JOURNAL OF MATERIALS SCIENCE 29 (1994) 5773–5778

Coating of polymethylmethacrylate with transparent SiO_2 thin films by a sol–gel method

R. MIZUTANI, Y. OONO, J. MATSUOKA, H. NASU, K. KAMIYA
Department of Chemistry for Materials, Faculty of Engineering, Mie University, Tsu-shi, Mie-ken 514, Japan

In order to improve the surface characteristics of polymethylmethacrylate (PMMA), oxide thin-film coatings were applied using the sol–gel dip-coating technique. The $Si(OC_2H_5)_4$ (TEOS), $CH_3Si(OC_2H_5)_3$ (MTES) or $Ti(O\text{–}i\text{–}C_3H_7)_4$ (TIP) was used as a starting material for SiO_2 or TiO_2 coating. The hardness of the alkoxy-derived oxide-coated PMMA was increased from 200 MPa for non-coated PMMA with increasing film thickness. By optimizing the heating conditions and the hydrolysis conditions, and by repeating the dip-coating/heating processes, a hardness as high as 325 MPa was achieved in the PMMA triply coated with the TEOS-derived SiO_2 film using the withdrawal velocity of 0.30 mm s^{-1} and heat treatment at 80 °C. The increase in hardness with the thickness of coating film was saturated before reaching that of bulk silica-dried gel (ca. 500 MPa), which may be due to the increased porous nature of the thick films.

1. Introduction

The coating of semiconductors, metals, glasses and ceramics with oxide thin films is one of the most important applications of the sol–gel process, and has been extensively studied [1–4]. The substrate material is provided with new functionality and its surface characteristics improved by the sol–gel coatings [1–6]. Because the sol–gel technique enables the fabrication of oxide materials at relatively low processing temperatures compared to the conventional methods, it is expected that the oxide coating may also be applicable to organic plastics.

Many organic polymers having good properties with respect to the main application, sometimes fail in practical use because of their surface softness. For an example, transparent synthetic polymers which are prepared with excellent optical applications can only be used for limited optical applications at the present time, because the optical quality is easily and rapidly degraded by the surface being scratched with dust or by mechanical contacts. Polymethylmethacrylate (PMMA) is one of the scratch-resistant organic polymers, but its hardness is still far from that of oxides or metals. Therefore, much effort has been made to overcome these disadvantages by applying metal or oxide coatings using techniques such as electrodeposition and chemical vapour deposition (CVD). The sol–gel coating of organic plastics based on ORMOSIL (organic/inorganic composite SiO_2) is also one of the improvements [7].

In present study, silicon or titanium oxide thin-film coating was applied to PMMA substrate using the sol–gel dip-coating technique to increase the surface hardness. The effects of the composition of the starting solution, heating conditions, hydrolysis conditions, and repetition of the dip-coating/heating process, on the surface hardness of the resultant oxide-coated PMMA, was investigated.

2. Experimental procedure

Oxide thin-film coatings were applied to polymethylmethacrylate (PMMA, Asahi Kasei Co. DELPET 80N) substrates using the sol–gel dip-coating technique.

For the SiO_2 composition, commercially available tetraethyl-ortho-silicate, $Si(OC_2H_5)_4$ (TEOS) or monomethyl-tri-ethoxy-silane, $CH_3Si(OC_2H_5)_3$ (MTES) were used as starting material without further purification. Alkoxide–H_2O–C_2H_5OH–HCl solutions of various compositions (in molar ratio, see Table I) were prepared. First, the alkoxide was diluted with half of the prescribed amount of anhydrous ethyl alcohol. Then, the remaining half of ethyl alcohol containing the desired amount of water and HCl (catalyst), was slowly added to the above solution using a burette whilst stirring at room temperature, so that a clear solution resulted.

For the TiO_2 coating, titanium-tetra-isopropoxide, $Ti(O\text{–}i\text{–}C_3H_7)_4$ (TIP) was used as a starting material. The solution consisting of TIP, H_2O, C_2H_5OH and HCl in the molar ratio of 1:6:6:0.8 (Table I) was prepared in a similar manner to that for the SiO_2 composition. The solutions used for the dip-coating were aged for about 2 h at room temperature before use.

PMMA substrate (40 mm × 20 mm × 3 mm), which was ultrasonically cleaned with distilled water beforehand, was dipped into the solution, held there for 10 s, and then pulled up vertically. The withdrawal

0022-2461

TABLE I Composition (molar ratio) of starting sol solution used in the experiment

Alkoxide[a]	Amount of chemicals in molar ratio to alkoxide		
	H_2O	C_2H_5OH	HCl
TEOS	6	6	0.03
	3	6	0.03
	2	6	0.03
MTES	6	6	0.01
TIP	6	6	0.80

[a] TEOS, $Si(OC_2H_5)_4$; MTES, $CH_3Si(OC_2H_5)_3$; TIP, $Ti(O\text{-}i\text{-}C_3H_5)_4$.

velocity was varied in the range 0.15–0.8 mm s^{-1}. The assembly used for the dip-coating is shown schematically in Fig. 1.

The gel-coated PMMA substrate was dried in an ambient atmosphere for 5 min, and then heated at 80 °C (just below the glass transition temperature of PMMA) for 6 h, or at 120 °C for 5 min. Heat treatment at 120 °C for longer than 5 min was not carried out because the PMMA substrate exhibited viscous flow.

The thickness of the coating films was measured with a stylus profilometer (Kosaka Laboratory Ltd. SE-3B); thickness values obtained at several portions of the film were averaged. The surface of the sol–gel-coated PMMA was examined with an optical microscope and a scanning electron microscope (SEM, Hitachi S-2300)

The hardness of the oxide-coated PMMA was measured using a Vickers hardness tester (Akashi Manufacturing Co. Type MVK-E). In the measurements, the applied load was set to 10 g and the loading time was kept constant for 15 s. The diagonal length of the pyramidal indentation was transformed to the Vickers hardness in the conventional manner. Because the depth of indentation was about 0.7 μm, while the coating film thickness was 0.5 μm at most, as will be seen below, the hardness thus obtained corresponds neither to that of the oxide coating film itself, nor to that of PMMA, and might not have any strict physical meaning. However, in the present work, this value is used as a measure of the hardness of the composite surface layer for practical purposes and referred to as the "apparent hardness".

3. Results and discussion

3.1. General aspect of the coating films

In Fig. 2, logarithm of the thickness of the TEOS-derived SiO_2 film, MTES-derived SiO_2 film and TIP-derived TiO_2 film deposited on PMMA substrate and heat treated at 120 °C for 5 min, is plotted against logarithm of the withdrawal velocity used in the dip-coating.

It has been reported that the thickness, t, of the coating films applied by the sol–gel dip-coating method is a function of several experimental parameters as follows

$$t = K(\eta V/\rho g)^{\alpha} \qquad (1)$$

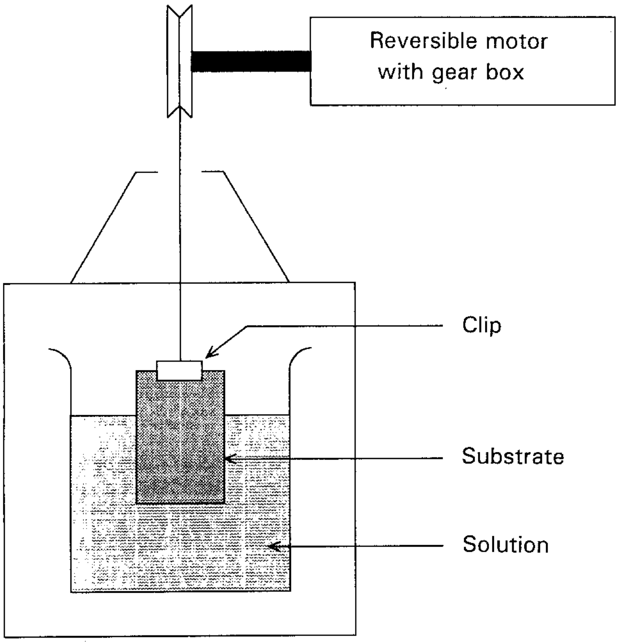

Figure 1 Schematic illustration of the apparatus for dip-coating.

where η is the viscosity of the sol, V the withdrawal velocity, ρ the density of the sol, g the gravitational acceleration, and K is a constant. The exponent, α, in equation 1 is controversial, and is reported to be 1/2 or 2/3 [8, 9].

The slope of the log t–log V relation for three different coating films in Fig. 2 falls in the range of 1/2 to 2/3, being consistent with previous works. However, the thickness itself differs from each other at the same withdrawal velocity, which is attributed to the difference in η and ρ of the starting sol.

The MTES-derived coating film was colourless and transparent, and crack-free as seen in Fig. 3a. The TEOS-derived film was also colourless and transparent up to the thickness of about 0.2 μm, but in the thicker film only, cracks were occasionally observed (Fig. 3b). TIP-derived TiO_2 coating film was also transparent but slightly tinted due to the light interference effect. The TiO_2 film is more crackable than SiO_2 film, and many cracks or creeks were observed in the film with a thickness of 0.38 μm, as seen in Fig. 3c. This may result from a higher sensitivity for hydrolysis of TIP than TEOS and MTES, which leads to the gradient of the gelation velocity in the sol film or shrinkage rate in the gel film along the vertical direction to the coating film.

When Scotch tape tightly stuck to the oxide film-coated PMMA was stripped off quickly and strongly, the film was not peeled off from any of the coating films. Moreover, no sign of ripping of the film was noticed under the optical microscope even after Vickers pyramid indentation. This indicates that the adherence of the coating film to the PMMA substrate is large enough for practical uses. However, this argument is rather qualitative, and a quantitative evaluation of the bonding of the film to the PMMA substrate remains to be made.

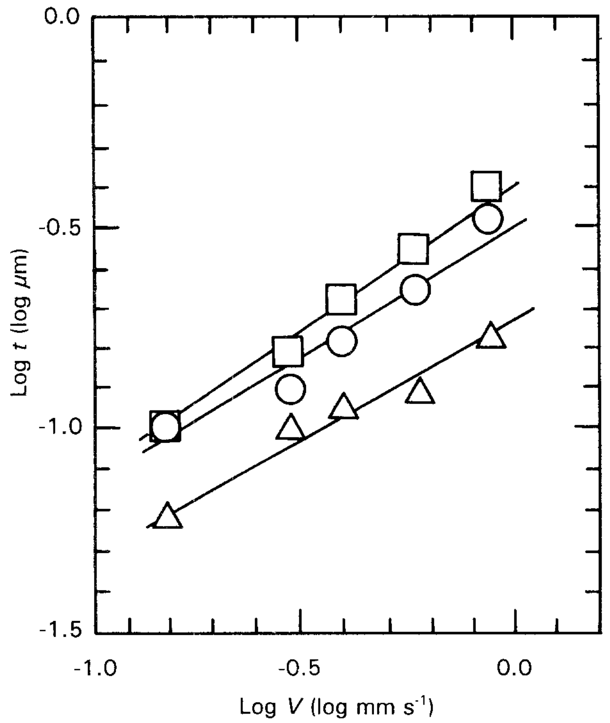

Figure 2 Logarithm of the thickness of oxide film deposited on PMMA substrate plotted against logarithm of the withdrawal velocity used in the dip-coating. (△) MTES-derived SiO_2 film, (○) TEOS-derived SiO_2 film, (□) TIP-derived TiO_2 film.

3.2. Hardness of the oxide-coated PMMA

3.2.1. *Effect of the starting material and thickness of the coated film*

Fig. 4 shows the apparent hardness of the PMMA coated with SiO_2 and TiO_2 films prepared from different sources, plotted against the thickness of the films. Here, TEOS-derived SiO_2 film was prepared from the sol with an H_2O/TEOS molar ratio of 6, and the coated PMMAs were heat treated at 120 °C for 5 min.

The hardness of the TEOS-derived SiO_2-coated PMMA increased with increasing film thickness. On the other hand, little thickness-dependence of the hardness was observed for the MTES-derived SiO_2-coated PMMA. It has been reported that Si–CH_3 bonds in the MTES-derived SiO_2 gels are not ruptured at temperature as low as 120 °C [10]. Thus the remaining Si–CH_3 bonds may provide the film with elasticity or flexibility and be attributable to low hardness.

The PMMA coated with TiO_2 film is of medium hardness. As can be seen, the hardness decreased with increasing film thickness above 0.25 μm. The lower hardness of the TiO_2-coated PMMA than that of the TEOS-derived SiO_2-coated PMMA may arise from the porous nature of the deposited film originating from the rapid gelation. The decrease in hardness at a film thickness of 0.38 μm may be caused by the occurrence of numerous creeks or cracks, which can be observed in Fig. 3c.

The size of the film fragments is smaller than that of the indentation by Vickers pyramid, so that the ultimate load supported by the film fragment is considered to become small compared to that by the crack-free film.

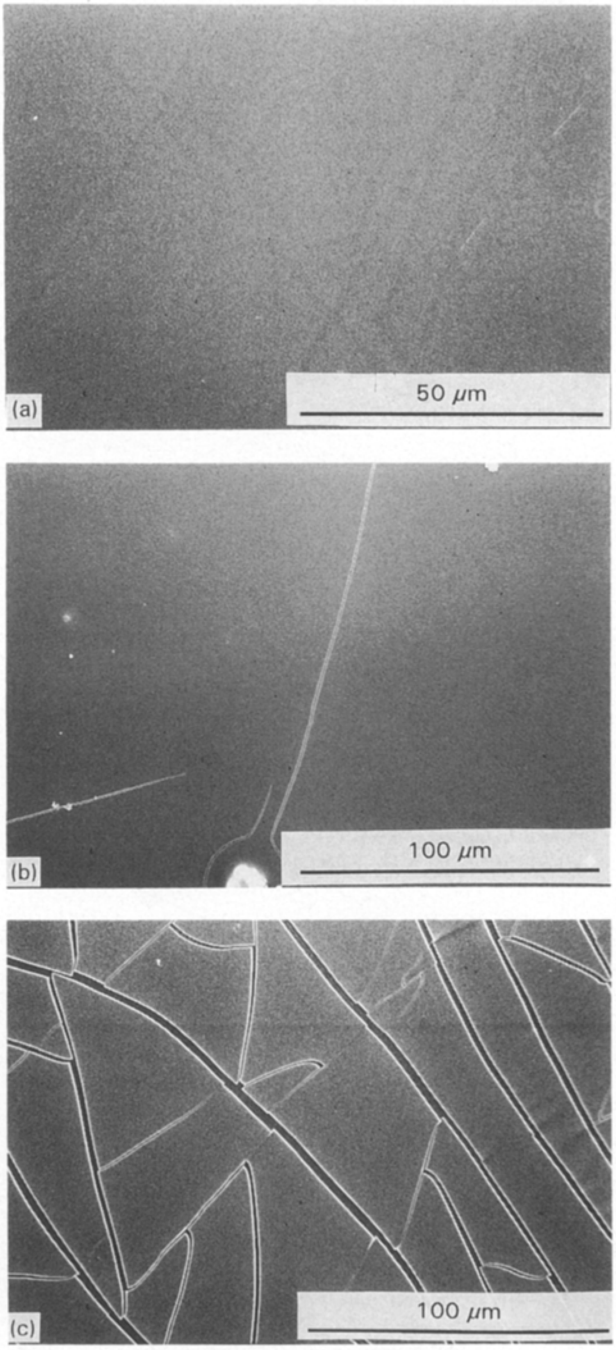

Figure 3 Scanning electron micrographs of the surface of the oxide film deposited on PMMA substrate and heat treated at 120 °C for 5 min. (a) MTES-derived SiO_2 film, (b) TEOS-derived SiO_2 film, (c) TIP-derived TiO_2 film.

Even in the TEOS-derived SiO_2-coated PMMA, the rate of increase of the hardness becomes smaller as the thickness of the coating film is increased, which may be due to the increase of the porous nature in the thick films.

It is obvious from the above results that of the three, the TEOS-derived SiO_2-coated PMMA shows the highest apparent hardness. Therefore, in the following sections, we are concerned only with TEOS-derived SiO_2-coated PMMA.

3.2.2. *Effect of the heating conditions*

The apparent hardness of TEOS-derived SiO_2-coated PMMA heat treated under two different conditions is

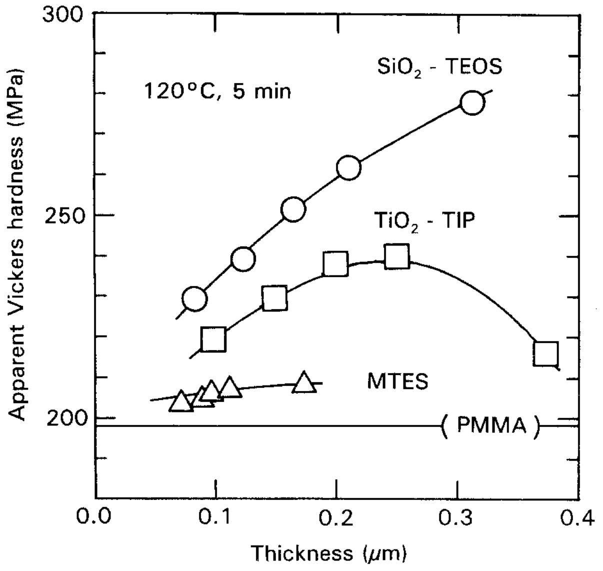

Figure 4 The apparent hardness of the PMMA coated with SiO_2 and TiO_2 films prepared from different sources plotted against the thickness of films.

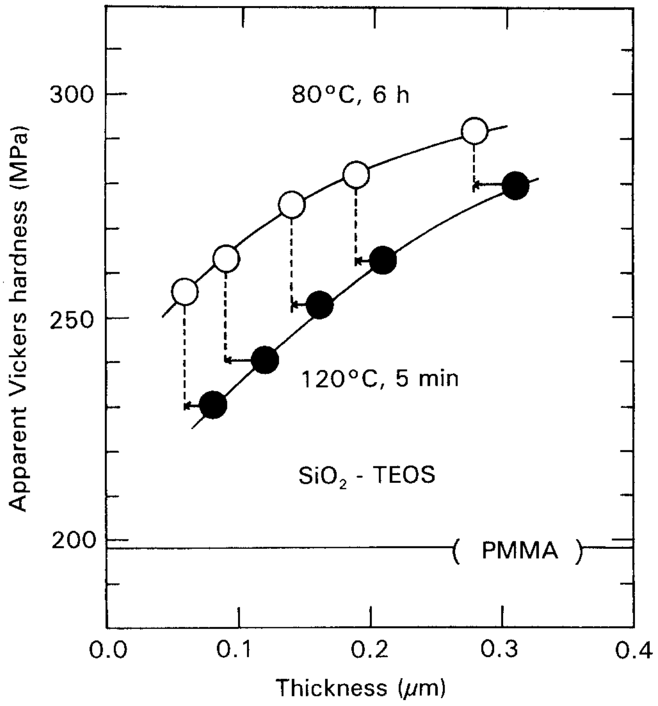

Figure 5 The apparent hardness of TEOS-derived SiO_2 coated PMMA heat treated under two different conditions, plotted against the coating film thickness.

shown in Fig. 5 as a function of coating film thickness. It is seen that heat treatment at 80 °C for 6 h is more effective for increasing the apparent hardness of the coated PMMA than that at 120 °C for 5 min. It is also noticed that the thickness of the coating film heat treated at 80 °C is smaller than that treated at 120 °C when compared at the same withdrawal velocity used in the dip-coating process (the difference in thickness is indicated by an arrow in Fig. 5). Namely, heat treatment at 80 °C for a long time accelerates more intensively the condensation reaction between Si–OH bonds in the film and make the film more dense than treatment at 120 °C for a short time, this being reflected in the increased apparent hardness.

A greater increment of hardness was not achieved by heating for more than 6 h. It was impossible to heat treat the coated PMMA above 80 °C for a long time owing to the occurrence of viscous flow. Eventually, it is concluded that the heat treatment at 80 °C for 6 h is suitable for providing the SiO_2 coating on PMMA with the highest apparent hardness.

3.2.3. Effect of hydrolysis conditions

The apparent hardness of the PMMA coated with the SiO_2 film prepared from TEOS sols hydrolysed with different amounts of water (in molar ratio to TEOS, r) is shown as a function of the coating film thickness in Fig. 6. The gel-coated PMMA was heat treated at 80 °C for 6 h (the ultimate condition for obtaining the highest hardness). It is seen that the hardness increased with increasing film thickness for all three hydrolysis conditions, but that the rate of increase differs. In particular, the rate of increase of hardness for the specimen prepared at $r = 2.0$ is relatively small compared to the other two. It is also seen that a larger amount of water used for hydrolysis of TEOS results in a harder SiO_2-coated PMMA.

It has been reported that an H_2O/TEOS molar ratio of 2.0 does not lead to the completion of the hydrolysis of TEOS and a considerable amount of ethoxy group remains in the film as $Si–OC_2H_5$ bonds, even after heat treatment at 80 °C [11]. Then, the $Si–OC_2H_5$ bonds act like $Si–CH_3$ bonds in the MTES-derived SiO_2 film, and provide the film prepared at $r = 2.0$ with elasticity, causing the lower

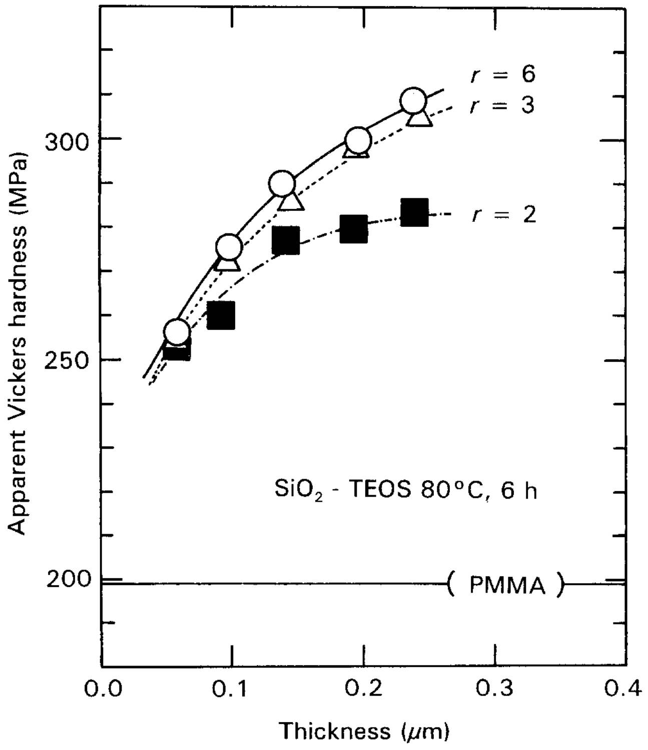

Figure 6 The apparent hardness of PMMA coated with the SiO_2 films prepared from TEOS sols hydrolysed with different amounts of water, as a function of the coating film thickness.

apparent hardness than other films prepared at $r = 3.0$ and 6.0. The high hardness of the SiO_2-coated PMMA prepared at $r = 6.0$ is consistent with the previously reported fact that a larger amount of water added for hydrolysis of TEOS leads to the formation of a rigid three-dimensional gel network.

3.2.4. Effect of the repetition of the dip-coating/heating process

In the above sections, the thickness of the coating film was varied by changing the withdrawal velocity of the PMMA substrate. Here, the thickness of the TEOS-derived SiO_2 coating film was changed by repeating the process consisting of dip-coating, drying and heat treating at 80 °C for 6 h.

Results of the hardness measurement are shown in Fig. 7, and compared with the SiO_2-coated PMMA prepared by a single dip-coating process using different withdrawal velocities. The hardness is higher in the sample prepared by multiple dip-coating than that by single dip coating. This result indicates that the repeated deposition of a thin, dense layer is more effective for increasing the hardness of the coated PMMA than one deposition of a less dense film with an equivalent thickness, although the process is time-consuming.

The combined effect of the withdrawal velocity and multiple dip-coating process on the hardness of resultant SiO_2-coated PMMA is seen in Fig. 8. All the coated PMMAs were heat treated at 80 °C for 6 h. The numbers in or adjacent to the symbols in the figure denote the number of times the dip-coating/heating process was repeated. The highest apparent hardness is attained in the PMMA triply coated with the SiO_2 film using the withdrawal velocity of 0.30 mm s^{-1}. The increase in hardness from about 200 MPa for non-coated PMMA to 325 MPa corresponds to the three-step increments in the scale of pencil hardness, which is a convenient method for examining the resistance to scratching.

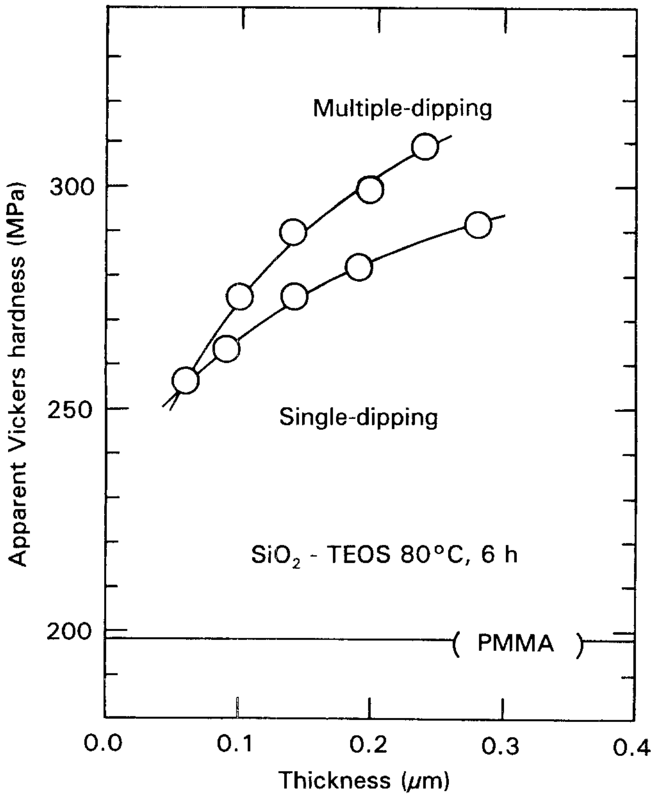

Figure 7 The apparent hardness of PMMA coated with the SiO_2 films prepared by repeating the process consisting of dip-coating, drying and heating at 80 °C for 6 h, plotted against film thickness.

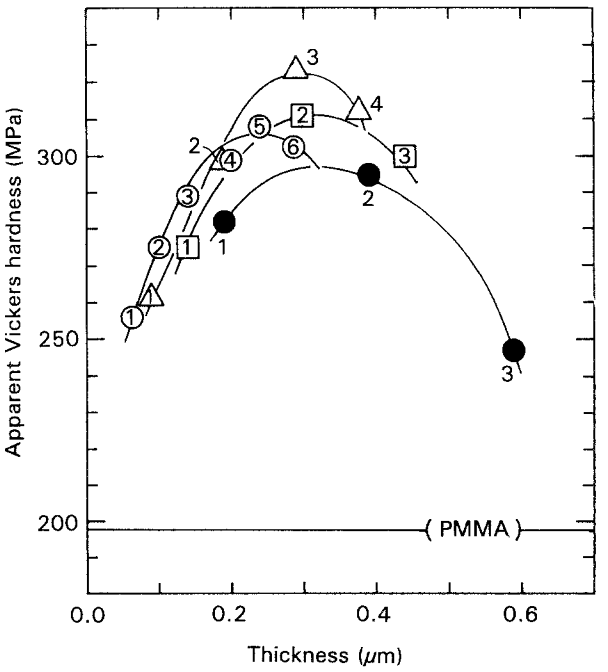

Figure 8 The apparent hardness of PMMA coated with SiO_2 films prepared by multiple dipping, using different withdrawal velocities, plotted against film thickness. (○) 0.15 mm s^{-1}, (△) 0.30 mm s^{-1}, (□) 0.40 mm s^{-1}, (●) 0.60 mm s^{-1}.

The obtained hardness (325 MPa) is, however, even lower than that (~ 500 MPa) of TEOS-derived bulk silica-dried gel. This is due to the smaller thickness of coated film than the indentation depth, to the microporous nature of the gel-derived film, and to the effect of the remaining OH.

4. Conclusion

The SiO_2- and TiO_2-coated PMMA substrates prepared by the sol–gel method using various alkoxide sources showed higher hardness than uncoated PMMA. Among them, the TEOS-derived SiO_2-coated PMMA showed the highest apparent hardness. This is because the TEOS-derived SiO_2 film can be prepared most homogeneously and has few cracks or creeks even when the film thickness is increased to 0.3 μm.

The heat treatment near the glass transition temperature, 80 °C for 6 h, considerably accelerated the condensation among Si–OH bonds in the films and made them dense, which was reflected in the increased apparent hardness.

The repeated deposition of a thin, dense layer was more effective for increasing the hardness of the coated PMMA than a single deposition of a film with an equivalent thickness using a faster withdrawal velocity. The maximum apparent hardness obtained in the present study is 325 MPa, which is about 1.6 times larger than that of uncoated PMMA.

References

1. H. DISLICH, in "Sol–gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty Shapes", edited by L. C. Klein (Noyes, Park Ridge, New Jersey, 1988) p. 50.
2. C. J. BRINKER and G. W. SCHERER, in "Sol–gel Science" (Academic Press, Boston, MA, 1990) p. 787.
3. S. SAKKA and T. YOKO, in "Chemistry, Spectroscopy and Applications of Sol–Gel Glasses", edited by R. Reisfeld and C. K. Jørgensen, Vol. 77 (Springer, Berlin, 1992) p. 89.
4. S. SAKKA, K. KAMIYA, K. MAKITA and Y. YAMAMOTO, *J. Non-Cryst. Solids* **63** (1984) 223.
5. K. IZUMI, H. TANAKA, M. MURAKAMI, T. DEGUCHI, A. MORITA, N. TOHGE and T. MINAMI, *ibid.* **121** (1990) 344.
6. J. MATSUOKA, R. MIZUTANI, H. NASU and K. KAMIYA, *J. Ceram. Soc. Jpn* **100** (1992) 47.
7. M. SCHMIDT, B. SEIFERLING and G. PHILIP, in "Ultrastructure Processing of Advanced Ceramics", edited by J. D. Mackenzie and D. R. Ulrich (Wiley, New York, 1988) p. 651.
8. I. STRAWBRIDGE and P. F. JAMES, *J. Non-Cryst. Solids* **82** (1986) 366.
9. Idem, *ibid* **86** (1986) 381.
10. M. MURAKAMI, K. IZUMI, T. DEGUCHI, A. MORITA, N. TOHGE and T. MINAMI, *J. Ceram. Soc. Jpn* **97** (1989) 91.
11. H. YOSHINO, K. KAMIYA and H. NASU, *J. Non-Cryst. Solids* **126** (1990) 68.

Received 12 October 1992
and accepted 26 August 1993