Hybrid Coating and Characterization of Silica Precursor Film on PBT Substrate by Sol-Gel Method Using Polysilazane

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Silica, silica/polymethylmethacrylate (PMMA) hybrid, and silica-particle blend silica films were successfully prepared on polybutylene terephthalate (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 in detail by scanning electron microscopy and Fourier transform infrared spectroscopy. Mechanical properties of silica and silica/PMMA hybrid thin films also were examined by the pencil scratch hardness tests.

Key words: Polysilazane, dip-coating, Silica thin film

1. INTRODUCTION

Recently, there has been an increase in interest in the effects of heat on tableware used to prepare and serve warm meals in cafeterias in schools, companies, and hospitals. Plastics, such as melamine, ABS, and polycarbonate, and ceramics have both been used in such tableware. Plastic tableware is of interest because ceramic tableware is easily damaged. However, plastic tableware has low heat resistance. Therefore, it is less durable when used for cooking using a heating cookware such as a microwave oven. Polybutylene terephthalate (PBT) has received attention as a material for tableware with improved heat resistance.

PBT's excellent mechanical properties compared to ordinary plastic tableware, such as strength and abrasion-resistance, are well known. However, the problem of stains from colored food components has not been solved in either PBT tableware or ordinary plastic tableware. In addition, the heat resistance and mechanical properties of PBT need improvement in order for it to be used at higher temperatures. We have noted that by coating silica using polysilazane, a dense silica film is easily obtained at temperatures below 100 °C. It was reported [1–3] that perhydropolysilazane (PHPS) leads to formation of a dense silica film at a lower temperature than that required for silicon alkoxides such as tetraethyl orthosilicate. In this study, silica thin films were successfully prepared on PBT substrates by dip coating using PHPS as a silica source. The effect of thermal treatment on conversion from PHPS to silica was investigated by scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy. In addition, silica, silica/polymethylmethacrylate (PMMA) hybrid, and silica-particle blend silica films were prepared, and their mechanical properties were investigated, with the goal of improving their flexibility and durability.

2. EXPERIMENTAL

PBT substrate was processed into 8.0 cm × 4.0 cm ×

0.3 cm pieces and then cleaned with acetone. After cleaning, the substrates were coated with white acrylic urethane resin by spray coating and then heated for 1 h at 130 °C. PHPS/xylene solution (NL110A, AZ Electronic Materials) was diluted with xylene and adjusted to 10 mass%. A coating solution with PMMA (BR-82, MW. 150,000, Mitsubishi Rayon) added to the PHPS solution was prepared. In addition, silica particles were dispersed to prepare a third PHPS coating solution. Dip coating was carried out using a desktop coating device (RV-6SL, Mitsubishi Electric). PBT substrates were dip coated with these coating solutions at a dipping time of 10 s and withdrawal rate of 10 mm/min. The dip-coated substrates were dried at room temperature for 30 min. After drying, the PBT substrates were heated at 170 °C for 1.5 h using an electric furnace or a water oven. The water oven (AX-HCI HEALSIO, Sharp Corporation) was used to heat the substrates in a steam atmosphere.

The thermally treated substrates were characterized by SEM, FT-IR spectroscopy, and a pencil hardness test. An SEM (S-2300, Hitachi) was used to observe the surface and cross-section of the silica thin films. An FT-IR spectroscope (FTIR-8300, Shimadzu) was employed to characterize the films. The scratch resistance of the silica coating was characterized using a commercial pencil hardness tester (No. 533, Yasuda Seiki Seisakusho). Pencil scratch hardness was measured based on JIS-K5600-5-4, using pencils with hardness from 6B to 9H.

3. RESULTS AND DISCUSSION

SEM images of a silica film, silica/PMMA hybrid film, and silica-particle blend silica film on PBT substrate are shown in Fig.1. The formation of two layers on the PBT substrate is clearly indicated. Both the silica film and the silica/PMMA hybrid film were 100 nm thick and had smooth surfaces. Fig.2 show the SEM images of the surfaces of these films. A few cracks were observed on each surface. Shallow, narrow cracks, about

Fig.1 SEM images of silica film (a), silica/PMMA hybrid film (b), and silica-particle blend silica film (c) on PBT substrate

0.2 μm wide, were observed in the silica/PMMA hybrid film. PBT substrate coated with only PHPS developed large, deep cracks, 1.5 μm wide, in the film after conversion from PHPS to silica. This is due to the large difference in thermal expansion coefficient between the silica film and PBT substrate. The surface of the silica-particle blend silica film was not smooth, but no cracks were observed on the film. It is thought that silica particles were buried in the cracks and linked silica particles.

Fig.3 shows the change in IR spectra for silica films coated on a silicon wafer using 10 mass% PHPS solution. Silica film (a) was heated at 170 °C using an electric furnace in air, and silica films (b) and (c) were heated using a water oven in a steam atmosphere. Absorption bands at 2200, 830, 1080 cm^{-1} can be assigned to the Si-H, Si-N, and Si-O-Si vibrations respectively, and 2350 cm^{-1} is assigned to C=O vibration. The reaction rate for the PHPS-to-silica transformation can be determined by the disappearance

of Si-H (and Si-N) vibrations and the emergence of the Si-O-Si vibration in an IR spectroscopic analysis. The absorption peak for Si-O-Si vibration increased with increasing thermal treatment time in a steam atmosphere. This spectrum appeared in silica film (a); however, Si-H and Si-N vibrations also appeared in the film. This result suggested that thermal treatment in a steam atmosphere is more effective for the formation of silica from PHPS compared with heating in air.

Using 5 mass% PHPS solution, 5 mass% PHPS/4 mass% PMMA solution, and 5 mass% PHPS/1 mass% silica-particle blend solution as a coating solution, silicon wafers were dip coated. After coating, the wafers were heated at 170 °C for 30 min using the water oven in a steam atmosphere. Fig.4 shows IR spectra for these films prepared on silicon wafers. The absorption peak of Si-O-Si antisymmetric stretching vibration was observed in all samples, and the formation of silica was confirmed. The absorption peak of Si-O-Si vibration was smaller in the silica/PMMA hybrid film than in the

Fig.2 SEM images of the surface of silica film (a), silica/PMMA hybrid film (b), and silica-particle blend silica film (c) on PBT substrate coated by acrylic urethane resin

Fig.3 Effect of thermal treatment on the conversion from PHPS (10 mass%) to silica by heating (a) in an air atmosphere at 170 °C for 30 min, (b) in a steam atmosphere at 170 °C for 30 min, (c) in a steam atmosphere at 170 °C for 90 min.

Fig.4 FT-IR spectra for silica films coated on silicon wafers: (a) 10 mass% PHPS solution, (b) 5 mass% PHPS and 4 mass% PMMA solution, and (c) 1 mass% silica-particle blend/10 mass% PHPS solution

silica and silica-particle blend silica films. This suggested that the addition of PMMA inhibited the conversion to silica. Furthermore, the absorption peak of Si–N vibration was smaller in the silica-particle blend silica film than in the silica film. This is thought to be due to the high conversion from PHPS to silica by the addition of silica particles.

Table 1 lists the thickness and pencil scratch hardness grade of the silica films. The pencil scratch hardness grade of the silica film derived from 10 mass% PHPS was 2B before thermal treatment, but increased up to H with thermal treatment at 170 °C for 1.5 h. The pencil scratch hardness grade of the silica/PMMA hybrid film (5 mass% PHPS, 4 mass% PMMA) was lower than that of the silica film (10 mass% PHPS). This is thought to result from the low conversion to silica due to the addition of PMMA, as suggested by the IR data shown in Fig.4. The pencil scratch hardness grade of the silica-particle blend silica (10 mass% PHPS, 1 mass% silica particles) was 2B before thermal treatment, but increased to 3H with thermal treatment. This result suggested that silica particles support the bonding of silica to silica.

The effect of silica particle addition on the mechanical properties of silica film derived from PHPS was investigated. Fig.5 shows the effect of pencil scratch

hardness of silica films with added silica particles. The pencil scratch hardness of silica films derived from 10 mass% PHPS and 1.0 mass% silica particles improved from H to 3H, but the hardness decreased with the addition of silica particles over 1 mass%. Fig.6 shows SEM photograph of silica film derived from 10 mass% PHPS and 2.5 mass% silica particles on a PBT substrate. The surface of this silica-particle blend silica film was not smooth, and the film thickness was 200 nm. Cracks were not observed on the film surface. These results suggest that the addition of a large amount of silica particles effectively increased the film thickness, however, it decreased the film's hardness.

4. CONCLUSIONS

Coating solutions were prepared by adding PMMA and dispersing silica particles in a PHPS solution. Silica film, silica/PMMA hybrid, and silica-particle blend silica films were coated on PBT substrates by dip coating, using solutions containing PHPS, PHPS/PMMA, and PHPS/dispersed silica particles, respectively. Thermal treatment in a steam atmosphere was effective in converting PHPS to silica, but it introduced large, deep cracks in the film. The conversion to silica was inhibited by the addition of PMMA, but crack formation was reduced. The silica-particle blend silica film showed

Table 1. Film thickness and pencil scratch hardness of silica, silica/PMMA hybrid, and silica-particle blend silica films

film	Thickness (nm)	Pencils hardness (Before treatment)	Pencil hardness (After treatment)
Silica film	100	2B	H
Silica / PMMA hybrid film	100	6B	B
Silica particle brend silica film	160	2B	3H

Fig.5 The effect of silica particle addition on pencil scratch hardness of silica film

less crack formation and improved pencil scratch hardness. These results show that the silica-particle blend silica films have the best characteristics among these coating films. However, excessive supply of silica particles decreased the film hardness. Therefore, the optimum concentration of silica particles added to the PHPS is 1.0 mass%.

Fig.6 SEM image of the surface of silica film derived from 10 mass% PHPS and 2.5 mass% silica particles

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