Preparation and Characterization of Silica Films on PBT Substrate
by Dip Coating with PDMS/PHPS Solution

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Silica films were successfully prepared on a polybutyleneterephthalate (PBT) substrate by dip coating using a perhydropolysilazane (PHPS) / polydimethylsilazane (PDMS) solution. The effect of thermal treatment on conversion from PDMS / PHPS to silica was investigated in detail by using SEM and FT-IR. The prepared Silica film had a thickness of 160 nm with a smooth surface and was crack free at 50 mass% of PDMS. The color pollution on silica films was characterized using a color meter. The resistance to color pollution was highest when the PDMS content was 25 mass%. The mechanical properties of silica films were also examined by performing pencil hardness and Vickers hardness tests. The Vickers hardness of the silica film decreased with increasing PDMS content. The pencil hardness of the silica film was 9 H, regardless of the PMDS content.

Key words: polysilazane, polydimethylsilazane, dip coating, silica, thin film

1. INTRODUCTION

Plastic tableware is currently used in many public facilities such as schools, workplaces, hospitals, hotels and airplanes. Plastics such as melamine and polycarbonate are widely used to manufacture such tableware. These plastics are often heated with food in a microwave or steam oven at temperatures higher than 150 °C. Due to its low heat resistance, plastic tableware is easily damaged at such high temperatures. An engineering plastic such as polybutyleneterephthalate (denoted as PBT) is expected to become a material used for tableware because of its high heat resistance. Furthermore, it is well known that PBT has excellent mechanical properties such as strength and abrasion resistance.

However, color pollution due to food materials often takes place in PBT tableware or other plastic tableware when it is heated with food in a microwave or steam oven at temperatures above 150 °C. Applying a coating to the plastic seems to be an effective solution to this problem. From the viewpoint of cost, the sol-gel method is expected to be a solution, and silicon alkoxides such as tetraethylorthosilicate (denoted as TEOS) have been used as starting materials. The use of TEOS, however, often leads to the formation of cracks in silica film because the oxygen in TEOS accelerates the combustion in the film during heating under an air atmosphere. We have noted that oxygen-free perhydropolysilazane (denoted as PHPS) is a precursor of silica film.

It has been reported [1-3] that PHPS leads to the formation of a dense silica film at a lower temperature than that required for TEOS. However, when PHPS was coated on a plastic substrate, cracks formed on the silica films during the conversion to silica because of the different thermal expansion coefficients of the silica and PBT plastic substrate. We found that this formation of cracks in silica film on a PBT substrate was improved to some degree by the addition of polymethylmethacrylate (denoted as PMMA) [4]. Slight color pollution was observed due to the existence of cracks when PBT tableware was heated with curry paste in a microwave oven.

In this study, polydimethylsilazane (denoted as PDMS) was used as an alternative to PMMA in order to obtain crack-free silica film. It was expected that the addition of PDMS would reduce the formation of cracks in comparison to PMMA. We experimented with the preparation of silica films on a PBT substrate by dip coating using a PDMS / PHPS solution. In this study, the effects of PDMS on the conversion from PHPS to silica and the formation of cracks on silica film were investigated. The mechanical properties and resistance to color pollution of silica film were also examined.

2. EXPERIMENTAL

PBT substrate (80 mm x 40 mm x 3 mm) was cut from a PBT plate and then cleaned with acetone. After cleaning the substrate, the acrylic urethane resin was coated on a PBT substrate by spraying. Additionally, the PBT substrate was heated for 1 h at 130 °C. PHPS (NL120, (H3NSi)n, AZ Electronic Materials) and PDMS (MHP-20DB, (C2H6NSi)n, AZ Electronic Materials) were used as coating reagents. The viscosity of the PHPS and PDMS was 0.89 mPa·s and 0.88 mPa·s, respectively. They were both diluted to 10 mass% with a dibutyl ether solution. PDMS solution was added to separate volumes of the PHPS solution to yield PDMS solutions with a PDMS content ranging from 0 to 50 mass%. These solutions were coated on PBT substrates by dip coating. A desktop coating device (RV-6SL,
Mitsubishi Electric) was used as a dip coating machine. The rate of pulling up was 0.16 mm/s. After coating, the samples were dried at room temperature for 600 s and then heated at 170 °C for 0.5 h in an electric furnace under a vapor atmosphere. The microwave oven (AX-ICL, HEALSIO, Sharp) which was heated using vapor was used as an electric furnace.

The surface and microstructure of the silica films were observed by a SEM (JSM-6390, JEOL). The crystallization process of silica was observed by an FT-IR (FTIR-8300, Shimadzu). The mechanical properties of the silica film were characterized using a pencil hardness tester (No. 533, Yasuda Seiki Seisakusho) and Vickers hardness tester (AVK-A, Akaishi). Pencil hardness was measured based with the use of a JIS-K5600-5-4 with pencils ranging in hardness from 6 B to 9 H. Compressive strength was measured by Vickers with a load of 10 kg. Color pollution was evaluated by visual observation and a color meter (CM-7300d, Konica Minolta). The difference in color (ΔE) between the reference and sample was measured by a color meter.

3. RESULTS AND DISCUSSION

The influence of PDMS on the crystallization to silica during heating was observed by an FT-IR. Figure 1 shows the IR spectra of silica film obtained from a PHPS and a PDMS / PHPS solution. PHPS was easily crystallized to silica by heating with steam in a microwave oven. Among the absorption spectra observed in silica film prepared from PHPS, the absorption bands at 2200 cm⁻¹, 1080 cm⁻¹, and 830 cm⁻¹ can be assigned to the Si-H, Si-O, and Si-N vibration bands, respectively. The IR spectrum of 2350 cm⁻¹ is also assigned to the C-O vibration. These spectra suggest that the conversion from PHPS to silica takes place in the film. New absorption bands appeared at 800 cm⁻¹ and 1270 cm⁻¹ in the silica films prepared from PDMS solution. These bands correspond to the vibration band of Si-CH₃. These absorption spectra increased with an increase in the PDMS content in the PHPS solution. This result suggests that PDMS remains in silica film without the crystallization to silica during heating. It is considered that PDMS may be blended in silica film as an amorphous polymer. Therefore, when the PDMS content is increased, the absorption band of Si-O broadens.

The effect of the addition of PDMS on the surface and microstructure of silica film was examined. Figure 2 shows SEM photographs of silica films cast on a PBT substrate. Silica film prepared from a PHPS solution had a smooth surface and a large crack that was approximately 0.1 μm wide. On the other hand, the silica films prepared from a PHPS / PDMS solution also had a smooth surface, regardless of the PDMS content. Crack-free silica film was also obtained by the addition of PDMS solution. It became clear that the addition of PDMS reduced crack formation in silica film. Because the viscosity of PHPS was equal to that of PDMS, an amorphous PDMS that is homogenously blended into PHPS might not be influenced by the difference between the thermal expansion of silica film and the PBT substrate.

Figure 3 shows the fracture surfaces of silica film cast on PBT substrates. SEM photographs show that silica film strongly adhered to the PBT substrate regardless of the PDMS content. The thickness of the silica film prepared from PHPS solution was around 120 nm, as observed by a SEM. The thickness of silica film prepared from
Fig. 3 Fracture surface of silica film prepared from PHPS solution and PHPS solution with indicated PDMS content

PHPS solution was approximately 160 nm. It was found that the thickness of the silica film increased with the addition of PDMS.

The effect of the addition of PDMS on the color pollution of silica film was investigated. Generally, if it was not coated with silica film, PBT tableware turned dark yellow when heated with curry paste in the microwave oven. The coating of silica film on PBT tableware led to a reduced degree of color contamination from food materials. In this study, curry paste, which has a strong capacity to induce coloration, was used to confirm the effect of resistance to coloration. Figure 4 shows the change in $\Delta E$ values of silica film after samples were heated with commercial curry paste in the microwave oven. The $\Delta E$ value decreased up to 25 mass% of PDMS with increasing PDMS content. On the contrary, they increased from 30 mass% of PDMS with increasing PDMS content. The $\Delta E$ value increased up to 28 at 50 mass% of PDMS. The color pollution was clearly observable by the naked eye. On the other hand, it was found that the $\Delta E$ value was less than 10 at 25 mass% of PDMS. The resistance to color pollution was highest at 25 mass% of PDMS. When the $\Delta E$ value was less than 10, the color pollution was not observable by the naked eye on the PBT substrate. It was considered that the addition of PDMS promoted the flexibility of the silica film.

However, the excessive addition of PDMS led to results that showed a decreased effect by PDMS.

The effect of the addition of PDMS on the mechanical properties of silica film was examined. Figure 5 shows the relation between Vickers hardness and PDMS content. The Vickers hardness of silica film prepared from PHPS solution was 555 kgf/mm², while that of silica film prepared from PHPS/PDMS solution decreased to 463 kgf/mm² with an increase in the PDMS content. The Vickers hardness of silica film decreased remarkably when the PDMS content exceeded 25%. This may result from the flexibility of silica film due to the presence of PDMS. It was considered that the amorphous area in the silica film increased with increased PDMS content and the flexibility of the silica film then increased.

Table 1 lists the relation between the pencil hardness of silica film and its PDMS content. The pencil hardness of silica film prepared from PHPS solution was 9 H, and that of silica film prepared from PDMS/PHPS was also 9 H. The pencil hardness of silica film was independent of the PDMS content. Although the amorphous area was introduced to the silica film by the addition of PDMS to PHPS, it was also found that the silica film exhibited a high degree of pencil hardness. Table 2 lists the relation between the pencil hardness of silica and its PMMA content. The pencil hardness of silica film decreased to 4 H when the PMMA content increased up to 50 mass%.

Fig. 4 Relation between $\Delta E$ and PDMS content

Fig. 5 Relation between Vickers hardness and PDMS content
It was clear that the pencil hardness of silica film prepared from PHPS / PMMA solution [5, 6] was lower than that of silica film prepared from PHPS / PDMS solution.

4. CONCLUSIONS
Silica film was coated on PBT substrates by dip coating with a PHPS / PDMS solution. The thickness of the silica film that was coated with the PHPS solution once was 120 nm. The thickness of the silica film increased to 160 nm with the addition of PDMS. The silica film was crystallized to silica, but its crystallinity decreased with an increase in the PDMS content. PDMS existed in an amorphous form without crystallization to silica. The silica film exhibited excellent adhesive properties on a PBT substrate. When PDMS solution was added, a crack-free silica film was obtained. The AE value was lowest at 25 mass% of PDMS. The excess addition of PDMS led to color pollution. It was found that the optimum PDMS content was 25 mass%. The Vickers hardness of the silica film decreased with increasing PDMS. Silica film prepared from PDMS / PHPS exhibited higher pencil hardness than that silica film a PHPS / PMMA solution.

REFERENCES

Table 1 Relation between PDMS content and pencil hardness

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<th>Contents of PDMS</th>
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<td>9 H</td>
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<tr>
<td>25 mass%</td>
<td>9 H</td>
</tr>
<tr>
<td>50 mass%</td>
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Table 2 Relation between PMMA content and pencil hardness

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<td>8 H</td>
</tr>
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<td>25 mass%</td>
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<td>50 mass%</td>
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