Surface Hardness and Transparency of Poly(methyl methacrylate)-Silica Coat Film Derived from Perhydropolysilazane

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ABSTRACT: To prepare hard and transparent poly (methyl methacrylate)-silica coat film on glass or polycarbonate substrates, poly(methyl methacrylate-co-2-hydroxyethyl methacrylate) random copolymers and perhydropolysilazane (PHPS) were blended in solution. Then the solution was cast on the substrates. The grafting of PHPS onto 2-hydroxyethyl methacrylate unit was analyzed by ^{1}H NMR spectroscopy. Surface hardness and transparency of the coat film were measured by nano-indentation method and UV-Vis spectroscopy, respectively. Surface hardness of coat film depended on the volume fraction of silica in the coat film, and reached 2.7 GPa when the volume fraction of silica was 76.4%. Transparency of the coat films prepared with PHPS was almost 100%, indicating that the coat film prepared with PHPS was highly transparent not only on glass substrate but also on the polycarbonate substrate. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3388–3395, 2007

**Key words:** coatings; composites; hardness; silicas; transparency

INTRODUCTION

Organic-silica nanocomposites have been developed to improve the properties, such as mechanical strength,[1–3] thermal resistance,[4–6] etc., of organic polymers. In general, a sol-gel method is the most convenient method to prepare organic-silica nanocomposites.[7–10] However, the silica prepared by the sol-gel method contains many lattice defects, which reduce the transparency of the composites.

Not only silica but also clay[11–14] and polyhedral oligomeric silsesquioxane (POSS),[15–18] which is the smallest unit of quartz (silica glass), have been hybridized with organic polymers. It is possible to synthesize organic-silica nanocomposites by blending perhydropolysilazane, ($-SiH_2-NH-$), PHPS, which is a preceramic material of silica for an insulator of electric devices, with organic polymers having hydroxyl groups.[19] Chemical structure of PHPS is shown in Scheme 1.[19] Scheme 2 shows the general scheme of synthesis of organic-silica nanocomposite with PHPS. PHPS is soluble in many organic solvents, such as xylene, toluene, THF, pyridine, etc., and reactive with hydroxyl group. Graft copolymer with organic truck and PHPS branches is spontaneously formed by blending PHPS and the organic polymer having hydroxyl group in the solution because Si—H group of PHPS is reactive with hydroxyl group. It is well known that the graft copolymer with incompatible sequences forms microphase separation in solid state.[20] The microphase-separated film with PHPS and organic domains is obtained by casting the blend solution on a substrate. The film is converted to organic-silica nanocomposites by calcination of PHPS. When glass transition temperature is higher than the calcination temperature, the morphology of microphase separation is not changed by calcination. It is possible to convert PHPS to silica at low temperature, which is in a range from room temperature to 100°C. Therefore, the organic-silica nanocomposite with similar morphology to organic-PHPS film is obtained. There are two major advantages of this method: (1) The graft copolymer, which governs the morphology of microphase separation of nanocomposites, is spontaneously formed in the blend solution. (2) The calcination system is very clean. For calcination of PHPS, no catalysts except for moisture are required.

On the basis of this concept, PMMA-silica,[19,21] PS-silica,[22] P4VP-silica,[23] and P2VP-silica[23] nanocomposites have been synthesized. The morphology of microphase separation of composites was governed by the volume fraction of the organic sequence,[21] solvent selectivity of organic sequence[23] as well as many organic block, and graft copolymers. However, strict control by Molau's law[20] was not succeeded because of the multi-functionality of PHPS with hydroxyl group. In case of PS-silica nanocomposites, highly

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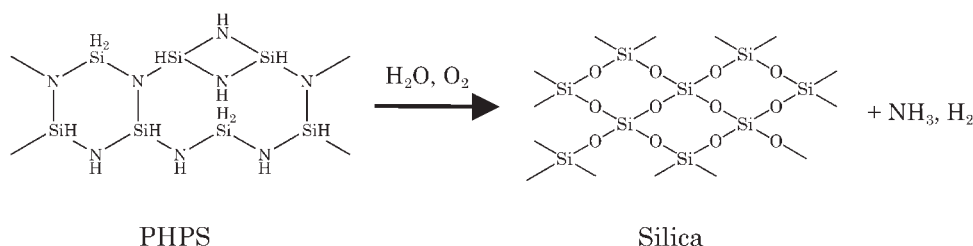
Scheme 1 Structure of PHPS and synthesis of silica by calcination of PHPS.

transparent composites with hard surface (0.75 GPa) were formed on a glass substrate.[22] This suggests that the organic-silica nanocomposite formed from the graft solution of PHPS and organic polymer will be a good coating material. Silica prepared from PHPS is a transparent and hard coat material on metals[24–26] and other inorganic sustrates.[27,28] However, the adhesion between silica and the substrate of organic polymer is very poor because of large difference between their δ values.[19,29] The organic-silica nanocomposite will improve the adhesion of the composites and the substrate of organic polymer.

Three major questions about the coating with graft solution of PHPS and organic polymer with hydroxyl group are raised. First, whether it is possible to prepare transparent and hard coat film with organic polymer other than polystyrene on a soft substrate or not. Second, whether their surface is harder than that of sol-gel coat film or not. Third, the mechanism of grafting of PHPS is unclear. To clarify these, in this work, the coat films of PMMA-silica nanocomposite were prepared on the hard and soft substrates and the surface hardness and trans-

parency of the coat films were investigated. Additionally, the grafting of PHPS onto hydroxyl group was analyzed by FTIR and ^{1}H NMR.

For the organic polymer, poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) [P(MMA-*co*-HEMA)] synthesized by conventional radical polymerization with α,α'-azobisisobutyronitrile (AIBN) or copper-mediated atom transfer radical polymerization were used. Glass and polycarbonate plates were chosen as the hard and soft substrates, respectively. The graft solution was cast on the substrate by a flow coating method. The surface hardness and transparency of coated substrate were measured by nano-indentation and UV-Vis spectrometry, respectively.

EXPERIMENTAL

Materials

α,α'-Azobisisobutyronitrile (AIBN, Kanto, 97%), tetraethoxysilane (TEOS, Tokyo Chemical Industry, 98%), Hydrochloric acid (Kanto, 35–37.0%), dimethylsulfoxide (DMSO, Kanto, 98%), and phenyl iso-
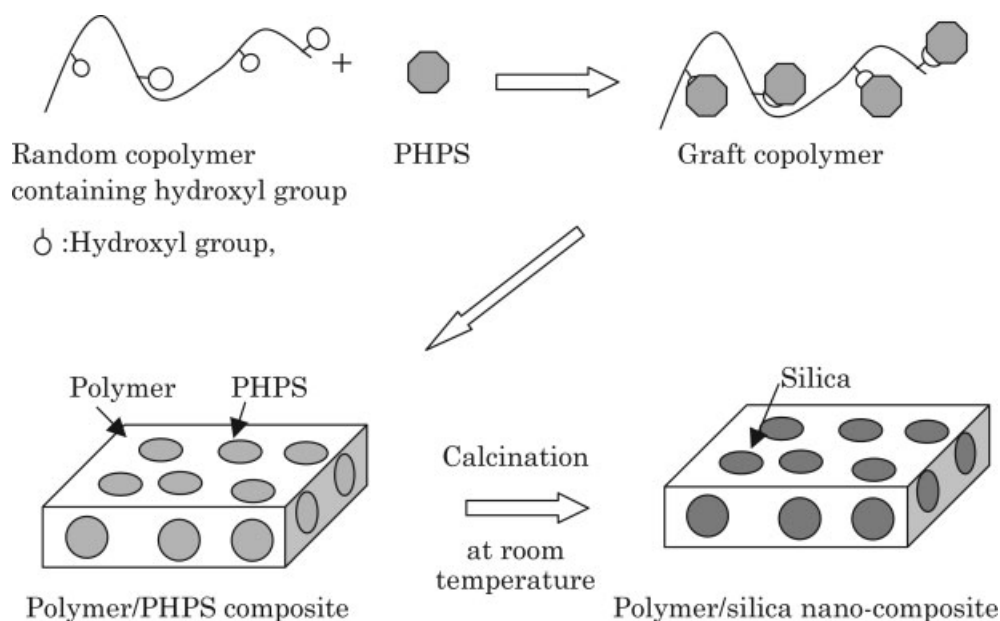
Scheme 2 Synthetic concept of nanocomposites of organic polymer and silica glass by hybridization of PHPS and random copolymer containing hydroxyl group.

TABLE I
Characteristics of P(MMA-*co*-HEMA) Random Copolymer

Sample no.	$\overline{M_n} \times 10^{-4}$ [a]	$\overline{M_w}/\overline{M_n}$ [a]	Content of HEMA (mol %)
RA2	4.5	1.30	14.5
P(MMA-*co*-HEMA)1	2.3	1.46	15.1
P(MMA-*co*-HEMA)2	3.3	1.26	13.7

RA2 was synthesized by using ATRP technique,[19] P(MMA-*co*-HEMA)1 and P(MMA-*co*-HEMA)2 were synthesized by free radical polymerization with AIBN.

[a] $\overline{M_n}$ and $\overline{M_w}/\overline{M_n}$ are number-average molecular weight and polydispersity, respectively, determined by GPC.

cyanate (Kanto, 98%) were used as received. Tetrahydrofurane (THF, Kanto, 99.5%), *n*-hexane (Kanto, 96%), cyclohexane (Kanto, 99.5%) were dried with sodium metal (Kanto) and distilled under vacuum before use. Benzene (Kanto, 99.5%), ethyl acetate (Kanto, 99%), methyl methacrylate (MMA, Tokyo Chemical Industry, 99%), and 2-hydroxyethyl methacrylate (HEMA, Tokyo Chemical Industry, 95%) was purified by distillation under vacuum.

Perhydropolysilazane [PHPS] solution (AZ Electronic Materials, NN-110, PHPS 20 wt % solution in Xylenes, number-average molecular weight of PHPS, 700; density, 0.92 g/mL) was used as received.

Poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) [P(MMA-*co*-HEMA)] random copolymer, RA2, was previously synthesized by copper-mediated atom transfer radical polymerization and characterized elsewhere.[19] Two types of P(MMA-*co*-HEMA) random copolymer, P(MMA-*co*-HEMA)1 and P(MMA-*co*-HEMA)2 were synthesized by free radical polymerization with AIBN. The typical procedures of P(MMA-*co*-HEMA)1 are shown as follows: Benzene (130 mL), MMA(16.5 mL), HEMA (2.5 mL), and AIBN (0.45 g) were sealed in a vacuum flask. The solution was heated at 60°C for 20 h. After reaction, the solution was poured to hexane (500 mL) to precipitate P(MAA-*co*-HEMA). HEMA con-

tents were measured by ^{1}H NMR spectrometer (BRUKER DPX300, 300 MHz) with DMSO-*d* by using the peak at 3.8 ppm originated methylene group next to hydroxyl group of HEMA and the broad peak in a range from 0.6 to 2.2 ppm originated methylene group of backbone and methyl group attached to backbone. Number-average molecular weight and molecular weight distribution were measured by GPC as follows: To protect hydroxyl group, a small amount of phenyl isocyanate was added to polymer-THF solution with 0.1 wt % of polymer concentration. Then the solution was stirred for overnight, and loaded to GPC. THF was used as an eluent. Flow rate and temperature was 0.6 mL/min and 35°C, respectively. Column oven, L-7300 (HITACHI); refractive index detector, L-2490 (HITACHI); pump, L-7100 (HITACHI); Column, TSKgelG5000H$_{HR}$ (TOSOH). Characteristics are listed in Table I. P(MAA-*co*-HEMA)s were freeze-dried with benzene before use.

Substrates

Glass, slide glass with 76 and 26 mm in height and width. Polycarbonate [PC] plate: IUPILON SHEET: NF-2000 Color: 552A (Mitsubishi Engineering-Plastics) with 75 and 25 mm in height and width.

Preparation of coat film

Coating on glass

P(MMA-*co*-HEMA) was dissolved in dry THF and certain amount of NN-110 was added under nitrogen. The solution was stirred for 24 h under nitrogen. Then, 2 mL of the solution was cast on glass substrate and gradually dried for 24 h under air at room temperature. The ingredients of coat solution are listed in Table II.

Coating on PC plate

P(MMA-*co*-HEMA) was dissolved in dry ethylacetate and certain amount of NN-110 was added under nitrogen. The solution was stirred for 24 h under

TABLE II
Ingredient of Coat Solutions

Code	Substrate[a]	Polymer type	Solvent (vol %)[b]				Polymer concentration (wt %)	PHPS concentration (wt %)
			THF	EtAc	CH	Xy		
Glass1	Glass	RA2	100	0	0	0	1.0	0.0
Glass2	Glass	RA2	99.2	0	0	0.8	0.99	0.19
Glass3	Glass	RA2	97.9	0	0	2.1	0.95	0.46
Glass4	Glass	RA2	95.9	0	0	4.1	0.93	0.89
Glass5	Glass	RA2	93.9	0	0	6.1	0.93	1.32
Glass6	Glass	RA2	82.5	0	0	17.5	0.77	3.7
PC-1	PC	P(MMA-*co*-HEMA)1	0	47.4	23.1	29.5	4.6	6.6

[a] PC corresponds to polycarbonate plate.
[b] THF, tetrahydrofurane; EtAc, ethyl acetate; CH, cyclohexane; Xy, xylenes.

TABLE III
Conditions of PMMA-Silica Synthesis
by Sol-Gel Reaction

Sample code	Sol-gel-1
Polymer weight (mg)	609.9
TEOS (mL)	0.9
DMSO (mL)	18
H_2O (mL)	0.14
Methanol (mL)	0.64
HCl (mL)	0.02

Polymer, P(MMA-co-HEMA)2; $[H_2O]/[TEOS] = 1.94$; $[HCl]/[TEOS] = 0.06$; $[TEOS]/[OH] = 5.01$; $[Methanol]/[H_2O] = 2.03$; reaction time, 75°C; reaction temperature, 6 h.

nitrogen. A certain amount of dry cyclohexane was added dropwise to the solution. Then, 2 mL of the solution was cast on PC plate and gradually dried for 24 h under air at room temperature. The ingredients of coat solution are listed in Table II.

Coating on glass by the sol-gel method

P(MMA-co-HEMA) was dissolved in DMSO. Methanol, water, TEOS, and HCl aq. were added. The mixture was refluxed at 75°C for 6 h. Then, 2 mL of the solution was cast on the glass substrate, and heated at 100°C for 5 h. Content of coat solution for the sol-gel method is listed in Table III.

Analysis

FTIR measurement

Graft copolymers were recovered by precipitation of the sampled solutions with *n*-hexane and dried. Content of PHPS in the polymer was measured with a Fourier-transfer infrared spectrometer (Jasco, FTIR-410) by using absorption at 835 and 1730 cm^{-1} originated Si—N bonding in PHPS and carbonyl group in PMMA, respectively.

^{1}H NMR measurement

25.4 mg of P(MMA-co-HEMA)2 was dissolved in 0.5 mL of CDCl$_3$ in an NMR tube. Then, 0.2 mL of NN-110 was added to the solution under dry nitrogen. After 24 h, the solution was measured by ^{1}H NMR (JEOL, GLX-400, 400 MHz).

Nano-indentation

Surface hardness of the coat films were recorded with a nano-indentor (triboscope, Hysitron) attached to an atomic force microscope (AFM, SPM9500J2, Shimazu). The hardness measurements were per-

formed with a load ranging from 50 to 5000 μN, corresponding to a contact depth from 50 to 1200 nm.

UV-vis measurement

Transparency of the coat film was recorded with a UV-VIS spectrometer (Jasco, V-530) in a range from 350 to 1100 nm. The glass substrate or the PC plate was used for a reference.

RESULTS AND DISCUSSION

P(MMA-*co*-HEMA) random copolymers

In this work, three type of P(MMA-*co*-HEMA), RA2, which was previously synthesized, P(MMA-*co*-HEMA)1 and P(MMA-*co*-HEMA)2, which were newly synthesized in this work, were used. The characteristics of P(MMA-*co*-HEMA) random copolymers are listed in Table I. HEMA contents of P(MMA-*co*-HEMA)1 and P(MMA-*co*-HEMA)2, 15.1 and 13.7 mol %, respectively, were close to that of RA2, 14.5 mol %. PMMA-silica nanocomposite with well-ordered microphase separation was formed with PHPS and P(MMA-*co*-HEMA) RA2.[19] The polydispersity of all polymers was in a range from 1.26 to 1.52, which was narrow enough to form the well-ordered microphase separation.

Reaction between PHPS and hydroxyl group

Coat solutions were prepared based on the ingredients listed in Tables II and III. No solutions gelled before coating. The reaction of PHPS with hydroxyl group of P(MMA-*co*-HEMA) provides P(MMA-*graft*-PHPS) in the coat solutions. To confirm the formation of P(MMA-*graft*-PHPS) in solution, FTIR measurements were carried out. Figure 1 shows the FTIR spectra of P(MMA-*co*-HEMA)2 series. The product containing organic polymer was recovered from the
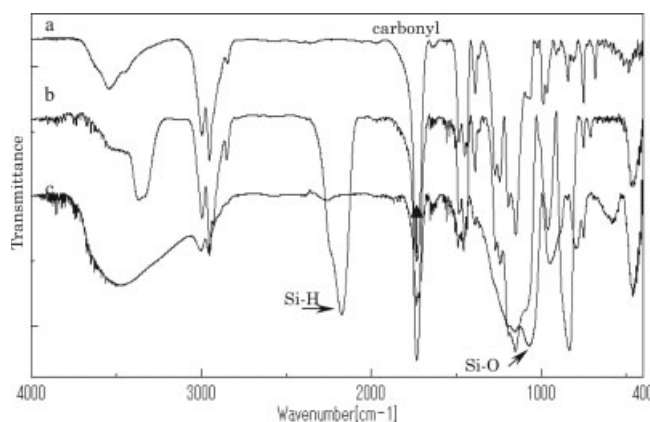

Figure 1 FTIR spectra (a) P(MMA-*co*-HEMA)2, (b) P(MMA-*graft*-PHPS), and (c) PMMA-silica composite.
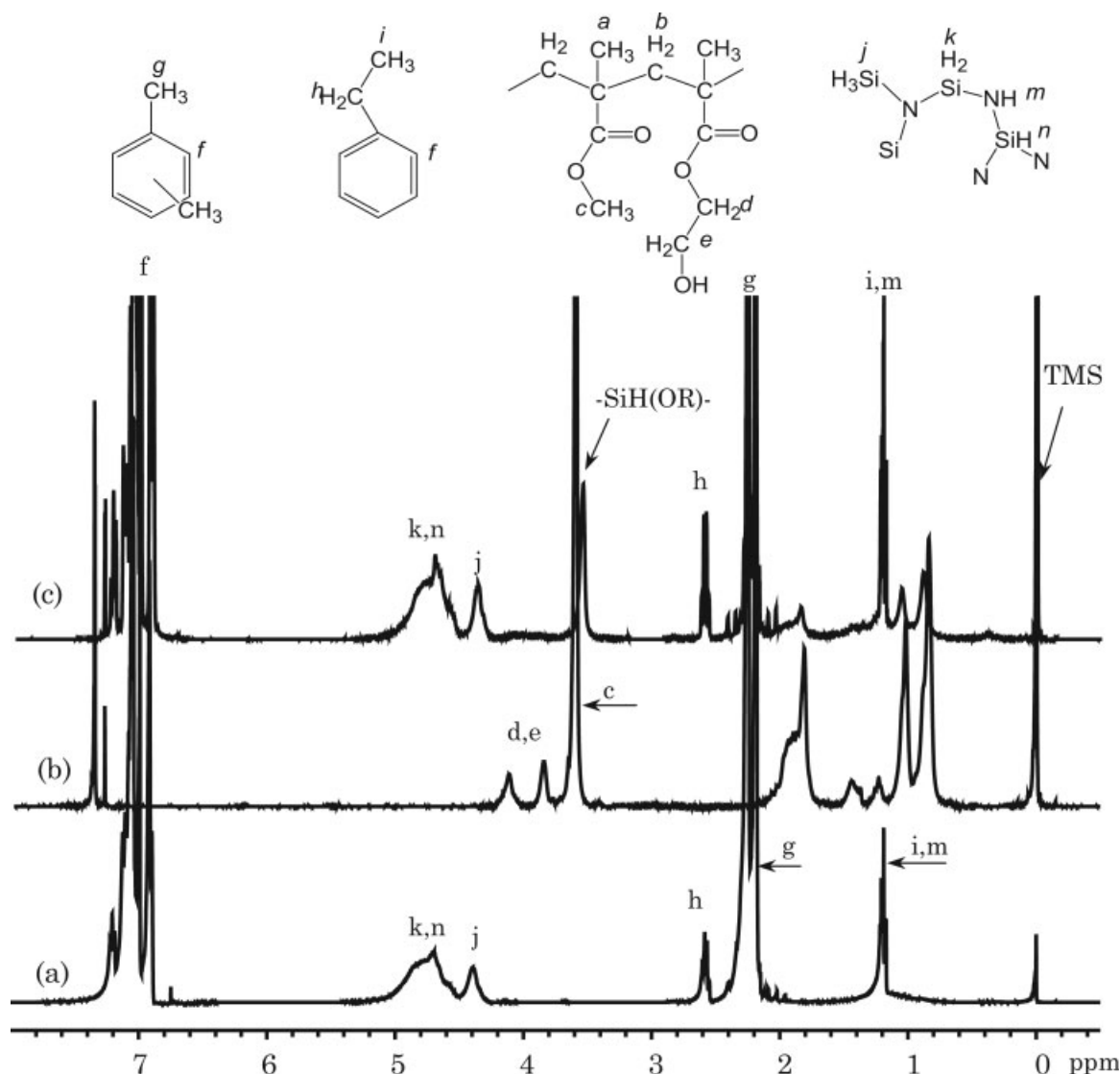
Figure 2 ¹H NMR spectra of (a) NN-110, (b) P(MMA-*co*-HEMA)2, (c) a mixture of P(MMA-*co*-HEMA)2, and NN-110.

coat solution by precipitation with hexane, which is a good solvent for PHPS and nonsolvent for P(MMA-*co*-HEMA) and the graft copolymer. For the precipitant [Fig. 1(b)], Si—H peak owing to PHPS appeared at 2170 cm⁻¹, indicating that PHPS was grafted onto P(MMA-*co*-HEMA)2.

To calculate the degree of grafting of PHPS onto P(MMA-*co*-HEMA), ¹H NMR measurements were carried out. Figure 2 shows the ¹H NMR spectra of NN-110, P(MMA-*co*-HEMA)2, and the blend solution of P(MMA-*co*-HEMA)2 and NN-110. The solvent was CDCl₃. Polymer concentration and PHPS concentration was 3.8 and 5.4 wt %, respectively. Since xylene was the solvent of NN-110, the volume fractions of CDCl₃ and xylenes were 75.3 and 24.7 vol %, respectively. For NN-110 solution, the peak at 4.3 ppm corresponds to SiH₃ group, the peak at 4.8 ppm corresponds to SiH and SiH₂ groups, and the broad peak at 1.2 ppm corresponds to NH group

of PHPS.[30] The peaks of methyl and phenyl groups of xylene are observed at 2.2 and 7.0 ppm. The peak at 2.6 ppm corresponds to methylene group of ethyl benzene, which is an impurity in xylene. It should be noticed that the peak of methyl group of ethyl-benzene overlaps with that of NH group at 1.2 ppm. It is possible to estimate the peak area at 1.2 ppm owing to ethylbenzene by using the peak of methyl-ene group at 2.6 ppm. Taking account of peak area owing to ethylbenzene, the peak area of NH group at 1.2 ppm was estimated. From the peaks of SiH, NH, and methyl group of xylenes, the concentration of NH and SiH units in NN-110 was found 2.15 and 7.36 mol/L, respectively. The molar ratio of SiH to NH was 2 : 0.58. The theoretical molar ratio of SiH:NH of PHPS is 2 : 1. The experimental amount of NH group was less than that of theoretical value. As shown in Scheme 1, PHPS is not a linear but a branch molecule. Therefore, the experimental
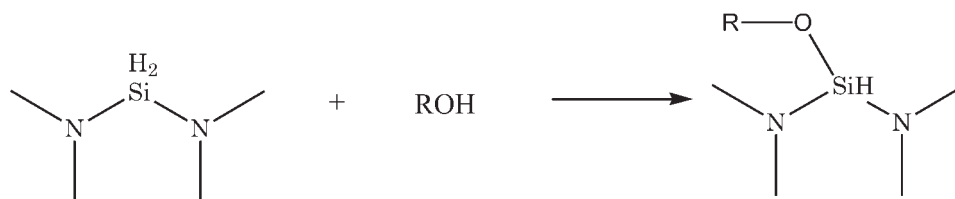
Scheme 3 Reaction of hydroxyl group and PHPS.

value of NH group would be less than the theoretical value.

For the blend solution of P(MMA-co-HEMA)2 and NN-110, the peaks owing to P(MMA-co-HEMA)2 and PHPS are observed. The new peak owing to N—Si(OR)H—N appeared at 4.7 ppm, indicating that condensation occurred between hydroxyl group of HEMA and N—SiH$_2$—N in PHPS (Scheme 3). For P(MMA-co-HEMA)2, the ratio of total peak areas of methylene group of HEMA at 3.8 and 4.1 ppm to methoxy group of MMA at 3.6 ppm was 0.177. In contrast, for the blend solution, the ratio of total peak areas of methylene group of HEMA to that of methoxy group of MMA was 0.085. Theoretically, the molar content of methylene and methoxy groups should be constant. The reduction of ratio of peak area of methylene of PHEMA was due to the decrease of the mobility of HEMA by grafting PHPS. Thus, the degree of grafting was not determined by ^{1}H NMR.

Calcination of film

The coat film was prepared on the substrate by casting and drying the coat solution on the substrates. The formation of PMMA-silica nanocomposites on the substrate was investigated by FTIR. Figure 1(c) shows FTIR spectra of the coat film pealed from the glass substrate of Glass4. In contrast to P(MMA-graft-PHPS) [Fig. 1(b)], the Si—H peak at 2170 cm^{-1} vanished in the composite, novel peak owing to Si-O appeared at 1100 cm^{-1}, indicating that silica was formed by calcination of PHPS by drying at room temperature. It has been reported that PHPS was gradually converted to silica at room temperature.[19] In case of polystyrene-silica nanocomposite prepared with PHPS, PHPS was converted to silica within 24 h at room temperature.[22] Consequently, the calcination of PHPS in the coat film was completed by 24 h. Further heat treatment for calcination was not carried out.

Transparency of the film

All coat films including Sol-gel-1, which was prepared by the sol-gel method, looked like transparent. Transparency is an important feature for coat film. For quantitative analysis, transmittance of the coat film was measured by UV-vis spectrometry. The substrate was used for reference. The results are shown in Figure 3. The transmittance of the coat film Sol-gel-1 was gradually increased from 60 to 94% by increasing the wavelength from 350 to 1100 nm, respectively. Especially, the transmittance in a visible range (380–780 nm) was in a range from 61.5 to 83%. In contrast, all coat films prepared with PHPS were highly transparent; their transmittance was almost 100% in a wide range. The volume fraction of silica in the composites of Sol-gel1, Glass5, and PC-1 were very close, ∼ 49 vol %. Thus, the good transparency of Glass5 and PC-1 was not resulted in the volume fraction of silica but the type of preparation of silica. In case of PHPS series, transparency of the coat film was independent on either the volume fraction of silica or the type of substrate (Glass1 and Glass5, Glass5, and PC-1, respectively). It should be notice that the coat solution for PC plates contains 23.1 vol % of cyclohexane, which is a nonsolvent for polycarbonate, to prevent the dissolution of polycarbonate plate to the coat solution.

Surface hardness of the film

Finally, the surface hardness and elastic modulus of coat film were measured by nano-indentation (Fig. 4). Figure 4 shows the curves of surface hardness and elastic modulus versus displacement depth of Glass1, Glass5, and PC-1. In case of Glass1, the surface hardness and elastic modulus were almost constants. The
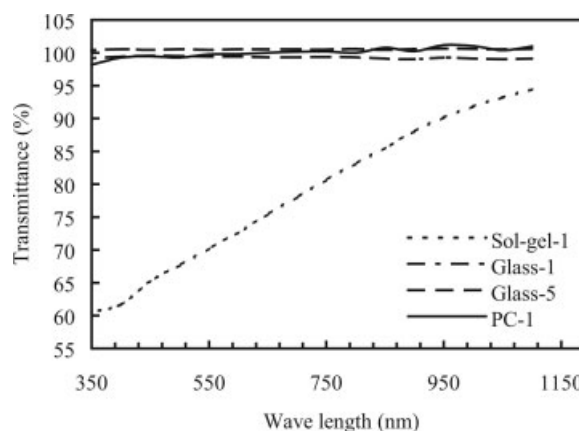

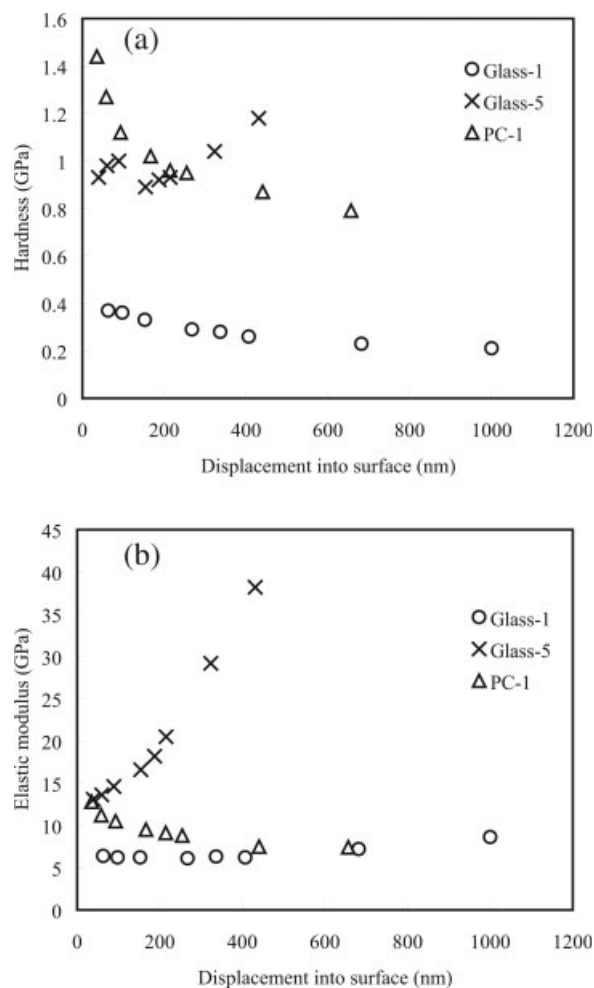**Figure 3** UV-vis spectra of PMMA-silica coat films.

Figure 4 Surface hardness and elastic modulus of coat film measured by nano-indentation. (a) Surface hardness and (b) elastic modulus.

substrate was glass and the thickness of coat film was 4.41 μm. Mechanical properties, such as surface hardness, elastic modulus, etc., of coat film were affected on the surface hardness of the substrate when the displacement depth was larger than 20% of thickness of coat film.[31] The surface hardness and elastic modulus of soda-lime glass, ∼ 5.5 and 70–73 GPa, respectively, at room temperature,[32,33] were higher than those of coat film. The slight change of surface hardness and elastic modulus by increasing the displacement depth would be due to the influence of glass substrate. However, the influence was small because the coat film was thick. In case of Glass5, the surface hardness was constant till 200 nm of displacement depth, and then drastically increased by increasing the displacement depth. The elastic modulus was increased by increasing the displacement depth. The thickness of coat film was 0.95 μm. 200 nm of displacement depth corresponds to ∼ 20% of film thickness. The coat film of Glass5 was thinner than that of Glass1, the strong influence

of glass substrate was observed over 200 nm of displacement depth. In other words, since the surface hardness and elastic modulus of glass substrate were larger than the coat film, these values were gradually increased by increasing the displacement depth over 200 nm.

In case of PC-1, the surface hardness and elastic modulus till 200 nm were drastically decreased and gradually decreased by increasing the displacement depth. The thickness of coat film of PC-1 was 4.14 μm. Thus, the influence of PC substrate till 200 nm of displacement depth would be small. According to Malzbender et al., the drastic decrease of surface hardness and elastic modulus near surface was related to the change in material properties because of in-diffusion of water.[34] The drastic decrease of PC-1 near surface would not be due to the influence of substrate but the moisture in atmosphere. The surface hardness and elastic modulus of PC were ∼ 0.16 and 2.4 GPa, respectively.[35] Since the surface hardness and elastic modulus of PC substrate were smaller than the coat film, these values were gradually decreased by increasing the displacement depth over 200 nm.

For quantitative discussion, the surface hardness and elastic modulus at 140 nm of displacement depth were compared. The results are shown in Table IV. The surface hardness was clearly improved by increasing the silica contents. Similar tendency was observed in the case of polystyrene-silica composites prepared with PHPS.[22] The surface hardness of coat film on glass was 2.7 GPa, when the volume fraction of silica was 76.4% (Glass6). The surface hardness of pure silica coat film prepared by the sol-gel method on polyester was 1.45 GPa, when the thickness of the silica coat was 128 nm.[36] The composites of P(MMA-co-HEMA) and PHPS with 76.4% of silica was harder than the pure silica coat. The surface hardness of pure silica prepared with PHPS was 3.2 GPa, when PHPS was converted to silica at room temperature for a month. Thus, the PMMA-silica nanocomposites prepared with PHPS showed good hardness. It should be notice that the surface hardness of coat film onto polycarbonate plate, 0.96 GPa, was close to that of the coat film onto glass substrate, 1.0 GPa, when the content of silica in the coat film was ∼ 50%. This indicates that the surface hardness of coat film did not depend on the substrate but the silica content. The surface hardness of coat film of polystyrene-silica composite with 28.6 vol % of silica (47.2 wt % of silica) was 0.74 GPa. The surface hardness of coat film with PMMA-silica composite with 24.6 vol % of silica was 0.75 GPa (Glass3). The surface of PMMA-silica composites was as hard as those of the PS-silica prepared with PHPS. In conclusion, the hard coated surface was provided on glass and polycarbonate substrates from

TABLE IV
Characteristics of Coat Film

Code	Substrate[a]	Polymer type	Volume fraction of SiO_2[b]	Thickness (μm)	Hardness (GPa)[c]	Elastic modulus (GPa)[c]
Glass1	Glass	RA2	0.0	4.41	0.33	6.2
Glass2	Glass	RA2	11.3	1.12	0.53	12.4
Glass3	Glass	RA2	24.6	0.68	0.78	13.0
Glass4	Glass	RA2	39.4	0.97	0.85	12.5
Glass5	Glass	RA2	49.3	0.95	1.00	14.6
Glass6	Glass	RA2	76.4	0.77	2.7	65.3
PC-1	PC	P(MMA-*co*-HEMA)1	49.2	4.14	0.96	9.1

[a] PC corresponds to polycarbonate plate.
[b] Volume fraction of silica in coat film.
[c] Force except for PC-1, 200 μN; force for PC-1, 750 μN.

the blend solution of P(MMA-*co*-HEMA) and PHPS by coating and drying on the substrate at room temperature.

CONCLUSIONS

PMMA-silica nanocomposites were prepared on glass substrate and polycarbonate plate by casting the blend solution of PHPS and P(MMA-*co*-HEMA) random copolymers with in a range from 13.7 to 15.1 mol % of HEMA content. The grafting of PHPS onto P(MMA-*co*-HEMA) in the blend solution was confirmed by FTIR. The molar ratio of [N—H] : [Si—H] of PHPS was not 1 : 2 but 0.58 : 2 because of its branch structure. All coat films prepared with PHPS were highly transparent. The surface hardness of coat film did not depend on the substrate but the silica content and type of preparation of silica. Higher the volume fraction of silica, harder the surface is. When the volume fraction of silica was 76.4%, the surface of coat film reached 2.7 GPa, which was larger than that of pure silica coat film prepared by sol-gel method. By using selective solvent, which was bad for the polycarbonate and good for P(MMA-*co*-HEMA) and PHPS, it was possible to coat the polycarbonate plate with the composite.

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