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The Effect of Thermal Treatment on Conversion to Silica of Silica / Polymethylmethacrylate Hybrid Films Prepared by Sol-Gel Method Using Perhydropolysilazane

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Silica/polymethylmethacrylate (PMMA) hybrid thin films were successfully prepared on polybutyleneterephtalate (PBT) substrate by dip-coating using perhydropolysilazane (PHPS) as a silica source. The effect of thermal treatment on conversion from PHPS to Silica was investigated by SEM and FT-IR in detail. Ultraviolet radiation in conversion to silica of thin film was most effective compared with heating in electric furnace. Mechanical properties of silica and silica/PMMA hybrid thin films also were examined by vickers hardness and pencil scratch hardness.

Key words: sol-gel method, silica, polysilazane, dip coating, hybrid film

1. INTRODUCTION

Recently, the method in which the tableware that dished up the ingredient is heating cooked and offer a warm meal is spreading in the school lunch of the school, the company cafeteria and the hospital. Both of plastic such as melamine, ABS and polycarbonate and pottery has been used in tableware. The plastic tableware is paid to attention because pottery is heavily damaged easily. However, the heat-resistance of plastic tableware is low. Therefore, when the heating cooking of the microwave oven is done, the low degree of durability becomes a problem. Polybutyrene terephthalate (PBT) is paid to attention as a material for tableware to improve heat-resistance in the heating cooking of tableware.

It is well-known that PBT has excellent mechanical properties such as strength and abrasion-resistance compared with ordinary plastic tableware. However, the problem that various coloring matters in the food component pollute PBT has not been solved in PBT tableware still as well as ordinary plastic tableware. In this work, silica coating to the surface of tableware was examined to prevent pollution with the food coloring matter of plastic tableware including PBT. Silica coating to the PBT substrate was done by dip coating method in consideration of the economy, productivity and the easiness of the coating to the complex shape substrate. Perhydropolysilazane (PHPS) was used as silica source.

It was reported [1-3] that PHPS led to formation of dense silica film at lower temperature than silicon alkoxide such as tetraethylorthosilicate (TEOS). Silica coating at lower temperature is advantageous for the coating to plastic tableware with low heat-resistance. We reported that the contamination of color components derived from the curry could be significantly improved on PBT substrate by coating PHPS/PMMA hybrid film [4]. Recently, it was reported that the ultraviolet treatment was effective for the low temperature formation of ceramic film derived from sol-gel route [5,6]. In this paper, the heating condition in coating of PHPS to the PBT substrate was examined and then formation process of silica film was observed from PHPS during heating by an ultraviolet irradiation. Furthermore, the mechanical properties of silica film were also described.

2. EXPERIMENTAL

Xylene solution for PHPS (NL110A, AZ electronic materials) was diluted with the xylene and it has been adjusted to 10mass%. Polymethylmethacrylate (PMMA, BR-82, MW. 150,000, Mitsubishi Rayon) was also added to prepare PHPS coating solution. The contents of PMMA ranged from 0 to 10mass%. PBT substrate was processed to 8.0cm×4.0cm×0.3cm and then cleaned with the acetone. After cleaning, white acrylic urethane resin was coated on PBT substrate by spray coating. This was heated for 1h at 130°C. The dip coating was

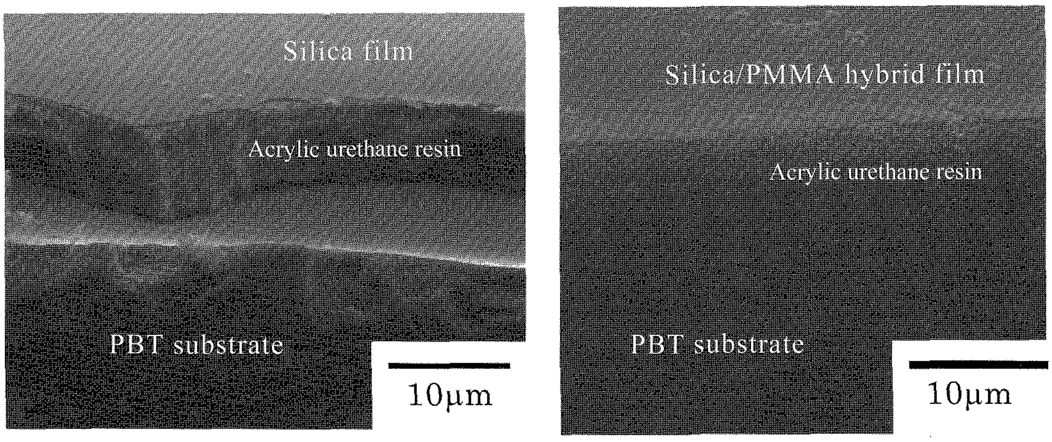

Fig.1 SEM photograph of silica film (a) and silica/PMMA hybrid film (b) on PBT substrate coated by acrylic urethane resin

carried out by using the desk-top type coating device (RV-6SL, Mitsubishi Electric). It was set at 5s in the impregnation time of PBT substrate to PHPS coating solution. The withdrawal speed of PBT substrate ranged from 1 to 5mm/s. After coating, PBT substrate was heated by Ultraviolet (UV) irradiation or electric furnace at 100°C. Handy type UV curing device (4000W, 365nm, Sen Lights) was used as UV irradiation. The irradiation time ranged from 32 to 160s.

The change of the combination between Si and O was observed by using FT-IR (FTIR-8300 Shimadzu) to order to examine the process in which PHPS changes to the silica. The surface of PHPS was observed by scanning electron microscope (SEM, S-2300, Hitachi). The mechanical properties of PBT substrate coated by PHPS were examined by pencil scratch hardness tester (No.553 Yasuda-seikiI-seisakusho) and vickers hardness tester (AVK-A, Akashi). The pencil scratch hardness was measured based on JIS-K5600-5-4. The pencil with hardness from 6B to 9H was used. The compressive strength was measured at 5kg load.

3. RESULTS AND DISCUSSION

PHPS and PHPS/PMMA solution were coated on the silicon wafer (8.0cm ×4.0cm×0.3cm) and heated by UV irradiation and electric furnace at 160°C to investigate the conversion process of silica from PHPS and PHPS/PMMA. Figure 1 shows SEM photographs of silica film (10mass%PHPS) and silica/PMMA hybrid film (5mass%PHPS/4mass%PMMA) on PBT substrate. Both silica film and silica/PMMA hybrid film had smooth surface with thickness of 100nm. Figure 2 show the change of IR spectra for silica films coated on silicon wafer using 10mass% PHPS solution. The absorption spectrum derived from antisymmetric stretching vibration of Si-O-Si (about 1060cm^{-1}) was observed in all samples and the formation of silica was confirmed. This spectrum increased with increasing irradiation time.

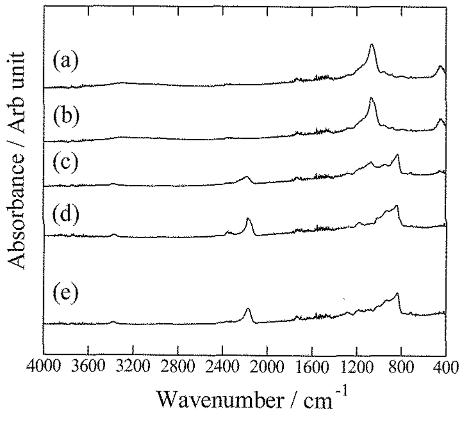

Fig.2 Effect of thermal treatment on the conversion from PHPS (10mass%) to silica by UV irradiation for (a)160s, (b)80s (c)32s, (d)0s and (e)only heating at 100°C for 160s

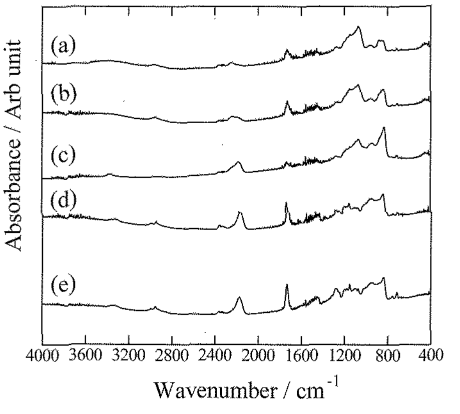

Fig.3 Effect of thermal treatment on the conversion from PHPS (5mass%) /PMMA (4mass%) to silica by UV irradiation for (a)160s, (b)80s (c)32s, (d)0s and (e)only heating at 100°C for 160s

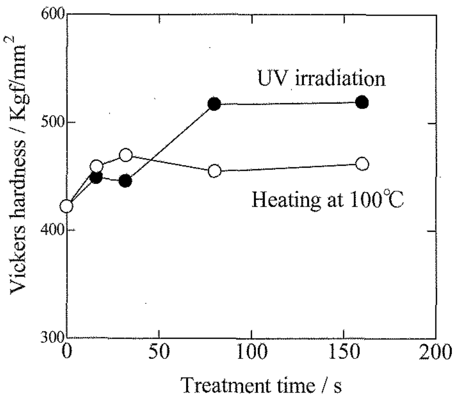

Fig.4 The change of vickers hardness as a function of treatment time, (•) UV irradiation and (○) heating at 100°C

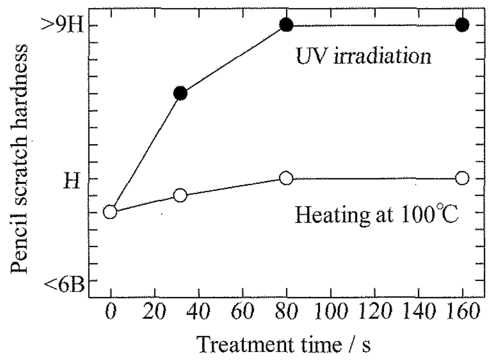

Fig.5 The change of pencil scratch hardness for silica film as a function of treatment time, (•) UV irradiation and (○) heating at 100°C

The surface temperature increased up to 100°C using by the infrared radiometer thermometer. However, no spectrum derived from antisymmetric stretching vibration of Si-O-Si was observed in film which was only heated at 100°C. It was found that UV irradiation was effective for the formation of silica from PHPS compared with heating in electric furnace. This result suggested that UV irradiation has the effect which accelerates the reaction of PHPS and moisture in the air atmosphere in order to convert to silica. PHPS/PMMA was coated on silicon wafer and heated by UV irradiation and electric furnace at 100°C.

Figure 3 show the change of IR spectra for silica/PMMA hybrid films coated on silicon wafer using 5mass% PHPS (4mass%PMMA) solution. The absorption spectrum derived from antisymmetric stretching vibration of Si-O-Si was also observed by UV irradiation. The absorption spectrum derived from antisymmetric stretching vibration of Si-O-Si was lower and broader than that observed in Fig.2. No spectrum derived from antisymmetric stretching vibration of Si-O-Si was observed in film which was only heated at 100□C. This result suggested that the addition of PMMA inhibited the conversion to the silica.

The effect of UV irradiation on mechanical properties of silica film or silica/PMMA hybrid film derived from PHPS or PHPS/PMMA was investigated. Figure 4 shows the relation between vickers hardness of silica film derived from 10mass% PHPS and treatment time by UV irradiation. To compare the effect of UV irradiation, the vickers hardness of silica film which was only heated at 100°C was examined. The vickers hardness of silica film was 420kgf/mm^2 before UV irradiation. The vickers hardness increased up to 520kgf/mm^2 at more than 80s of irradiation time. On the other hand, the vickers hardness was only to slightly improve in the heating at 100°C.

Figure 5 shows the relation between pencil scratch hardness of silica film derived from 10mass% PHPS and treatment time by UV irradiation. The pencil scratch hardness of silica film was 2B before UV irradiation. The pencil scratch hardness increased up to 9H at more than 80s of irradiation time. On the other hand, the pencil scratch hardness was only to slightly improve from 2B to H in the heating at 100°C. It was found that the adhesive property between silica film and substrate was significantly improved by UV irradiation.

Figure 6 shows the relation between pencil scratch hardness of silica/PMMA hybrid film derived from 5mass% PHPS and 4mass% PMMA and treatment time by UV irradiation. The pencil scratch hardness was lower than that obtained from PHPS. This results in low conversion to silica by the addition of PMMA, as shown in Fig.3. However, the use of silica/PMMA hybrid film led to the suppression of contamination by color component from curry compared with silica film because the flexibility of silica film was improved by the addition of PMMA [4].

It is assumed that the difference of thermal expansion coefficient between silica/PMMA film and PBT

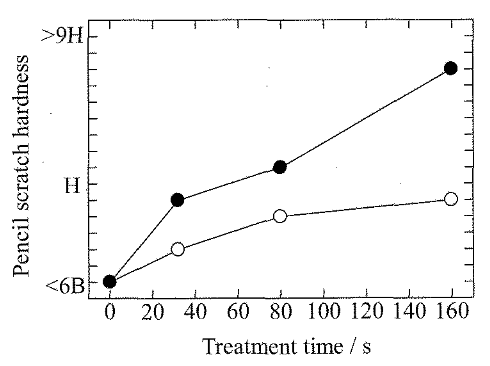

Fig.6 The change of pencil scratch hardness for silica/PMMA hybrid film as a function of treatment time, (•) UV irradiation and (○) heating at 100°C.

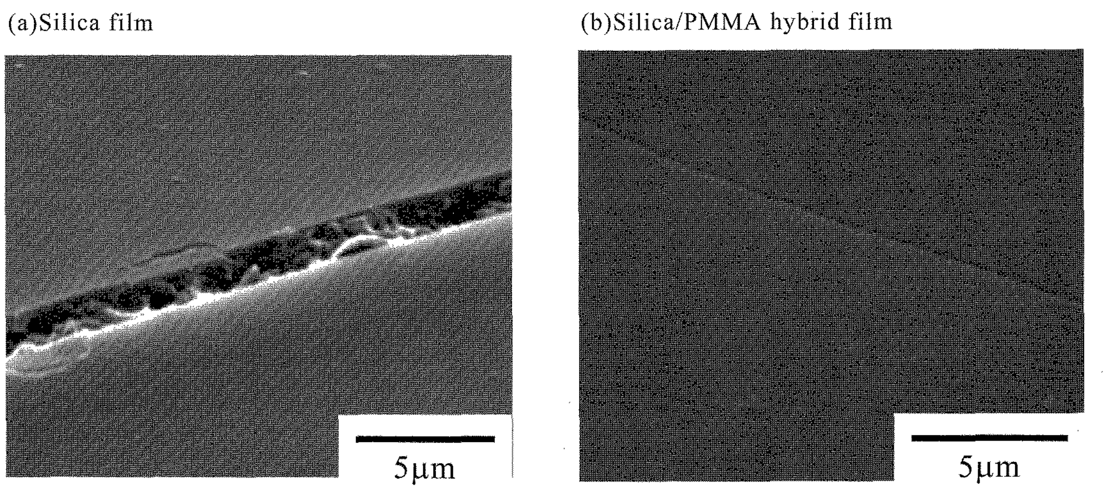

Fig.7 SEM photographs of surface on silica film (a) and silica/PMMA hybrid film (b) on PBT substrate coated by acrylic urethane resin

substrate is small. Figure 7 shows SEM photographs of surface on silica film (10mass%PHPS) and silica/PMMA hybrid film (5mass%PHPS/4mass%PMMA). The formation of crack with narrow width and shallow was observed in silica/PMMA hybrid film by the addition of PMMA. The width of crack was about 0.2μm. When only PHPS was also coated on PBT substrate, a large and deep crack with 1.5μm of width was developed in a film under conversion from PHPS to silica. It is thought that the difference of thermal expansion coefficient between silica film and PBT substrate is great. The pollution of color matter was observed in the area which crack arose. Therefore, silica/PMMA hybrid film in which the pollution of color matter is not very much generated is useful for practical application.

4. CONCLUSION

Silica and silica/PMMA hybrid thin films were coated on PBT substrate by dip-coating using PHPS and PHPS/PMMA solution. UV irradiation was effective for the conversion from PHPS to silica, but the crack with large and deep was introduced in the film. The conversion of silica was inhibited by the addition of PMMA, but the formation of crack was improved. Both pencil scratch hardness and vickers hardness of silica and silica/PMMA hybrid film was improved by UV irradiation. These values of silica film were higher than that of silica/PMMA hybrid film.

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