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Preparation and characterization of organic–inorganic hybrids and coating films from 3-methacryloxypropylpolysilsesquioxane

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3-Methacryloxypropylpolysilsesquioxane (MA-PS) was prepared by acid- or base-catalyzed hydrolytic polycondensation of 3-methacryloxypropyltrimethoxysilane (MAS). MA-PS coating film was prepared by dip-coating on organic, metal and inorganic substrates, including poly(ethylene terephthalate), aluminum, stainless steel, and glass. The coating films on poly(ethylene terephthalate) and glass showed high adhesive strength. The hardness of coating films increased with increasing heat treatment temperature, whereas they decreased with increasing H_2O/MAS molar ratio. The refractive index of coating films increased with increasing heat treatment temperature. In addition, flat and transparent free-standing films (0.24–0.27 mm thickness) were prepared from MA-PS that were crack-free after heat treatment at 1000 °C.

Keywords: 3-methacryloxypropylpolysilsesquioxane; organic–inorganic hybrid; coating film; free-standing film; adhesive strength; hardness; refractive index

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1 INTRODUCTION

Organic–inorganic hybrid materials have been drawing attention as unique materials because of their novel characteristics provided by the combination of both organic and inorganic polymers. Organic–inorganic hybrids are classified in two categories from the viewpoints of domain sizes and chemical bonding. Organic–inorganic microcomposites are prepared by physical mixing of micrometer-sized organic and inorganic components. On the other hand, polymer hybrids are characterized by the formation of chemical bonds between organic and inorganic components to establish a mixing of organic and inorganic polymers at the molecular level.[1–9] Polymerization of carbo- and sila-functional monomers is often applied in the preparation of silicon-based organic polymer hybrids by a tandem polymerization and a simultaneous polymerization of both organo- and sila-functional groups in the monomer.

3-Methacryloxypropyltrimethoxysilane (MAS) has been expected to be a good precursor for polymer hybrids because it has both methacrylate and trimethoxysilyl groups in a molecule. Bobonneau and co-workers[9] reported that hydrolytic polycondensation of MAS provides linear or cyclic 3-methacryloxypropylsilsesquioxane (MA-PS) oligomers. Ishida and co-workers[10] reported that the reaction under neutral or basic conditions results in the formation of rubber-like solids or insoluble precipitates. In addition, we have reported the preparation of free-standing films from MAS via two processes: (1) polymerization of a methacrylate group followed by hydrolysis provided soft or flexible gel films, in which the tensile strength decreased with increasing carbon chain length; (2) hydrolysis of a methoxy group followed by polyaddition of a vinyldene group gave a tough hybrid gel plate with short carbon chain length.[11] Unfortunately, we were unable to design a simultaneous polymerization process.

In this work, the preparation of MA-PS and its application as a coating agent and a ceramic precursor were investigated according to the Scheme 1. A tandem polymerization of the hydrolysis and a subsequent polyaddition process

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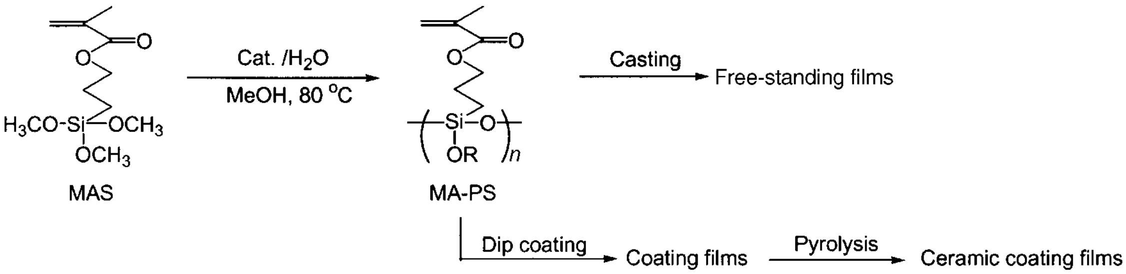

Scheme 1 Preparation of hybrid films from MAS.

was utilized, since we can expect the preparation of hybrid coatings and hard ceramic materials by this route.

2 EXPERIMENTAL

2.1 Reagents

MAS (Shin-Etu Chemical Industry Co., Ltd) was purified by distillation. Methanol and tetrahydrofurane (THF) (Wako Pure Chemical Co., Ltd) were dried and purified by conventional methods. Other reagents were used without further purification.

2.2 Preparation of MA-PS

Into a four-necked flask equipped with a stirrer, nitrogen inlet and outlet tubes, MAS and methanol were placed and stirred for 10 min at 0 °C. Water and catalyst (hydrochloric acid, ammonia (aq.), triethylamine, diazabicyclooctane, or sodium hydroxide) were added and stirred for 10 min. Then, the mixture was stirred at 70 °C for several hours at a fixed rate under a regulated nitrogen flow.[12] The highly viscous liquid thus obtained was dissolved in THF followed by filtration to remove an insoluble product as a white powder. A highly viscous liquid of MA-PS was obtained by evaporating the solvent under reduced pressure.

2.3 Preparation of coating films

The substrates utilized for coating were polypropylene (PP), high-density polyethylene (HDPE), poly(ethylene terephthalate) (PET), 6-Nylon, aluminum, stainless steel, soda-lime glass, quartz glass and silicon wafer. These substrates were cleaned in acetone for 30 min under ultrasonic irradiation. The substrate was immersed in an MA-PS 20 wt% acetone/methanol (w/w = 1) or methyl ethyl ketone solution and then pulled up at a rate of 80 mm min^{-1}. This process was repeated several times. The coating films thus obtained were dried at 80 °C for 24 h and then at 100 °C for 12 h. The coating films were placed in an electrical furnace and heated under nitrogen flow (50 ml min^{-1}) at a heating rate 5 °C min^{-1} with a hold for 1 h at each temperature.

2.4 Preparation of free-standing films

An MA-PS 20 wt% acetone/methanol (w/w = 1) solution was poured onto a polytetrafluoroethylene–polyperfluoroalkylvinylether copolymer (PFA) shale and heated at 80 °C for 21 days. The free-standing films were placed on an alumina boat and heated using an electric furnace under nitrogen flow (50 ml min^{-1}) at a heating rate of 5 °C min^{-1} with a hold for 1 h at each temperature.

2.6 Instruments

Gel permeation chromatography (GPC) was performed by using a High-performance liquid chromatography (Nihon Seimitsu Kagaku Co. Ltd or Shimadzu Co. Ltd): column (TOSOH G5000HXL/G3000HXL or Polymer Science Mixed D); solvent: THF; flow rate: 1.0 ml min^{-1}; detector: RI-3H (Nihon Bunseki Kogyo Co., Ltd.) or SPD-10A (Shimadzu Co. Ltd). Polystyrenes were used as standards.

Infrared (IR) spectra were recorded by the carbon tetrachloride solution method or the transmission mode (KBr disk method or by coating films on a silicon wafer) using a JEOL JIR-5300 spectrophotometer or a JASCO FT/IR 410 spectrophotometer.

^{1}H and ^{29}Si nuclear magnetic resonance (NMR) spectra were recorded using JEOL JNM-PMX 60Si

Table 1 Hydrolytic polycondensation of MAS[a]

		Molar ratios			Molecular weight[b]		Crude yields (g)	
Run	Catalyst	Cat./MAS	H_2O/MAS	Temp. (°C)	M_n	M_w/M_n	MA-PS	Powder
1	HCl	1.05×10^{-1}	1.5	70	2200	1.6		
2				100	2200	1.6		
3				150	2300	1.7		
4				200	–	–[c]		
5	NH_3	1.0×10^{-1}	3.0	70	620	1.9	9.39	–
6		3.2×10^{-1}			780	2.1	9.19	–
7	NEt_3	1.0×10^{-1}	3.0	70	2100	2.0	7.89	–
8		2.7×10^{-1}			2400	2.0	7.79	–
9	DABCO	2.7×10^{-1}	3.0	70	6800	6.1	7.43	–
10	NaOH	5.4×10^{-5}	3.0	70	2700	1.6	7.76	–
11		2.7×10^{-3}			>35 000[d]	–[d]	7.27	–
12[e]		2.7×10^{-2}			9000	5.9	6.40	0.28
13[e]		5.7×10^{-2}			2900	2.1	6.10	0.27
14[e]		2.7×10^{-1}			390	1.0	0.18	4.97

[a] Scale of operation: MAS, 10.4 g (4.2×10^{-2} mol); MeOH, 14 ml. Temp.: 70 °C. Time: 3 h. Nitrogen flow rate: 360 ml/min^{-1}.
[b] Polystyrene standard.
[c] Gelation.
[d] Over the exclusion limit of the column.
[e] Methacryloxy group was hydrolyzed.

or JEOL JNM-AL300 instruments in chloroform-*d* or methanol-d_4 in the presence of tetramethylsilane as an internal standard.

Differential thermal analysis and thermogravimetry (DTA-TG) was performed using a Thermoflex (high-temperature type) TG8112BH (Rigaku Co., Ltd). The sample was heated at 10 °C min^{-1} to 1200 °C in an air atmosphere.

Adhesion was evaluated based on the Japanese Industrial Standard (JIS) K5400 by a cross cut tape test.[13] The pencil-hardness was also evaluated according to JIS K5400 by a pencil scratch test.

The thickness of the coating films was measured by surface shape gauge. The refractive index of the coating films was found by the ellipsometric parameter, measured by a Mizojiri Kogaku Kogyosho DVA-36VW spectroellipsometer. The measurement was carried out at 6328 Å with an He–Ne beam using the coating films on the silicon wafer. Transparency at 500 nm was measured by a JASCO UVIDEC-610 using the coating films on the quartz glass.

The cross-section of the coating films was observed using a Hitachi S-4500 field emission type scanning electron microscope (FE-SEM).

The peak areas of the T^1, T^2, and T^3 signals in ^{29}Si NMR spectra were calculated by means of deconvolution of the original spectra using Peak-Fit™ software with Gaussians.

3 RESULTS AND DISCUSSION

3.1 Hydrolytic polycondensation of MAS

MA-PS was hydrolyzed under nitrogen flow. As we have already reported, this method is a useful and convenient technique to produce high molecular weight polysilsesquioxane sols as a highly viscous liquid.[12,14,15] A key process is the introduction of nitrogen gas throughout the hydrolysis reaction. Gel formation is retarded by removing methanol and water during the hydrolysis, which will promote further condensation reactions to form gels.

Table 1 summarizes the results on the preparation of MA-PS. Hydrolysis was carried out in the presence of hydrochloric acid, ammonia, triethylamine, diazabicyclooctane, or sodium hydroxide. An MA-PS oligomer ($M_n = 2200$) was produced by the hydrolysis of MAS under acidic conditions (run 1). The M_n was almost constant even with increasing

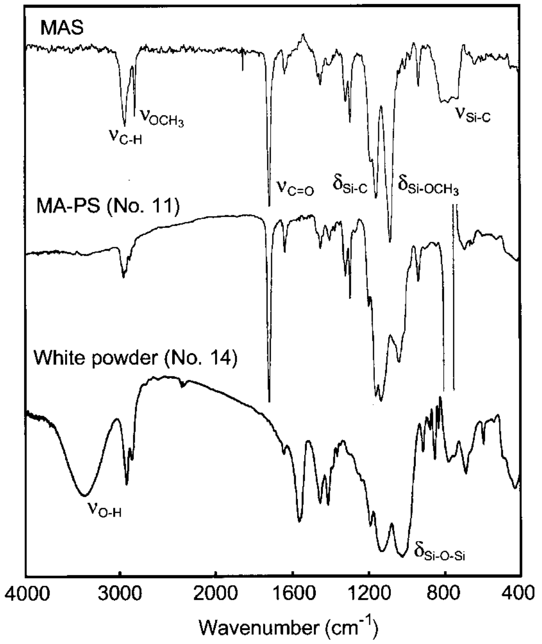

Figure 1 FTIR spectra of MAS, MA-PS (no. 11) and white powder (no. 14). (CCl_4 solution method for MAS and MA-PS and KBr disk method for white powder).

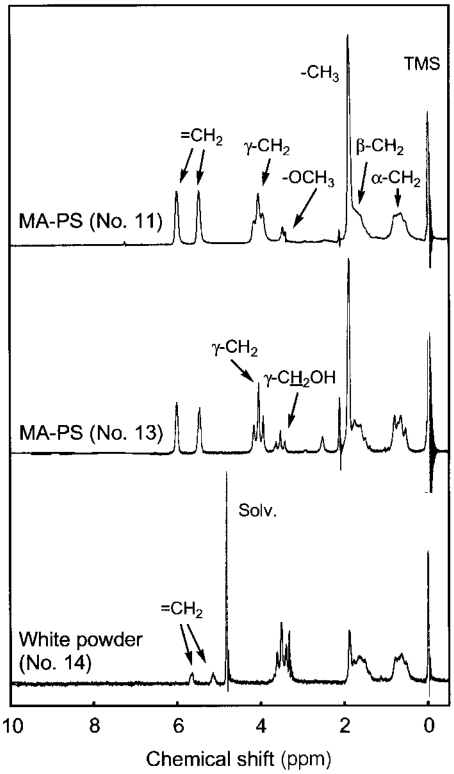

Figure 2 ^{1}H NMR spectra of MA-PS (nos 11, 13) and white powder (no. 14); (solvent: $CDCl_3$ for nos 11 and 13 and CD_3OD for white powder).

temperature (runs 2 and 3). MA-PS gelled at elevated temperatures (run 4). Hydrolysis of MAS in the presence of volatile bases provided MA-PS oligomers (runs 5–8). MA-PS polymers with a high M_n were produced when non-volatile bases were utilized as catalysts (runs 9–14). On hydrolysis under more severe conditions (runs 12–14), a white powder was produced with elimination of an ester group.

MA-PS (runs 10–14) was soluble in THF, chloroform, benzene, and acetone, and was insoluble in hexane and alcohols. MA-PS (runs 5–9) was soluble in every organic solvent used. The white powder (runs 12–14) was soluble in alcohols. Figure 1 shows the FTIR spectra of MAS, MA-PS (run 11) and white powder (run 14). The absorption peak intensity due to $\nu_{\mathrm{Si{-}OCH_3}}$ (1080 cm^{-1}) decreased in conjunction with the increasing peak intensity due to $\nu_{\mathrm{Si{-}O{-}Si}}$ (1130 cm^{-1}), which indicates the progress of hydrolytic polycondensation of MAS to form MA-PS. The disappearance of the absorption peak due to $\nu_{\mathrm{C{=}O}}$ and the appearance of the peak due to ν_{OH} indicate hydrolysis of the methacryloxy group to form 3-hydroxypropylpolysiloxane. The ^{1}H NMR spectra of MA-PS (run 11) and white powder (run 14) shown in Fig. 2 indicate signals due to α-CH_2, β-CH_2, —CH_3, γ-CH_2, and =CH_2 appeared at 0.7 ppm, 1.7 ppm, 1.9 ppm, 4.05 ppm, and at 5.5 and 6.05 ppm respectively. With increasing molar ratio of sodium hydroxide the 3-methacryloxy group is hydrolyzed to provide 2-hydroxy groups, which appear as a new signal due to γ-CH_2 with a small shift. In the spectrum of the white powder (run 14), the signals due to H_2C=, —CH_3, and γ-CH_2 become weak with the appearance of the signal due to γ-CH_2OH.

Based on the results shown in Table 1, sodium hydroxide was selected as the best catalyst to produce MA-PS polymers. The reaction condition was studied in detail by varying the molar ratio of water and sodium hydroxide against MAS. Table 2 summarizes the results on hydrolytic polycondensation of MAS using sodium hydroxide as a catalyst. MA-PS gelled on hydrolysis in run 15. With increasing H_2O/MAS molar ratio in runs 16–19, M_w and polydispersity (M_w/M_n) decreased uniformly, since the condensation rate is depressed to retard the gellation. The T^3% increased with

Table 2 Molecular weight and siloxane unit (T^n) of MA-PS prepared by sodium-hydroxide-catalyzed hydrolysis of MAS[a]

	Molar ratios		Molecular weight[b]		T^n composition (%)[c],[d]		
Run	H_2O/MAS	NaOH/MAS	M_w	M_w/M_n	T^1	T^2	T^3
15	1.3	1.80×10^{-3}	–[e]	–[e]	–[e]	–[e]	–[e]
16	1.5	1.80×10^{-3}	102 200	7.3	2	16	82
17	2.0	1.80×10^{-3}	76 000	3.8	0	1	99
18	3.0	1.80×10^{-3}	65 600	4.1	0	1	99
19	4.0	1.80×10^{-3}	30 800	2.2	0	6	94
20	2.0	1.35×10^{-3}	42 500	2.5	0	3	97
21	2.0	0.70×10^{-3}	13 300	1.9	2	10	88

[a] Scale of MAS in operation: 0.252 mol. Temp.: 70 °C. Time: 6.5 h. Nitrogen flow rate: 360 ml min^{-1}.
[b] Polystyrene standard.
[c] Calculated based on the peak area of ^{29}Si NMR spectrum.
[d] T^n denotes the unit structures $CH_2{=}(CH_3)C{-}COO(CH_2)_3Si(OSi)_n(OMe)_{3-n}$ (n = 1–3).
[e] Gelation.

increasing H_2O/MAS molar ratio; this suggests the formation of highly condensed polysilsesquioxanes. Comparing the results of runs 17, 20, and 21, the increasing concentration of sodium hydroxide yielded high molecular weight MA-PS with higher T^2 up to 16%.

Figure 3 shows the ^{29}Si NMR spectra of MA-PS prepared under various H_2O/MAS molar ratios in the presence of sodium hydroxide. Signals due to T^1, T^2 and T^3 appeared at −50.7 ppm, −57.5 to −60 ppm and −63 to −70 ppm respectively. Signals due to T^1 and T^2 decreased with increasing molar ratio. Signals due to T^3 were split into several peaks. According to Kelts *et al.*,[16] the signals at −64, −65.5 ppm and −66.5 ppm were assigned to a three-membered ring, a four-membered ring and a bridged four-membered ring respectively. The three- or four-membered ring increased in MA-PS with increasing H_2O/MAS molar ratio.

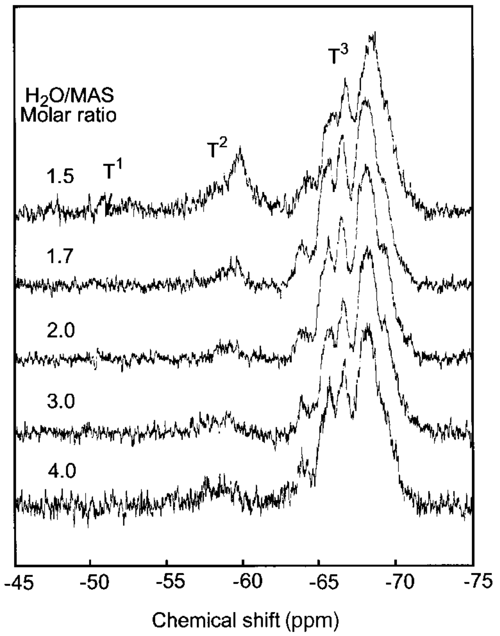

Figure 3 ^{29}Si NMR spectra of MA-PS prepared under various H_2O/MAS molar ratios; (solvent: $CDCl_3$).

3.2 Preparation of coating films

Table 3 summarizes the adhesion of MA-PS and the solubility parameters of organic polymers. MA-PS coating films were prepared successfully on PET and 6-Nylon, whereas there was no formation on PP and HDPE. Coating film formation was estimated by the difference of solubility parameters between polymer substrate and MA-PS, which indicates the difficulty of coating film formation on PP and HDPE substrates with a large solubility parameter deviation. On the other hand, coating films were prepared on aluminum, stainless steel, glass and silicon wafer by the formation of covalent bonds between silanol in MA-PS and hydroxy groups on the surface of the substrates.

Figure 4 shows the FE-SEM photographs of the cross-section of coating films prepared from MA-PSs run 17 (a) and run 21 (b) followed by heating at 100 °C for 12 h. These photographs reveal that uniform coating films with a very smooth surface were formed. The thicknesses of the coating films

Table 3 Adhesion of MA-PS coating films[a] and the solubility parameter of substrates and MA-PS

Substrate	Adhesion of MA-PS coating film	Solubility parameter of substrate
PP	No	8.02
HDPE	No	8.56
PET	Yes	11.7
6-Nylon	Yes	11.9–12.5
Aluminum	Yes	
SUS304	Yes	
Glass	Yes	
Silicon wafer	Yes	
MA-PS		13.3

[a] Solvent: methyl ethyl ketone. Pretreatment: ultrasonic washing with acetone or methanol for 1 h. Winding speed: 80 mm min^{-1}. Heating condition: 80 °C for 24 h.

were 0.84 μm (a) and 0.66 μm (b), since MA-PS with lower methoxy group content provides a dense and thick coating film by depressing the shrinkage on aging due to the elimination of the methoxy group.

Table 4 shows the adhesive strength and the pencil-hardness of coating films evaluated by JIS K5400. The coating films were prepared by hydrochloric acid (run 1) or sodium hydroxide (runs 16–19, 21) catalyzed hydrolysis of MAS. MA-PS (run 1) showed the maximum adhesion strength (point 10) for PET, aluminum, stainless steel, and glass but not for 6-Nylon. MA-PS (runs 16–19, 21) coating films showed the maximum adhesion strength (point 10) on PET and glass, whereas minium adhesion strength (point 0) was exhibited on 6-Nylon, aluminum and stainless steel. Comparing the adhesion strengths of PET and 6-Nylon, MA-PS adheres more strongly to PET than 6-Nylon probably because of dipolar–dipolar interaction between carbonyl groups in MA-PS and PET. Since adhesion strength of coating films on metal or glass substrates increases with increasing methoxy groups remaining in MA-PS, MA-PS in run 1 showed a stronger adhesion than those of MA-PS in runs 16–19 and 21. The pencil-hardness of MA-PS coating films on glass substrate was 6H or 7H, and it was almost the same regardless of the molecular weight of MA-PS.

Figure 5 shows the FTIR spectra of the coating films on a silicon wafer after heat treatment at various temperatures under nitrogen atmosphere. The coating film was crack-free even after pyrolysis at 1000 °C. With increasing heat treatment temperature, the absorption peaks due to ν_{OH}, $\nu_{\mathrm{C—H}}$, and $\nu_{\mathrm{C=O}}$ disappeared with an increasing peak intensity due to $\nu_{\mathrm{Si—O—Si}}$ and $\nu_{\mathrm{Si—C}}$. The hydroxy group and the organic groups disappeared by combustion at 500 °C and 800 °C respectively, which indicates the formation of an amorphous silica and silicon carbide coating film on the silicon wafer, as was suggested for heat treatment of vinylsilsesquioxanes.[15]

Figure 6 shows the transmittance at 500 nm of the coating films pyrolyzed at various temperatures. The transmittance decreased slightly up to 300 °C

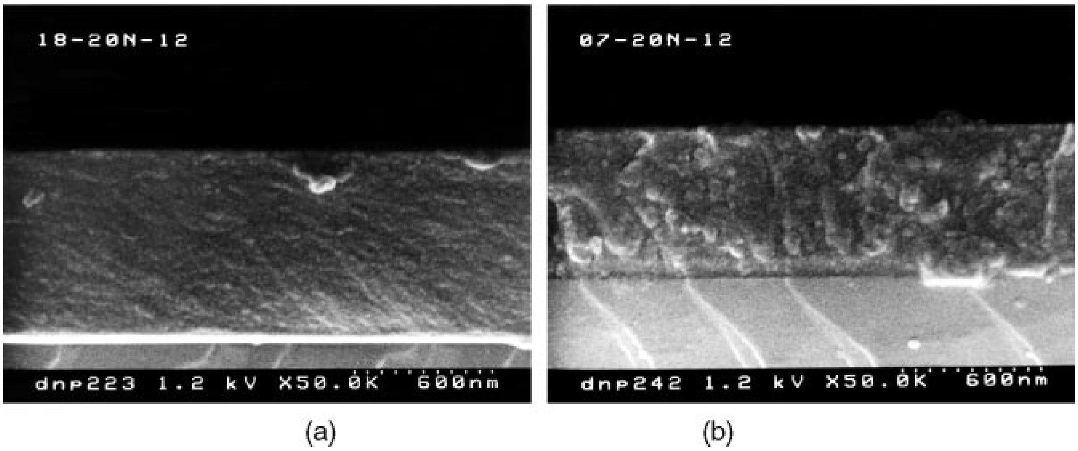

Figure 4 SEM photographs of cross-section of MA-CS (no. 17 (a) and no. 21 (b)) coating films.

Table 4 Adhesive strength and pencil-hardness of coating films[a,b]

Run no. of MA-PS	Adhesive strength[c,d] PET	6-Nylon	Aluminum	Stainless steel	Glass	Pencil-hardness[d,e]
1	10	0	10	10	10	7H
16	10	0	0	0	10	7H
17	10	0	0	0	10	7H
18	10	0	0	0	10	7H
19	10	0	0	0	10	6H

[a] Evaluated based on JIS K5400.
[b] No adhesions for PP and HDPE.
[c] Coating conditions: number of dipping, 1; winding speed, 80 mm min^{-1}.
[d] Coating films were heated at 80 °C for 24 h and then at 100 °C for 12 h.
[e] Coating conditions: numbers of dipping, 3; winding speed, 80 mm min^{-1}; substrate, soda-lime glass.

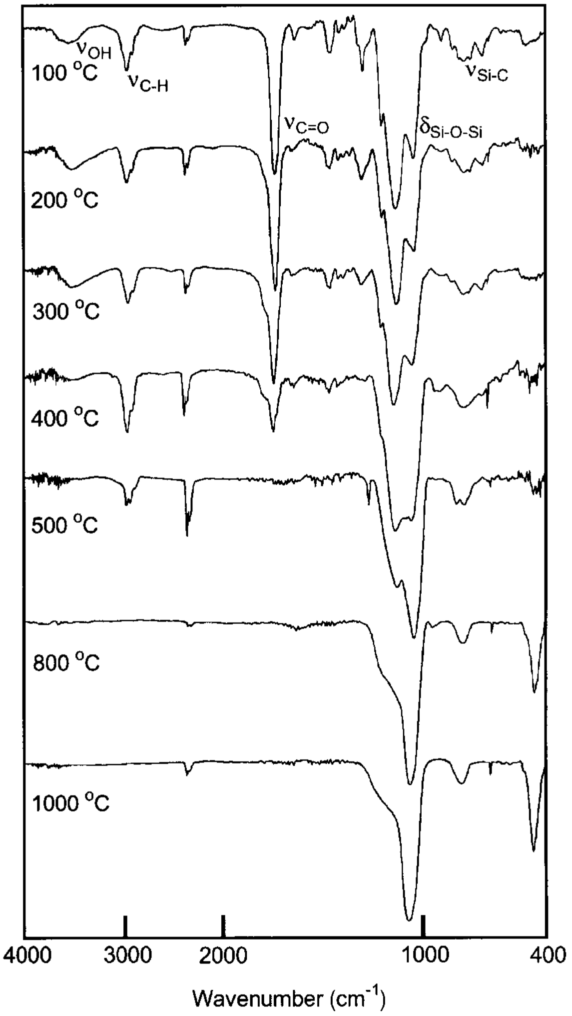

Figure 5 FTIR spectra of coating films on heating.

and rapidly up to 800 °C, which was due to the formation of carbon in the silica matrix caused by the combustion of 3-methacryloxypropyl and methoxy groups on pyrolysis. The transmittance significantly increased upto 1000 °C, which is caused by the combustion of carbon to provide a thin coating film of silica.

Table 5 shows the pencil-hardness of the coating films on a silicon wafers after heat treatment at various temperatures. The pencil-hardness of coating films increased with increasing heat treatment temperature and finally became 9H at a temperature of more than 800 °C, which is consistent with the combustion of 3-methacryloxypropyl and methoxy groups to provide a porous or low-density silica followed by densification. The pencil-hardness decreased with increasing molar ratio H_2O/MAS,

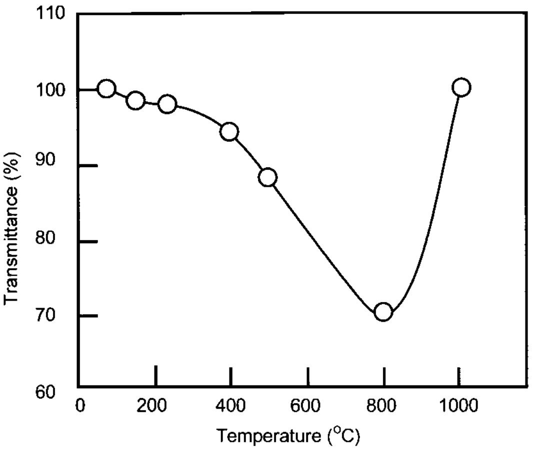

Figure 6 Transmittance of coating films on heating.

Table 5 Pencil-hardness of coating films on sintering at various temperatures[a,b,c]

Run no. of MA-PS	Pencil-hardness at each heat treatment temperature (°C)						
	100	200	300	400	500	800	1000
1	3H	5H	6H	7H	7H	9H	9H
16	5H	6H	7H	7H	9H	9H	9H
17	4H	6H	7H	4H	9H	9H	9H
18	4H	4H	6H	7H	9H	9H	9H
19	3H	3H	3H	5H	7H	9H	9H

[a] Evaluated based on JIS K5400.
[b] Coating conditions: number of dipping, 10; winding speed, 80 mm min^{-1}; substrate, silicon wafer.
[c] Coating films were sintered at 80 °C for 24 h and then 1 h at target temperature.

which is consistent with increasing T^3% of MA-PS to result in rapid densification to form silica.

Figure 7 illustrates the thickness (run 16) of the coating films on heat treatment, which decreased uniformly from 2.1 μm to 0.4 μm. The combustion of organic groups results in the formation of porous silica with shrinkage followed by densification of silica gel.

The refractive indices of the coating films (runs 16, 17 and 21), as shown in Figure 8, decreased at 200 °C; this is caused by the combustion of organic groups to form a porous silica. On raising the heat treatment temperature, the densification of silica provides a high-density silica and leads to an increase in the refractive indices. The refractive index increased more rapidly with increasing T^3% of MA-PS, which is caused by a rapid densification of silica on heat treatment.

3.3 Preparation of free-standing film

Figure 9 shows a photograph of a free-standing film. A flat, transparent, and flexible free-standing film (thickness 0.24–0.27 mm) was provided by aging hydrochloric-acid-hydrolyzed MAS (run 1) at 80 °C for 21 days in a PFA shale.

The free-standing film was then transformed to a ceramic film by sintering under a nitrogen atmosphere at 1000 °C to provide a crack-free film. With increasing heat treatment temperature, the film

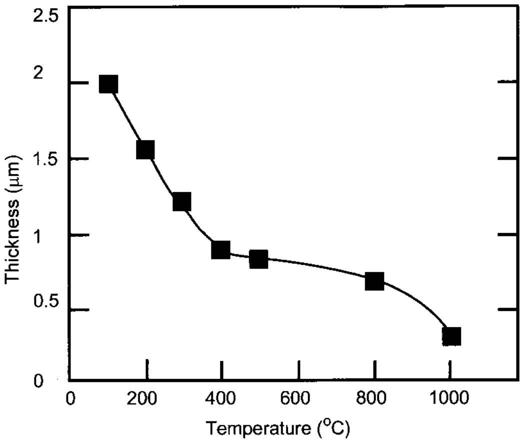

Figure 7 Thickness of coating film on heating.

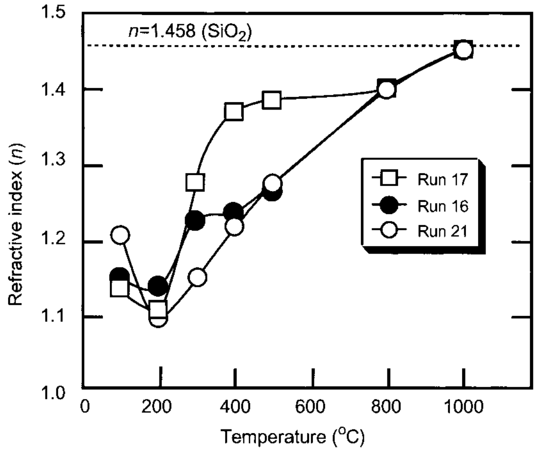

Figure 8 Refractive indices of coating films on heating.

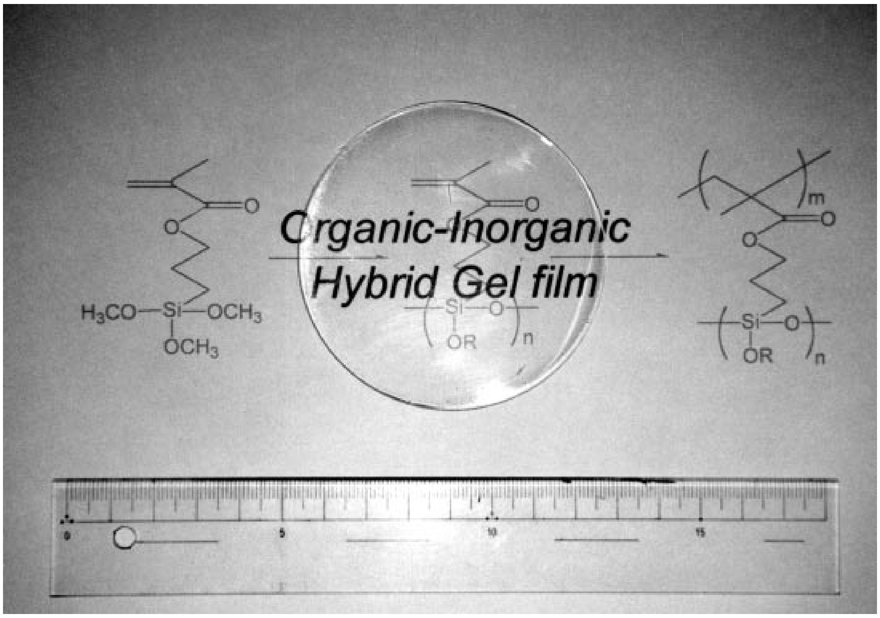

Figure 9 Photograph of MA-CS free-standing films.

became yellow, brown, black at 500 °C, and then purplish black at 1400 °C. The weight loss of the film at 1400 °C was 58%. The film was flexible up to 400 °C, and became rigid over 500 °C.

4 CONCLUSION

MA-PS was prepared by acid- or base-catalyzed hydrolytic polycondensation of MAS. When sodium hydroxide was employed as a catalyst, MA-PS was formed, while the methacryloxy group was hydrolyzed under high molar ratios of sodium hydroxide/MAS. MA-PS coating films were prepared on PET, 6-Nylon, aluminum, stainless steel, glass, and silicon wafer. Coating films on PET, metal and glass showed high adhesive strength. The hardness of the coating films increased with increase in sintering temperature and decrease in water/MAS molar ratio. The refractive index of the coating films increased with an increase in heat-treatment temperature.

Flat and transparent free-standing films were prepared from a 20 wt% acetone/methanol (w/w = 1) solution from MA-PS by casting onto PMP or PFA shale followed by ageing at 80 °C. These films provided crack-free ceramic films after the heat treatment at 1000 °C due to the formation of Si—O—C ceramics.

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REFERENCES

1. Kojiyama S, Tsubata H, Urayama K. *Bull. Chem. Soc. Jpn.* 1998; **71**: 961.
2. Sherman MA, Kennedy JP. *J. Polym. Sci.: Part A: Polym. Chem.* 1998; **36**: 1891.
3. Tadanaga K, Azuta K, Minami T. *J. Ceram. Soc. Jpn.* 1997; **105**: 555.
4. Chan CM, Cao GZ, Fong H, Sarikaya M, Robinson T, Nelson L. *Materials Research Society Symposium Proceedings*, vol. 576. MRS: Pittsburg, PA, 1999; 319.
5. Wojcik AB, Klein LC. *J. Sol–Gel. Sci. Technol* 1995; **4**: 57.
6. Zhou W, Dong JH, Qin KY, Wei Y. *J. Polym. Sci.: Part A: Polym. Chem.* 1998; **36**: 1607.
7. Kosemann R, Schmid HK, Wintrich E. *Better Ceramics Through Chemistry VI*, Brinker CJ, Clark DE, Ulrich DR (eds) *Materials Research Society Proceedings*, vol. 346. MRS: Pittsburg, PA, 1994; 915.

8. Etienne P, Denape J, Paris JY, Phalippou J, Sempere R. *J. Sol–Gel Sci. Technol*. 1996; **6**: 287.
9. Delattre L, Dupuy C, Bobonneau F. *J. Sol–Gel Sci. Technol*. 1994; **2**: 185.
10. Miller JD, Hoh K-P, Ishida H. *Polym. Composites* 1984; **5**: 18.
11. Abe Y, Honda Y, Gunji T. *Appl. Organomet. Chem.* 1998; **12**: 749.
12. Takamura N, Gunji T, Hatano H, Abe Y. *J. Polym. Sci.: Part A: Polym. Chem.* 1999; **37**: 1017.
13. Japanese Industrial Standards Committee. *Testing Methods for Paints*. JIS K5400, 1990; 74.
14. Abe Y, Hatano H, Gunji T. *J. Polym. Sci.: Part A: Polym. Chem.* 1995; **33**: 751.
15. Abe Y, Taguchi K, Hatano H, Gunji T, Nagao Y, Misono T. *J. Sol–Gel Sci. Technol*. 1994; **2**: 131.
16. Kelts L, Armstrong N. *J. Mat. Res.* 1989; **4**: 423.