1 wt% surface modified imogolite with P-HEMA was prepared. As a reference, the blend film with same imogolite content was prepared from PMMA and unmodified imogolite mixed solution. Fig. 8 shows the transparency of PMMA, PMMA/imogolite hybrid, and PMMA/imogolite blend films by light transmission measurement, and Table 2 indicates the haze value of each film estimated by haze meter. These results show the PMMA/imogolite hybrid film retained up the transparency of matrix film, being compared to PMMA/imogolite blend film. This difference in transparency can be attributed to the dispersibility of imogolite nanofibers in the polymer matrix. One of the factors to control the dispersibility is the affinity of interface

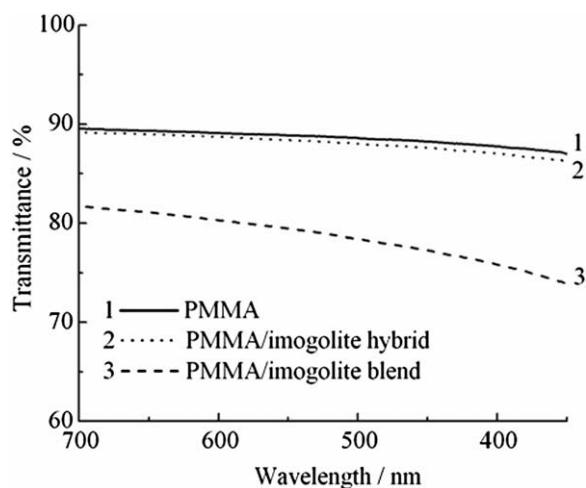


Fig. 8. Light transmittance of PMMA, PMMA/imogolite hybrid, and PMMA/imogolite blend films in the visible light region. Imogolite content was 1.0 wt%.

between PMMA matrix and the surface of PMMA grafted imogolite.

Finally, the mechanical properties of PMMA/imogolite hybrid film were investigated. Fig. 9 shows the temperature dependence of dynamic storage modulus (E') and loss tangent ($\tan \delta$) for PMMA, PMMA/imogolite hybrid, and PMMA/imogolite blend films. The PMMA/imogolite hybrid or blend film contained 1 wt% of modified or unmodified imogolite, respectively. The dynamic storage modulus of PMMA/imogolite hybrid film was approximately 1.5 times as high as that of PMMA film at all temperature range. Also, α_a -absorption temperature of the hybrid film was higher than that of PMMA film. Table 3 summarizes the tensile modulus, tensile strength, and elongation of PMMA, PMMA/imogolite hybrid, and PMMA/imogolite blend films evaluated by tensile test. Tensile modulus and ultimate strength of PMMA/imogolite hybrid were approximately 1.4 times as high as those of PMMA film. On the other hand, the tensile modulus and strength of PMMA/imogolite blend film were similar value with those of PMMA film. As the dispersibility of imogolite in the PMMA matrix was improved, the reinforcement effect of imogolite became remarkable in the case of PMMA/imogolite hybrid film. The elongation at break of PMMA/imogolite hybrid and blend film was smaller than that of the matrix polymer film, however, the hybrid film clearly showed larger elongation at break than the blend film. The reason of

Table 2

Haze value and transmittance of PMMA, PMMA/imogolite hybrid, and PMMA/imogolite blend films

Sample	Haze value	Transmittance (%) ^a
PMMA	0.59 ± 0.11	88.6
PMMA/imogolite (hybrid)	1.18 ± 0.07	88.0
PMMA/imogolite (blend)	3.37 ± 0.56	78.4

The content of imogolite in polymer matrix was 1.0 wt%.

^a Determined by light transmission measurement at $\lambda = 500$ nm.

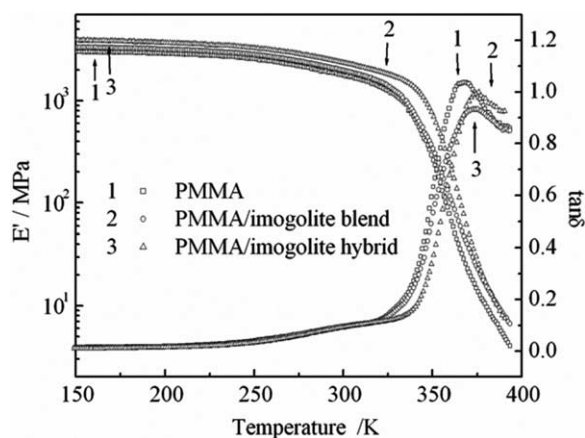


Fig. 9. Temperature dependence of dynamic storage modulus and loss tangent at 11 Hz for PMMA, PMMA/imogolite hybrid, and PMMA/imogolite blend films with 1.0 wt% imogolite contents.

Table 3

Tensile modulus, strength, and elongation of PMMA, PMMA/imogolite hybrid, and PMMA/imogolite blend films evaluated by tensile test

Sample	Modulus (GPa)	Strength (MPa)	Elongation (%)
PMMA	1.13 ± 0.05	27.6 ± 0.6	38.0 ± 13.7
PMMA/imogolite (hybrid)	1.55 ± 0.05	38.5 ± 0.8	21.0 ± 8.9
PMMA/imogolite (blend)	1.20 ± 0.08	27.7 ± 1.2	5.0 ± 1.2

The content of imogolite in polymer matrix was 1.0 wt%.

the difference in the elongation between these films seems due to the lack in interfacial defect between PMMA-grafted imogolite and matrix PMMA.

4. Conclusions

The authors have demonstrated the preparation of PMMA/imogolite hybrid by free radical polymerization in the presence of imogolite nanofibers, which were modified by methacrylate monomer with a phosphoric acid moiety. PMMA chains were successfully grafted from imogolite surface by polymerization of MMA monomer in the presence of the P-HEMA modified imogolite. Actually, the storage modulus at room temperature of PMMA imogolite hybrid film was 1.5 times as high as that of PMMA and PMMA/imogolite blend films, without loss of the transparency of hybrid film. The reinforcement effect can be attributed to the fine dispersion of imogolite nanofibers in polymer matrix and the good affinity between PMMA and PMMA grafted imogolite.

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