Effect of Solvent Composition on Transparency and Surface Hardness of Poly(methyl methacrylate)-Silica Nanocomposites Provided on Polycarbonate

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ABSTRACT: Poly(methyl methacrylate)-silica nanocomposites with 49 vol % of silica were prepared by blending poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) [content of 2-hydroxyethyl methacrylate: 15.1 mol %] with perhydropolysilazane in a ethylacetate/cyclohexane/xylene mixture, casting on polycarbonate (PC) substrates and drying for 24 h at room temperature. When the cyclohexane content in the solution was in a range from 21.7 to 32.3 vol %, composites were transparent in a wide range from 400 to 1000 nm of wavelength, the maximum surface hardness of composites on the substrate measured by nanoindentation was 1.07 GPa. Dynamic light scattering and viscometric analysis indicated that aggregates of poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) was formed in the mixture when the transparent composites were obtained on the PC substrates. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1498–1504, 2008

Key words: poly(methyl methacrylate); silicas; composites; polycarbonate; coating

INTRODUCTION

Polycarbonate (PC) is light, highly transparent, good biodegradable, and mechanically strong material, the application to many field in the place of glass is expected. The serious disadvantage of PC is bad antiscratching. To dissolve this problem, PC surface is generally coated with inorganic materials by gas phase or vacuum deposition (CVD and PVD).[1–8] Silica films prepared by CVD and PVD provided hard surface on the PC substrate. However, the coat layers did not adhere to the substrate because the solubility parameters and thermal expansion coefficients of the coating material and PC were too different.[4,5,8] To improve this problem, organic components were added to inorganic material. Highly transparent coat films were synthesized with metal alkoxides by sol–gel method or thermal cure and UV irradiational cure.[9–11] However, their process was complicated; they were not suitable for mass production and for coating on the rough surface with deep holes.

Silica is derived from perhydropolysilazane (PHPS) under ambient conditions (Scheme 1). PHPS is an oligomer with [SiH$_2$NH] of repeating unit with 700 of an average molecular weight. Because of the mild conditions for curing, PHPS is well used as a precer-amic material for silica insulator in electric devices. Organic-silica nanocomposites are formed with PHPS and organic polymer containing hydroxyl group. Scheme 2 shows the concept of synthesis of organic-silica nanocomposite with PHPS and organic polymer containing hydroxyl group. Si—H group in PHPS is highly reactive with hydroxyl group, PHPS is readily grafted onto the organic polymer containing hydroxyl group in solution. The graft copolymer with incompatible trunk and branch forms microphase separation in solid state.[12] Thus, microphase-separated film with the microdomains of organic polymer and PHPS is formed by casting the blend solution of PHPS and the organic polymer. When glass transition temperature of organic polymer is higher than the cure temperature (<100°C), curing of the composite resulted in the fixing of the morphology and the conversion of PHPS to silica. Based on this concept, poly(methyl methacrylate) (PMMA)-silica nanocomposites,[13–16] poly(2-vinyl pyridine)-silica nanocomposites, and polystyrene (PS)-silica nanocomposites[17] were synthesized.

There is a serious problem for using polymer-silica nanocomposites with PHPS as a coating material on PC. For coating, the composites were dissolved in a good solvent. The solubility of PMMA and PC were very similar, the selection of coat solvent, which was a good solvent for graft copolymer of PMMA and PHPS and a bad solvent for PC, was important. Ethyl acetate and xylene are good solvents for all sequences, and cyclohexane is a good solvent for
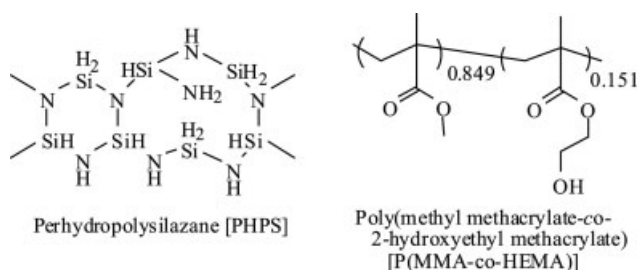
Scheme 1 Chemical structures of perhydropolysilazane and poly(methyl methacrylate-co-2-hydroxyethyl methacrylate).

PHPS and a bad solvent for both PMMA and PC. Addition of cyclohexane will prevent the damage of PC substrate. Taking into account the solvent composition of coat solution, micelle with PMMA core and PHPS shell will be formed in the coat solution. The structure of micelle will affect the microphase separation of coat film. Theoretically, the selectivity of solvent strongly influences the micelle formation of block and graft copolymer.[18] Therefore, the surface hardness and transparency of coat film will be controlled by the solvent composition of coat solution.

The purpose of this study is to clarify the effect of solvent composition of the preparation of hard coat film with PHPS. P(MMA-co-HEMA) with 15.1 mol % of HEMA was used for the organic polymer of composites. Volume fraction of silica in the composite was set to 49%. The aggregates formed in the coat solution were analyzed by dynamic light scattering (DLS) and viscometry. The surface hardness and transparency of coat films prepared with different solvent composition were measured by nanoindentation and UV–vis spectrometry, respectively.

EXPERIMENTAL

Materials

Ethyl acetate (Kanto, Japan, 99%), cyclohexane (Kanto, Japan, 99.5%), and benzene (Kanto, 99.5%) were dried with calcium hydride (Kanto, Japan, 95%) and distilled under vacuum before use.

Perhydropolysilazane (PHPS) solution (AZ Electronic Materials, Japan, NN-110, PHPS 20 wt % solution in xylene, 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, P(MMA-co-HEMA), was previously synthesized by free radical polymerization with α,α'-azobisisobutyronitrile and characterized elsewhere.[16] P(MAA-co-HEMA) was freeze-dried with benzene before use. HEMA content measured by ^{1}H NMR spectroscopy: 15.1 mol %, number-average molecular weight: 2.3 ×

10^4, and molecular weight distribution of random copolymer: 1.46.

Substrates: PC plate: IUPILON SHEET: NF-2000 Color: 552A (Mitsubishi Engineering-Plastics, Japan) with 75 and 25 mm in height and width.

Preparation of coat film

P(MMA-co-HEMA) was dissolved in dry ethyl acetate and PHPS solution was added under nitrogen. The solution was stirred for 24 h under nitrogen. Dry cyclohexane was gradually added to the solution. The solution was cast on three PC plates and gradually dried for 24 h at 20°C ± 2.5°C at RH = 32% ± 10%. The ingredients of coat solution are listed in Table I.

Analysis

#### DLS measurement of coat solution

The hydrodynamic of the aggregates in coat solution was measured with an electrophoretic light scattering spectrophotometer (Photal, Japan, ELS-8000) at 20°C with an angle of 90°.

Viscosity measurement of coat solution

The coat solution was gradually diluted with the mixture of ethyl acetate/cyclohexane/xylene with the same solvent composition to the coat solution till the polymer concentration became 0.01 wt %. Then the viscosity of the solution at each step was measured with an Ubbelohde viscometer at 25°C.

Nanoindentation

Surface hardness and elastic modulus of the coat film was recorded with a nanoindentor (triboscope, Hysitron, MN) attached to an atomic force microscope (AFM, SPM9500J2, Shimazu, Japan). The hard-
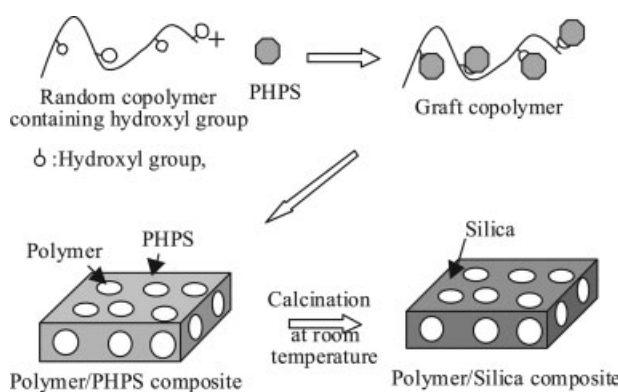
Scheme 2 Synthesis of organic and inorganic nanocomposite by using perhydropolysilazane.

TABLE I
Ingredient of Coat Solutions and Characteristics of Coat Films on Polycarbonate Substrates

	Coat solution					Coat film				
Code	Polymer concn. (wt %)	PHPS concn. (wt %)	Solvent (vol%)[a]			Film thickness (μm)	Volume fraction of SiO$_2$ (vol %)	Transparency (%)[b]	Hardness (GPa)[c]	Elastic modulus (GPa)[c]
			EtAc	CH	Xy					
PC-1	4.6	6.6	47.4	23.1	29.5	4.14	49.2	98.8	0.96	9.1
PC-2	4.2	6.1	51.3	21.7	27.1	5.06	49.3	99.4	0.93	8.7
PC-3	4.6	6.6	45.2	25.3	29.5	<6.0	49.2	–	–	–
PC-4	4.5	6.5	43.3	27.8	29.0	<6.0	49.4	–	–	–
PC-5	4.4	6.4	41.3	30.1	28.6	<6.0	49.3	–	–	–
PC-6	4.4	6.3	39.5	32.3	28.2	2.48	49.2	99.8	1.07	8.7
PC-7	4.3	2.1	49.9	40.8	9.3	<6.0	24.5	92.7	–	–

[a] EtAc, ethyl acetate; CH, cyclohexane; Xy, xylenes.
[b] Transmittance at 600 nm.
[c] Force 750 μN.

ness measurements were performed three times with a load ranging from 500 to 5000 μN, corresponding to a contact depth from 50 to 1200 nm with less than 0.05 and 0.15 of standard variations for surface hardness and elastic modulus, respectively.

UV–vis measurement

Transparency of the PC plate coated with composites was recorded with a UV–vis spectrometer (Jasco, V-530) in a range from 300 to 1100 nm. Error of each sample was less than 2%. Air was used for a reference.

Morphology observation by transmission electron microscopy

The ultra-thin film specimens with 60 nm thickness were cut out from the PC plate coated with composites with a microtome (Reinhert-Nissei Ultracut N). All the specimens were observed with a transmission electron microscope (Hitachi, H-7000) operating at 75 kV without staining.

RESULTS AND DISCUSSION

Preparation of coat solution

First, the composition of coat solution for transparent coat film was investigated. The ingredients of coat solution are listed in Table I. The solvent is a mixture of ethyl acetate, cyclohexane, and xylene. Again, ethyl acetate is a good solvent for polymer, PHPS. For readily grafting of PHPS on P(MMA-co-HEMA) in the coat solution and the suitable viscosity of coat solution for coating, the amount of ethyl acetate was determined by the concentration of polymer in polymer/ethyl acetate solution. The amount of xylene in coat solution is governed by the content of silica in the composites. Therefore, the main factor of the

composite of coat solution is the content of cyclohexane. It has been reported that grafting of PHPS onto P(MMA-co-HEMA) was completed by 24 h.[13] For grafting PHPS onto P(MMA-co-HEMA), P(MMA-co-HEMA), and PHPS were dissolved in an ethyl acetate and xylene mixture, and the solution was stirred for 24 h. Then, to prevent dissolution of the PC substrate to the coat solution, cyclohexane, which is a bad solvent for P(MMA-co-HEMA) and poly(carbonate) and a good solvent for PHPS, was gradually added to the solution. The graft copolymer will form the aggregate with PHPS shell and P(MMA-co-HEMA) core in solution. The PHPS shell will provide the hard surface on the PC plate. At 40.8 vol % of cyclohexane content (PC-7), the graft copolymer was precipitated. In contrast, the solutions with less cyclohexane content than 32.3 vol % were clear. However, the coat solution with less cyclohexane content than 20 vol % dissolved the PC substrate. Therefore, the optimum range of cyclohexane content was from 21.7 to 32.3 vol %.

Next, the coat solution was analyzed by DLS. Figure 1 shows DLS profiles of the coat solutions. The order of curves from bottom of Figure 1 corresponds to the cyclohexane content. In coat solution of PC-2 with 21.7 vol % of cyclohexane content, the hydrodynamic diameter of peak was less than 5 nm. The graft copolymer freely dissolved in the coat solution, the aggregate was not formed at 21.7 vol % of cyclohexane content. Over 23.1 vol % of cyclohexane content, new peaks over 100 nm appeared (PC-1 and PC-3-PC-6), indicating that the aggregates existed in the coat solutions. The increasing of cyclohexane content over 23.1 vol % increased the size of aggregates. It is reasonable because increasing of the content of the bad solvent for core sequence theoretically enlarges the aggregation number of graft or block copolymer in polymer micelle.[18–20] It should be noticed that the hydrodynamic diameter of aggregates at 32.3 vol % of cyclohexane content was close
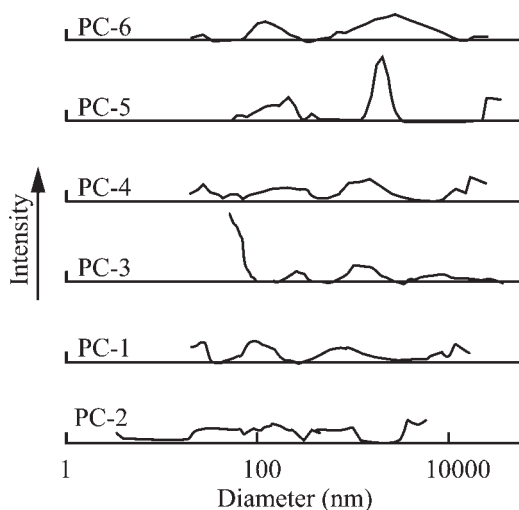
Figure 1 DLS profiles of coat solutions measured at 20°C.

Figure 2 Inherent viscosity of coat solutions measured with the Ubbelohode viscometer. Solution A: ethyl acetate/cyclohexane/xylene = 51.3/21.7/27.1 (v/v/v): PC-2 series. Solution B: ethyl acetate/cyclohexane/xylene = 39.5/32.3/28.2 (v/v/v): PC-6 series.

to 600 nm, suggesting that the solution may scatter the light. However, the coat solution was transparent. It would be due to the low difference of refractive indexes between the graft copolymer and solvent. The peaks corresponding to the aggregates were broad. In this work, P(MMA-*co*-HEMA) was synthesized by free radical polymerization, the distributions of molecular weight of P(MMA-*co*-HEMA) was 1.46. Therefore, the aggregates were polydispersed.

Concentration of graft copolymer is another important factor for the aggregation of polymers in selective solvent. To investigate the effect of graft copolymer concentration on the aggregate formation in the coat film, viscosity of coat solutions of volume fractions of ethyl acetate/cyclohexane/xylene = 51.3/21.7/27.1 (Solution A) and 39.5/32.7/28.2 (Solution B) was measured. The Solutions A and B correspond to PC-2 series and PC-6 series, respectively. Figure 2 shows the Fuoss-Mead plot[21] of Solutions A and B. The concentration, C, indicates the concentration of gloss of graft copolymer. In case of the Solution A, the slope of plots changed at 0.075 g/mL. Critical concentration to form the aggregate in Solution A was 0.075 g/mL. The concentration of graft copolymer of PC-2, 0.06 g/mL, was less than the critical concentration. Thus, the aggregate was not formed in the coat solution PC-2. On the way to drying, the aggregates may be formed. However, the formation of aggregate and the fixing of graft copolymer will be competitive in the composite. In case of the Solution B, the slope changed at 0.048 g/mL. The concentration of graft copolymer of PC-6, 0.06 g/mL, was higher than the critical concentration; the aggregates were formed in the coat solution PC-6. This agreed well with the DLS results. The slope of solution B was linear in a range from 0.048 to 0.094
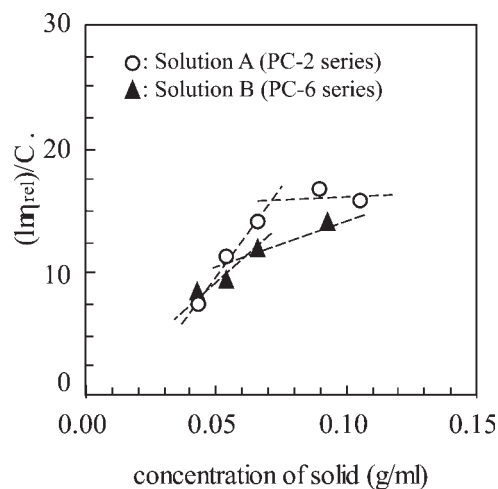
g/mL, the particle size will not be changed on the way to drying in the coat layer.

Transparency and surface hardness of coat film

The transparency and surface hardness of coat film were investigated. In case of PC-7, the coat film was powdery white. As described earlier, the graft copolymer was precipitated in the coat solution PC-7. Other coat films seemed transparent. For quantitative analysis, the transmittance of the authentic PC plates with and without washing with the coat solvent for PC-2 and the PC plates coated with composite was measured by UV–vis spectrometry. Figure 3 shows UV–vis spectra of the authentic PC plate, PC plate washed with solvent of PC-2 (PC-0), and PC
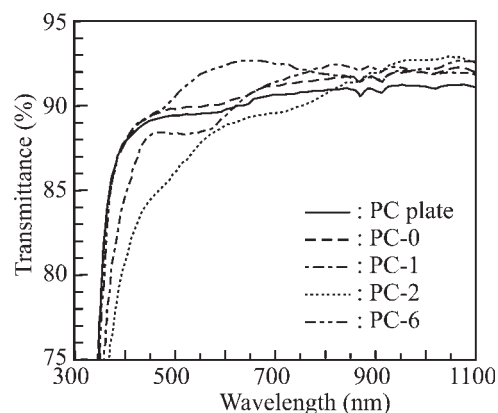

Figure 3 UV–vis spectra of authentic PC plate, PC plate washed with solvent for PC-2 (ethyl acetate/cyclohexane/xylene = 51.3/21.7/27.1 (v/v/v)), PC plates coated with PC-1, PC-2, and PC-6.

plates coated with PC-1, PC-2, and PC-6. The transmittance of these plates was close to that of authentic PC plate in the range from 400 to 1100 nm of wavelength, the solvent did not attack the surface of PC substrate. The drop of transmittance below 400 nm was due to the phenyl groups of PC (poly(bisphenol A carbonate)). Thus, an ethyl acetate/cyclohexane/xylene mixture with cyclohexane content in a range from 21.7 to 32.3 vol % was appropriate solvent for coating PC substrate. It should be noticed that the transmittance curves of the coated PC plates intercepted that of the authentic PC plate. The refractive indexes of PC, PMMA, and silica were 1.56 at 298 K, 589 nm,[22] 1.483 at 296 K, 632.8 nm,[23] and 1.46 at 587.6 nm,[24] respectively. The refractive index of coat film was lower than that of PC. The reduction of refractive index near the surface of plate by coating with composite decreases the reflectivity of film surface. Near 100% of transmittance, the effect of decreasing of reflectivity is not negligible. As a result, the curves of coated PC plate intercepted the authentic PC plate. However, the refractive index depends on wavelength. Additionally, the nanostructure of composite will influence the transmittance. Therefore, further discussion will be held elsewhere.

Surface hardness and elastic modulus of coat films of PC-1, PC-2, and PC-6 were measured by nanoindentation. Figure 4 shows the nanoindentation plots of surface hardness and elastic modulus measured at 750 μN of force. The standard variations of surface hardness and elastic modulus were 0.05 and 0.15, respectively. Surface hardness gradually and continuously decreased by increasing of displacement. At low displacement, the surface hardness of PC-2 was lower than PC-1 and PC-6. This indicates that the PC-2 was slightly softer than PC-1 and PC-6. When the displacement was larger than 20% of thickness of coat film, the surface hardness of substrate influenced that of coat film.[25] The thickness of coat film was in a range from 2.48 to 5.06 μm. To avoid the influence of substrate, the surface hardness, H, was determined at 200 nm of displacement. The H values measured with 750 μN of load are listed in Table I. The H values at 750 μN were ∼ 1. The silica contents of the coat films of this work were ∼ 49 vol %. To compare the H value of pure silica coat film with 128-nm thickness prepared on polyester, 1.45 GPa,[26] it is concluded that the hard coat films with organic-silica nanocomposite were formed on the PC substrate. The H value of PC-2 was slightly smaller than those of PC-1 and PC-6. As described earlier, the aggregates with PHPS shell were formed over 23.1% of cyclohexane content (PC-1 and PC-3–PC-6). By concentration of coat solution, silica matrix will be formed. To form hard surface, the formation of aggregates with PHPS shell is important. In conclusion, not only did the addition of cyclohexane pre-
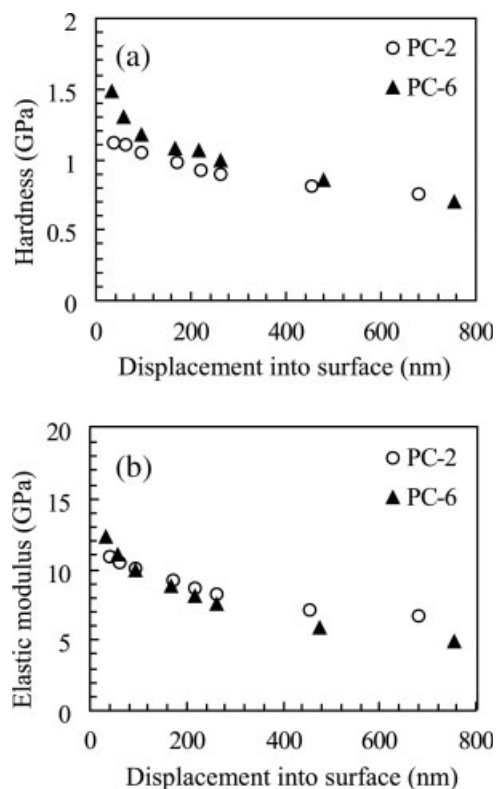

Figure 4 Surface hardness (a) and elastic modulus (b) of coat films of PC-2 and PC-6 on the polycarbonate substrates.

vent the attack of PC substrate, but also it increased the surface hardness.

Microphase separation of composite

The surface hardness strongly depends on the morphology of microphase separation of nanocomposites. Thus, the inner structure of composite was observed by transmission electron microscopy (TEM). In the composite, PHPS was converted to silica by drying at room temperature. Because of the higher electron density of Si atom than other atoms in the composites, silica domains were observed without staining by TEM at 75 kV. Figure 5 shows TEM micrographs of cross section of coat films of PC-2 and PC-6 on the PC substrate. White and dark regions correspond to PMMA-rich and silica-rich domains, respectively. In both specimens, the morphology was "PMMA-rich spheres in a silica-rich matrix." The silica-rich matrix provided hard surface. Additionally, PMMA-rich spheres, which reduce the hardness, did not exist near the surface but near the PC substrate. Therefore, hard surface was formed with the organic-silica nanocomposites with 49 vol % of silica. As described earlier, the aggregate was not formed in PC-2 but in PC-6. However, the morphology of both composites was PMMA-rich
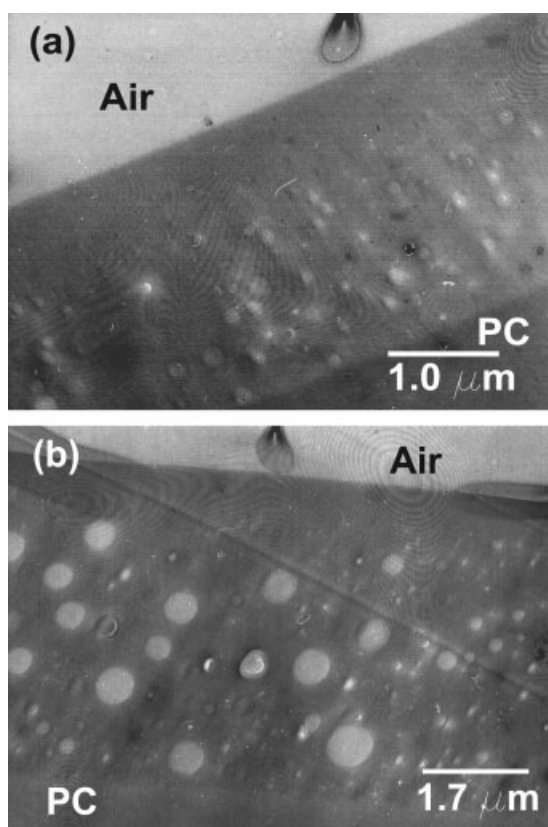
Figure 5 TEM micrographs of cross section of coat film of PC-2 and PC-6: (a) coat film of PC-2 and (b) coat film of PC-6.

PC, 9.5-11 $(cal/cm^3)^{1/2},[28]$ enhanced the localization of PMMA near the interface, the adhesion between composite layer and the PC substrate was increased. Diameters of PMMA-rich sphere were in a range from 0.05 to 0.4 μm for PC-2 and 0.1 to 0.6 μm for PC-6. The volume fractions of PMMA in PC-2 and PC-6 were very similar, ca. 49 vol %. However, the total area of white particles in the composites did not coincide. More total area of white region in PC-6 indicates that much amount of PMMA formed PMMA-rich spheres. In other words, in PC-6, the silica-rich matrix contained less PMMA. Again, the hardness of the composites originated from the silica network formed in the matrix. Reduction of PMAA content in the matrix increased the surface hardness. On the other hand, in case of PC-2, the formation of aggregate and fixing polymer in the coat film are competitive. The smaller particles observed for the coat film of PC-2 suggests that the formation of aggregate was incomplete and much amount of PMMA remained in the matrix. As a result, the surface hardness of PC-2 was lower than that of PC-6. Consequently, the formation of aggregates with organic polymer core-PHPS shell type aggregates in coat solution was important to form the hard surface.

spheres in the silica-rich matrix. This is explained as follows (Scheme 3): For PC-6, the aggregates with PMMA core-PHPS shell were condensed in the coat solution during drying. For PC-2, the critical concentration to form the aggregate was 0.075 g/mL, the aggregates were formed in the coat solution on the way to drying on the substrate. The molar ratio of PHPS to HEMA in feed was larger than 1.0. Solubility parameter of PHPS, 8.44 $(cal/cm^3)^{1/2},[13]$ was smaller than that of PMMA, 9.25 $(cal/cm^3)^{1/2}.[27]$ Excess PHPS was concentrated near the surface. The similar solubility parameters of PMMA, 9.25, and

CONCLUSIONS

To prepare transparent and hard coat film on the PC substrate, P(MMA-co-HEMA) and PHPS were dissolved in ethyl acetate/xylene mixture. Then, cyclohexane, which was a bad solvent for PMMA and PC and a good solvent for PHPS, was added to the solution. In the range from 23.1 to 32.3 vol % of cyclohexane content, PMMA core-PHPS shell type aggregates with 100–600 nm in the average diameter were formed. Cyclohexane in the coat solution prevented the dissolution of PC substrate. As a result, the surface of PC substrate was smoothly coated with PMMA/silica nanocomposites, and highly transparent coat film was obtained. The surface hardness
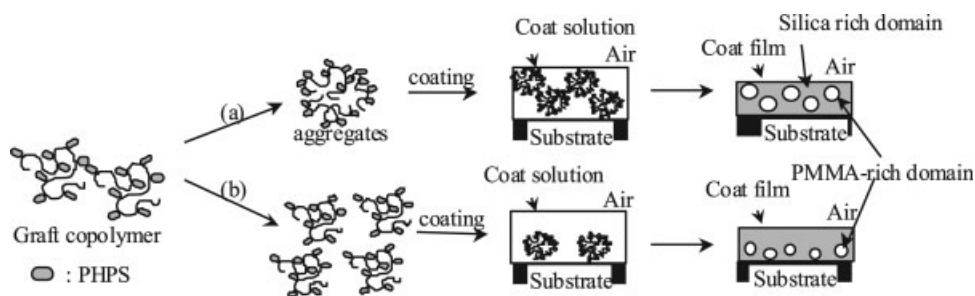
Scheme 3 Film formation mechanism of poly(methyl methacrylate)-silica coat film prepared from selective solvent systems: (a) PC-1 and PC-3-6 and (b) PC-2.

reached 1 GPa at 750 µN. Low cyclohexane content (21.7 vol %) did not induce the formation of aggregates in the coat solution, however, the morphology of the coat film was PMMA-rich spheres in the silica-rich matrix. It would be due to the formation of aggregates on the substrate during drying. The insufficient segregation of organic polymer decreased the size of PMMA-rich sphere and the surface hardness. Therefore, it was found that the addition of cyclohexane was useful not only to protect the PC substrate but also to increase the surface hardness.

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