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Synthesis of a poly(methyl methacrylate)/silica nano-composite by soaking of a microphase separated polymer film into a perhydropolysilazane solution

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Abstract

A novel synthetic method of poly(methyl methacrylate) (PMMA)/silica nano-composite with well-segregated PMMA and silica domains was proposed. To obtain the nano-composite, a poly(methyl methacrylate)-*block*-poly(2-hydroxyethyl methacrylate) (PMMA-*block*-PHEMA) film with PMMA and PHEMA domains was soaked into a pyridine/*m*-xylene/perhydropolysilazane (PHPS) mixture and calcinated at 90 °C under steam. PHPS was homogeneously introduced into the film and selectively converted to silica in PHEMA microdomains of the PMMA-*block*-PHEMA film. The morphology of the nano-composite was investigated by transmission election microscopy (TEM).
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1. Introduction

Polymer/silica nano-composites have been synthesized to provide new functionalities such as high transparency, high thermal stability, gas-barrier, shock resistance, etc. [1–6]. To synthesize highly-functionalised polymer/silica nano-composites, the control morphology of microphase separation of the composite is required. For example, highly ordered lamellae with polymer and silica is required for the gas-barrier film [7]. However, when organic materials were hybridised with silica, functionality of organic materials would be disturbed by silica that existed in organic domains although the thermal stability of the organic materials was increased [8]. To synthesize the material that required both functionality of organic materials and silica, it is necessary to segregate silica from organic domains.

In previous works, PMMA/silica nano-composites were obtained by casting a mixture of perhydropolysilazane (PHPS) and poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) (P(MMA-*co*-HEMA)) [9] or poly(methyl methacrylate)-*block*-poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) (PMMA-*block*-P(MMA-*co*-HEMA))

[10,11] in benzene or 1,4-dioxane. PHPS is a pre-ceramic material of silica and can be converted to silica without lattice defects lower than 100 °C. Density of the silica formed with PHPS calcinated at 90 °C was 1.3 g cm^{-3}. PHPS has following advantages for the synthesis of organic/silica nano-composites: (1) PHPS is highly reactive with hydroxyl groups. (2) PHPS is soluble in many solvents such as benzene, xylene, cyclohexane, pyridine, etc. By modifying the polymer with hydroxyl groups with PHPS, the organic/silica nano-composites are formed.

In these nano-composites, silica was segregated and formed microdomains with the clear interface against the organic domains. However, the small spherical silica particles (average diameter < 10 nm) were also observed in the organic microdomains of the PMMA/silica nano-composites obtained with PMMA-*block*-P(MMA-*co*-HEMA) because of the difficulty of removing PHPS that was not reacted with hydroxyl groups. Also, strict control of the morphology of the nano-composites was not achieved because intra- and inter-molecular crosslinking of the polymer was formed with PHPS in the mixture of polymer and PHPS. A PHPS molecule is reactive with more than one hydroxyl group. Thus, it is considered that the organic/silica nano-composites with well-designed structure can be

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obtained when the morphology of microphase separation of the polymer film was fixed before introduction of PHPS.

In previous works [12–14], colloidal silver was introduced into the crosslinked poly(2-vinyl pyridine) (P2VP) microdomains of the microphase separated polystyrene-*block*-poly(2-vinyl pyridine) (PS-*block*-P2VP) diblock copolymer film by soaking the films into a AgNO$_3$/water/1,4-dioxane solution. Before and after soaking the film into the Ag$^+$ solution, the inner textures of the film did not change. When the colloidal silver was introduced in the PS-*block*-P2VP, Ag$^+$ was reacted with Br$^-$ ions in the P2VP domains and silver bromide was selectively precipitated in the P2VP domains. By this method, it is possible to synthesize the nano-composites with well-segregated PS and Ag microdomains. Therefore, if a polymer film was composed with the inert domains with PHPS and the domains with hydroxyl groups, PHPS will be selectively introduced in the domain with hydroxyl groups by soaking the film into a PHPS solution. Then, the nano-composite will be conveniently obtained with organic polymer, which is inert with PHPS, and silica (Fig. 1).

In this work, a new method to synthesize PMMA/silica nano-composites, which is the soak of a block copolymer film into a PHPS solution, is proposed. PMMA-*block*-PHEMA with 49.3 mol% of HEMA was chosen to form block copolymer films with PMMA and PHEMA lamellae. Then, the PMMA-*block*-PHEMA films were soaked into a pyridine/*m*-xylene/PHPS solution to form the PMMA/silica nano-composites. Since PHPS is reactive with hydroxyl groups, PHPS will selectively exist in PHEMA microdomains during the soaking. By calcination, PMMA/silica nano-composites will be obtained. The distribution of Si atom owing to PHPS in the composite film was measured by energy dispersive X-ray spectroscopy (EDX). The morphology of the nano-composites was investigated by transmission electron microscopy (TEM) and thermogravimetric analysis (TGA).
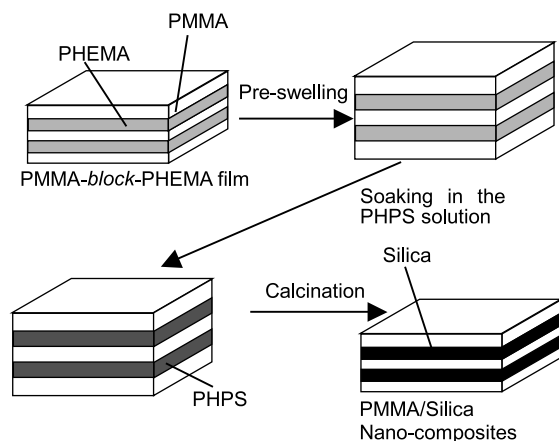

Fig. 1. The scheme of synthesis of nano-composites by a soaking method.

2. Experimental section

2.1. Materials

PHPS/xylene solution (NN-310, Clariant Japan Co., PHPS = 20 wt%, number average molecular weight (M_n) = 900) was used as received. PMMA-*block*-PHEMA (M_n = 56.8 (kg mol^{-1}), polydispersity index (M_w/M_n) = 1.56, volume fraction of PHEMA = 0.538, molar fraction of PHEMA = 0.493) was previously synthesized by copper-mediated atom transfer radical polymerisation (ATRP) [11]. PMMA (M_n = 55.5 (kg mol^{-1}), M_w/M_n = 1.73) was synthesized by free radical polymerisation initiated with 2,2′-azobisisobutyronitrile at 60 °C. PHEMA (M_n = 90.8 (kg mol^{-1}), M_w/M_n = 2.56) was synthesized by copper-mediated ATRP [15].

2.2. Introduction of PHPS into the polymer film

The PMMA-*block*-PHEMA films (10 mg, thickness: 50 μm) were obtained by casting the PMMA-*block*-PHEMA/1,4-dioxane/methanol = 1/50/50 (v/v/v) solution on a Teflon dish and gradually drying at room temperature. The PMMA-*block*-PHEMA film was completely dried at 130 °C for 8 h under vacuum. Before soaking the film into a PHPS solution, the film was pre-swollen in a pyridine (Py)/*m*-xylene (Xy) = 20/80 (v/v) mixture (4 ml) at room temperature for 24 h. After the pre-swelling, to introduce PHPS into the film, the film was soaked into a PHPS solution (2 ml, Py/Xy = 20/80 (v/v), [PHPS] = 0.16 mol l^{-1}) at room temperature for 72 h under dry N$_2$ atmosphere. After the introduction of PHPS into the film, the film was washed in a Py/Xy (= 20/80 (v/v)) mixture (4 ml) at room temperature for 72 h. Then, the film was dried at room temperature under N$_2$ atmosphere.

2.3. Calcination of the polymer/PHPS film

The film was exposed to a 5% triethylamine aqueous solution at room temperature for 5 min, and then heated at 90 °C for 3 h under steam. The introduced amount of silica was determined by gravimetry.

2.4. Characterization

The introduction of PHPS into the film and the conversion of PHPS to silica were estimated with a Fourier-Transfer Infrared spectrometer (JASCO, FT/IR-410) by using Si–H, carbonyl and Si–O–Si bonds observed at 2253, 1733 and 1070 cm^{-1}, respectively. Transmittance of the film was measured with a UV/VIS spectrometer (JASCO, V-530) at 600 nm. For EDX analysis, the cross-section of the film was spattered with carbon with an ion-spatter (JEOL, JEE-450D), and observed with a scanning electron microscope (Hitachi, S-800) at 15 kV. An element of Si on the cross-sectioned film was analysed with an

energy dispersive X-ray spectroscope (Philips, EDAX-PV9900) at 1.76 keV. For TEM observation, the ultra-thin film was prepared by cutting the film with a microtome (Leica, ULTRACUT-UCT) with glass knives. The TEM specimen of the PMMA-*block*-PHEMA was stained with OsO_4. The TEM specimen of the polymer/silica composite was observed without staining. Microphase separation of the films was observed with a transmission electron microscope (JEOL, JEM-200CX) at 120 kV. For TGA measurements, the specimen (2.5 mg) was sealed into an aluminium pan and measured with a thermogravimetric analyser (Seiko Instruments Inc., EXSTAR6000TG/DTA6300) under N_2 atmosphere. The measurement was conducted from 50 to 600 °C at a heating rate of 10 °C min^{-1}.

3. Results and discussion

To obtain the polymer film with PMMA and PHEMA lamellae, based on the Molau's law [16], PMMA-*block*-PHEMA with 0.538 of volume fraction of PHEMA was used in this work. For the film with lamellar structure, it is expected that PHPS is soaked into both PMMA and PHEMA domains. Fig. 2(a) shows a TEM micrograph of a cross-section of the PMMA-*block*-PHEMA film stained with OsO_4. The dark regions correspond to selectively stained PHEMA domains. The morphology of microphase separation of the PMMA-*block*-PHEMA film was not complete lamellae. Both the PMMA spheres and the PHEMA spheres were observed in a PHEMA matrix and a PMMA matrix, respectively. The average diameters of PMMA and PHEMA domains were 18.2 and 15.7 nm, respectively. It was considered that both PMMA and PHEMA domains would be continuous in the film. Consequently, a suitable polymer film for this work was obtained.

For the introduction of PHPS into the film, PHPS in the solution should be homogeneously diffusive in the film. For the homogeneous diffusion of PHPS in the film, the swelling of the film should be in an equilibrium state during the introduction of PHPS. Thus, the films were pre-swollen in the solvent without PHPS before the introduction of PHPS into the film. Degrees of swelling in the equilibrium state of PMMA-*block*-PHEMA and PHEMA films in a Py/Xy (= 20/80 (v/v)) mixture at 20 °C are listed in Table 1. The degree of swelling of the PMMA-*block*-PHEMA film was saturated at 24 h in this
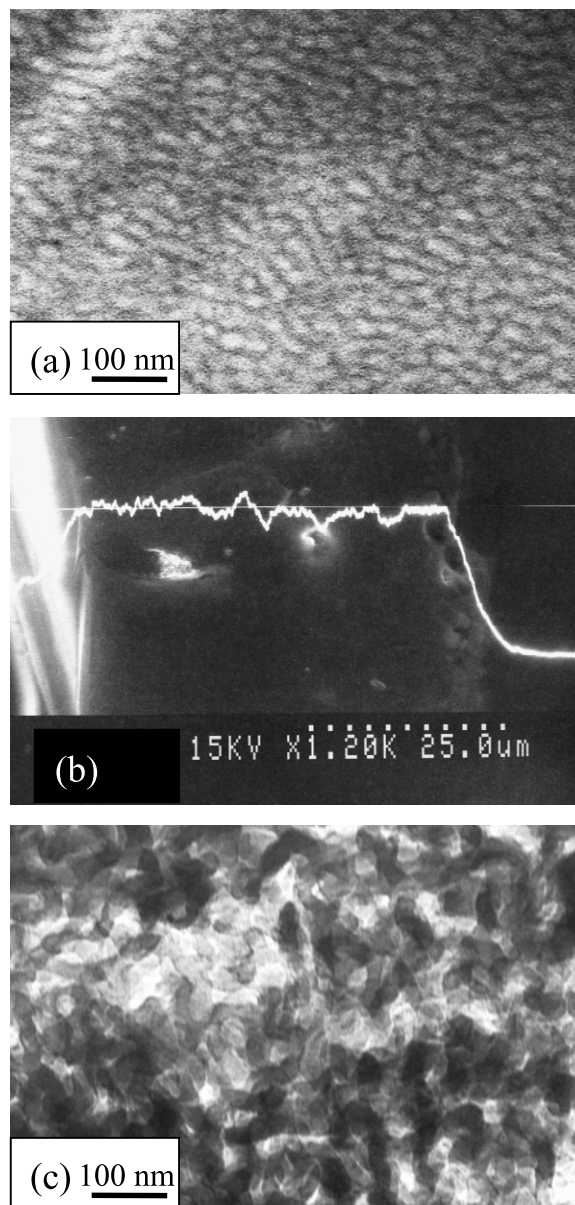

Fig. 2. Micrographs of PMMA-*block*-PHEMA and the composite. (a) A TEM micrograph of PMMA-*block*-PHEMA film stained with OsO_4. (b) An SEM micrograph and the results of EDX analysis (Si K_α line) of the nano-composite film. (c) A TEM micrograph of cross-section of the nano-composite film after calcination.

work. The pre-swelling of the film and introduction of PHPS into the film were carried out in a Py/Xy (= 20/80 (v/v)) mixture because the degree of swelling of the film was highest. The degree of swelling of PMMA was not obtained because PMMA was dissolved in the Py/Xy = 20/80 (v/v) mixture. Taking account of the degrees of swelling of the PMMA-*block*-PHEMA film and the PHEMA film, the swelling of PMMA-*block*-PHEMA film was mainly caused by the dissolution of PMMA in the Py/Xy mixture.

After pre-swelling of the PMMA-*block*-PHEMA film, the film was soaked into the PHPS solution to introduce

Table 1
Degrees of swelling of PMMA-*block*-PHEMA, PMMA and PHEMA in a Py/Xy = 20/80 (v/v) mixture at 20 °C at 24 h

PMMA-*block*-PHEMA	PMMA	PHEMA
2.43	–[a]	1.24

[a] Dissolved.

PHPS into the film. Then, the film was washed in the Py/Xy = 20/80 (v/v) mixture to remove the un-reacted PHPS from the film. After washing, the film was dried under N$_2$ atmosphere. After drying, a calcination of the film was carried out at 90 °C for 3 h. A weight ratio of the calcinated film to the original PMMA-*block*-PHEMA film was 1.28. The increase of the weight of the film by hybridisation by this method corresponds to the introduced amount of silica. Taking account of the introduced amount of silica and the molar fraction of PHEMA in PMMA-*block*-PHEMA, 0.493, the molar ratio of PHPS introduced to the hydroxyl groups to PHEMA was 0.054.

The calcination of PHPS to silica in the PMMA-*block*-PHEMA was investigated by FT-IR measurements. Fig. 3 shows the FT-IR spectra of PMMA-*block*-PHEMA (Fig. 3(a)), the film after soaking into the PHPS solution (Fig. 3(b)) and the film after calcination (Fig. 3(c)). After soaking of the pre-swollen film in the PHPS solution, new peaks appeared at 2253 and 878 cm^{-1} owing to the bonds of Si–H and Si–N of PHPS, respectively, indicating the introduction of PHPS into the film. The peaks of the calcinated film at 1070 and 450 cm^{-1} owing to Si–O–Si indicate the conversion of PHPS to silica. When the composites were prepared by casting the blend solutions of PHPS and PMMA-*block*-PHEMA (M_n : 17.7 kg/mol, molar fraction of HEMA: 0.216) [10], PHPS in the composites was completely converted to silica without calcination during drying because the moisture could be easily absorbed into the blend solutions and was reacted with PHPS. The silica formed before formation of the microphase separation would cause unexpected segregation of silica in the film. On the other hand, by the soaking method, PHPS in the film was not completely converted to silica without calcination. Incomplete conversion of PHPS to silica in the film of this work without calcination suggests the hindrance of the unexpected segregation of silica in the film. After calcination, the peaks of Si–H bond (2253 cm^{-1}) and Si–N bond (878 cm^{-1}) were completely vanished. Consequently, an organic/silica composite was successfully obtained by

soaking the film into the PHPS solution and calcination of the film.

In order to investigate a distribution of silica in the organic/silica composite film, an EDX analysis of the film was carried out. An SEM micrograph and the result of EDX analysis of the cross-section of the organic/silica composite film are shown in Fig. 2(b). From the intensity of Si K$_\alpha$ line observed on the cross-section of the film, it was found that Si atom was homogeneously dispersed in the organic/silica film. Since the complete conversion of PHPS to silica by calcination was confirmed by the FT-IR measurement, all Si atoms in this work originated from silica. It was concluded that silica was macroscopically homogeneously introduced in the film.

Fig. 2(c) shows a TEM micrograph of an inner texture of the organic/silica composite film. Since the silica-rich domains are observed as dark regions by TEM without staining, the calcinated film was not stained. The organic/ silica composite was microphase separated with the organic (white regions) and silica-rich (dark regions) domains. The morphology of the composite film was similar to that of the PMMA-*block*-PHEMA. The average diameters of organic and silica-rich domains were 17.8 and 17.4 nm, respectively. They agreed well with the average diameters of PMMA and PHEMA domains of PMMA-*block*-PHEMA, respectively. Consequently, the organic/silica nano-composite with the similar morphology of the organic polymer was synthesized by the soaking method.

In order to investigate the transparency of the nano-composite, the transmittance of the PMMA-*block*-PHEMA and the nano-composite film was measured at 600 nm. The theoretical and experimental values of the transmittance of the PMMA-*block*-PHEMA and the nano-composite film were shown in Table 2. The theoretical values of the transmittance were calculated by Lambert–Beer law with the densities and the molar absorption coefficients of PMMA, PHEMA and silica. Densities of PMMA, PHEMA and the silica formed with PHPS calcinated at 90 °C were 1.188 [17], 1.289 [18] and 1.3 g cm^{-3}, respectively. The molar absorption coefficients of PMMA, PHEMA and silica at 600 nm were 2.6×10^{-4} [19], 2.6×10^{-3} [20] and 9.7×10^{-4} (l mol^{-1} cm^{-1}) [21], respectively. The PMMA-*block*-PHEMA film before hybridisation was transparent. The less experimental value of the transmittance of the PMMA-*block*-PHEMA film than
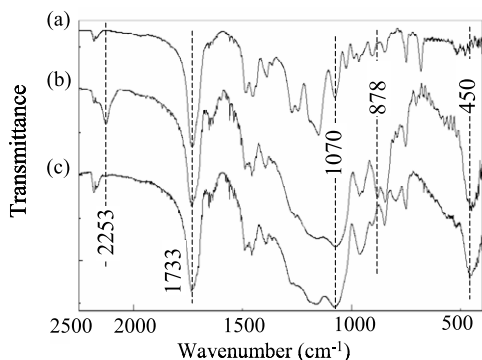

Fig. 3. FT-IR spectra of PMMA-*block*-PHEMA and the nano-composite films. (a) PMMA-*block*-PHEMA, (b) the nano-composite film before calcination, (c) the nano-composite film after calcination.

Table 2
Transmittance of the PMMA-*block*-PHEMA and the nano-composite films at 600 nm

Sample name	Theoretical value (%)	Experimental value (%)
PMMA-*block*-PHEMA	99.996	72.9
The nano-composite (dry)	99.996	12.7
The nano-composite (in *m*-xylene)	99.996	94.4

Thickness of the film: 50 μm.

the theoretical value of that was owing to the roughness of the surface of the film.

The film became opaque after hybridisation. Taking account of the theoretical value of the transmittance of the nano-composite, the nano-composite film should be transparent. The causes of opaqueness of the film were considered as followings: (1) The surface of the film was roughened during hybridisation. (2) Macrophase separation of polymer and silica was occurred in the film. (3) Birefringence was duplicately occurred in the film. To investigate the causes, the transmittance of the nano-composite film was measured in *m*-xylene, which refractive index at 20 °C (1.497) was close to that of PMMA (1.490 [22]). It was considered that PMMA was localized at the surface of the film because of the hydrophobicity of PMMA. If the main cause of opaqueness of the film is roughening of the surface of the film, the nano-composite film becomes transparent in *m*-xylene. As a result, the transmittance of the nano-composite film in *m*-xylene became 0.944, which was close to the theoretical value. Consequently, the main cause of opaqueness of the film was roughening of the surface of the film. It was considered that the roughening of the surface of the film was owing to the high degree of swelling of the film. The occurrence of macrophase separation and birefringence in the nano-composite film was negligible.

In order to investigate a selective introduction of silica to the PHEMA domains of the PMMA-*block*-PHEMA film by the soaking method, TGA measurements were carried out for PMMA, PMMA-*block*-PHEMA and the nano-composites synthesized by the soaking method and the solution method [11]. PMMA-*block*-PHEMA was gelated in the blend solution with PHPS, therefore, PMMA-*block*-P(MMA-*co*-HEMA) ($M_n = 50.0 \, kg \, mol^{-1}$, $M_w/M_n = 1.26$) was used instead of PMMA-*block*-PHEMA for the solution method [11]. The molar fractions of PMMA$_1$, PMMA$_2$ and PHEMA of PMMA$_1$-*block*-P(MMA$_2$-*co*-HEMA) were 0.576, 0.321 and 0.103, respectively. Since M_n and the molar fraction of PMMA$_1$ of PMMA$_1$-*block*-P(MMA$_2$-*co*-HEMA) were similar to those of PMMA-*block*-PHEMA used in this work, PMMA-*block*-P(MMA-*co*-HEMA) was a suitable model compound of PMMA-*block*-PHEMA used in this work.

Thermal degradation behaviours of PMMA, PMMA-*block*-PHEMA and the organic/silica nano-composites are shown in Fig. 4. For PMMA-*block*-PHEMA, the decrease of the weight near 100 °C corresponded to the evaporation of solvents and water. The char residues of the nano-composites at 600 °C synthesized by the soaking method and the solution method were 0.262 and 0.374 (w/w), respectively. Taking account of the weight fractions of silica in the nano-composites synthesized by the soaking method and the solution method, 0.220 and 0.318 (w/w), respectively, the char residues at 600 °C well agreed with the weight fractions of silica of each nano-composite. The organic polymer in the nano-composites did not exist at 600 °C.
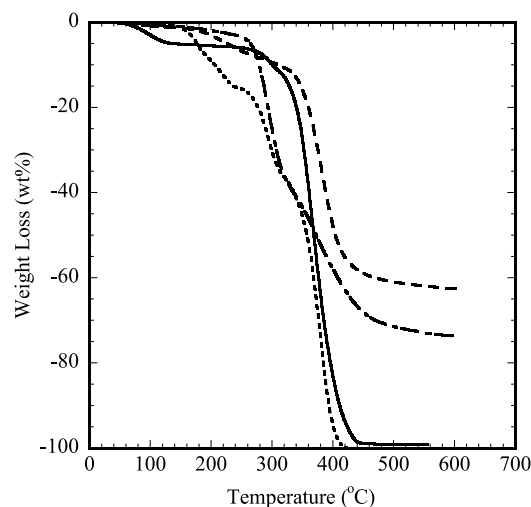

Fig. 4. TGA curves of PMMA-*block*-PHEMA and the nano-composites. PMMA-*block*-PHEMA (solid line), PMMA (dotted line), the nano-composite synthesized by the soaking method (one dotted broken line), the nano-composite synthesized by the solution method (broken line).

PMMA was thermally decomposed with three steps. The thermal degradation behaviour of the organic polymer of the nano-composite synthesized by the soaking method was similar to PMMA rather than PMMA-*block*-PHEMA, i.e. the nano-composite showed two-step thermal degradation in ranges from 240 to 340 °C and over 340 °C. According to Kashiwagi et al. the PMMA degradation of the first (in a range from 130 to 240 °C), second (in a range from 240 to 320 °C) and third (over 320 °C) steps was owing to the unzipping from the head to head linkage, the vinylidene chain end and random loci of the methacrylate chain, respectively [23]. For the composite synthesized by the soaking method, the degradation owing to the unzipping from the head to head linkage was not observed. On the other hand, for the composite synthesized by the solution method, the degradation was mainly occurred over 320 °C. It has been studied that the thermal stability of PMMA was improved with silica and hydroxyl groups [24,25]. Since it was impossible to remove un-reacted PHPS with hydroxyl groups of PHEMA unit, silica owing to un-reacted PHPS would exist in the organic domains by the solution method. Thus, it was considered that the thermal stability of the organic polymer in the composite synthesized by the solution method was increased by silica in the organic domains. However, the degradation of PMMA in the nano-composite synthesized by the soaking method was not disturbed by the hybridisation with silica. It was concluded that silica did not exist in the PMMA microdomains of the nano-composite synthesized by soaking method, in other words, the nano-composite with well-segregated PMMA and silica microdomains was synthesized. However, the effect of hybridisation of silica on the improvement of thermal stability of the nano-composite was not observed for the soaking method.

In conclusion, the PMMA/silica nano-composite was

synthesized by the soaking method. A microphase separated PMMA-*block*-PHEMA film was soaked in a Py/Xy/PHPS solution to selectively introduce PHPS into PHEMA domains. Introduction of PHPS into the film was confirmed as the increase of the weight and the appearance of the peaks owing to Si–H and Si–N bonds in the FT-IR spectra. The soaked film was calcinated under steam to convert PHPS to silica. The EDX analysis indicated that silica was macroscopically homogeneously dispersed in the film. The TEM observation of the film showed that, the nano-composite was composed with organic and silica micro-domains by the soaking method. The thermal degradation behaviour of the nano-composite synthesized by the soaking method revealed that the PMMA/silica nano-composite with well-segregated PMMA and silica microdomains was synthesized by the soaking method. It was concluded that the PMMA/silica nano-composite, which was macroscopically homogeneous and microscopically well-segregated, was synthesized by the soaking method.

Acknowledgements

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