Preparation of Thick Inorganic-organic Composite Films by Electrophoretic Sol-gel Deposition Using Organically Modified Silica Particles and Polyethylene Maleate

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Thick inorganic-organic composite films composed of organically modified silica particles and polyethylene maleate were prepared by electrophoretic sol-gel deposition. The optimum amount of polyethylene maleate added was 1 mass% and that of ammonia water was 1 mass% to obtain thick films of ca. 20 μm in thickness with no open spaces among the particles.

Development of techniques to prepare thick oxide films on the surface of a variety of substrates has recently been required in many fields of industry.[1-3] The electrophoretic sol-gel deposition is one of the most promising techniques to prepare such thick films.[4] This technique has some advantages as follows: thick films are obtained in short time, film thickness can easily be controlled by changing the electrodeposition time, the coating can be carried out for substrates with a complex form, and so on.[5-6] The films prepared by the electrophoretic sol-gel deposition are basically composed of monodispersed spherical particles, and have a lot of open spaces among these particles. If the open spaces can be filled with some organic polymers, a new type of inorganic-organic composite films with a unique character is expected to be obtained.

In the present study, we have tried to prepare thick inorganic-organic composite films by filling the open spaces of the original silica films with polyethylene maleate. For the electrophoretic deposition, coating sols containing the mixture of organically surface modified silica particles and polyethylene maleate were used.

We propose the optimum preparation condition to obtain thick inorganic-organic composite films and discuss the relation between the amount of ammonia water and polyethylene maleate in the coating sols and the microstructure of the films obtained.

Silica particles used in this study were prepared by the procedures reported previously:[7-8] monodispersed silica particles with an average diameter of 170 nm were obtained.[9] Organically surface modified silica particles were prepared by treating these silica particles with vinyltriethoxysilane (VTES) (Shin-Etsu Chemical Co., Ltd.) as follows. At first, the silica particles were dispersed in toluene solution of VTES. The mole ratio of the particles/VTES/toluene was fixed to be 5/1/150. Obtained suspension was then refluxed in a flask for 1 h to perform surface modification of the silica particles. Modified silica particles were separated from the solvent by centrifugation. The particles were washed with toluene for 3 times by re-dispersing and centrifugation. Washed particles were dried in vacuo at room temperature for 3 h and then heat treated at 120-150 °C for 6 h. From IR spectra of the modified particles, almost all of the silanol groups at the surface of the particles were replaced by vinyl groups.

Polyethylene maleate using the co-deposition with the organically modified silica particles was prepared from maleic acid (Wako Pure Chemical Industries, Ltd.) and ethylene glycol (Wako Pure Chemical Industries, Ltd.). Esterification was carried out in a flask by heating a mixture of 32.5 g of maleic acid (0.33 mol) and 18.6 g of ethylene glycol (0.30 mol) at 200 °C for 4 h with stirring. Dehydration polycondensation was performed by heating the mixture at 210 °C for 30 min under reduced pressure with stirring.

Sols for the electrophoretic deposition (coating sols) were prepared as follows. First, the particles were well dispersed in acetone solution of polyethylene maleate by stirring and applying ultrasonic wave. After the particles were dispersed completely in the acetone solution, 1% ammonia water was added. The amount of the ammonia water ranged from 0 to 5 mass% against the total weight of the coating sols. The amount of the particles added into the coating sol was 1 mass% and that of polyethylene maleate ranged from 0 to 5 mass%. The total amount of the coating sols was fixed to be 70 g. A stainless steel sheet (SUS430) was used as a coating substrate and a stainless wire (SUS304BA) as a counter electrode. Electrophoretic sol-gel deposition was carried out by applying 200 V for 1 min. Deposits on the substrate were weighed by using a micro-balance (Mettler M5SA). Observation of the microstructure for the surface of the thick silica films was performed by a scanning electron microscope (SEM) (JEOL JSM-5300).

Figure 1 shows the SEM photographs of thick inorganic-organic composite films prepared by changing the amount of polyethylene maleate and ammonia water. Each films have ca. 20 μm in thickness. Without polyethylene maleate, organically modified silica particles are regularly arranged on the substrate with the addition of 1 mass% ammonia water (a). However, a

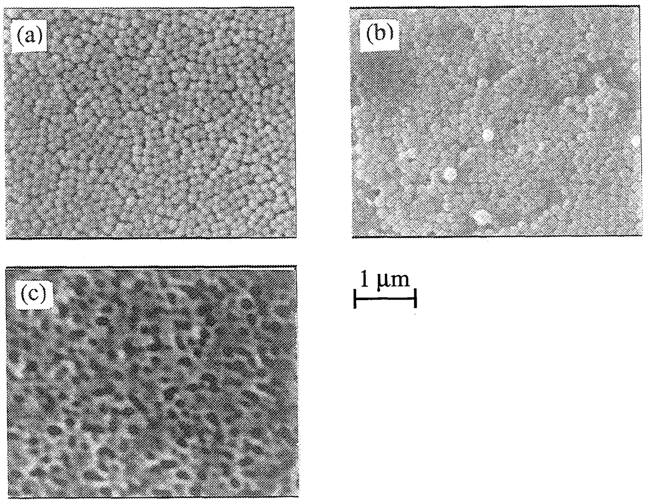

Figure 1. SEM photographs of thick silica films prepared by adding (a) 0 mass% polyethylene maleate and 1 mass% ammonia water, (b) 1 mass% of polyethylene maleate and 1 mass% ammonia water, and (c) 5 mass% of polyethylene maleate and 5 mass% ammonia water.

lot of open spaces exist among the particles in the films because the films were composed of only spherical particles aggregated. In contrast, the films prepared by adding 1 mass% polyethylene maleate and 1 mass% ammonia water have no openings by filling these spaces with polyethylene maleate (b). When the weight of polyethylene maleate was 5 mass% and the content of ammonia water was 5 mass%, many open spaces are observed and original silica particles are embedded (c).

Table 1 shows whether or not the electrophoretic deposition can be carried out by varying the amount of ammonia water and polyethylene maleate. The condition of thick films is also shown in Table 1. These were evaluated on the basis of the SEM observation. Without ammonia water, no electrophoretic deposition was observed at any polyethylene maleate content. Homogeneous thick films which consisted of regularly arranged particles were obtained at any polyethylene maleate content by adding 1 mass% ammonia water. Especially, thick inorganic-organic composite films without open spaces in the films were obtained at the amount of 1 mass% polyethylene maleate added, as shown in Figure 1 (b). More than 3 mass% of ammonia water was added, electrophoretic deposition could be carried out only by adding a specific amount of polyethylene maleate. Without polyethylene maleate, homogeneous films with open space were obtained. In the case that the polyethylene maleate content was 1 or 2 mass%, electrophoretic deposition could not be carried out since the particles were aggregated to precipitate at the bottom of the coating bath. When 5 mass% polyethylene maleate was added, the aggregation of the particles in the coating sols did not occur, so that the electrophoretic deposition was carried out. However, obtained films were heterogeneous and porous as shown in Figure 1 (c); the films had many open spaces with silica particles embedded.

Table 1. The ability of film formation and the condition of films prepared by the electrophoretic sol-gel deposition

Ammonia water / mass%	Polyethylene maleate / mass%	Film formation	Condition of films
0	0	×	-
0	1	×	-
0	2	×	-
0	5	×	-
1	0	○	homogeneous
1	1	○	homogeneous & filled the opening
1	2	○	homogeneous
1	5	○	homogeneous
3	0	○	homogeneous
3	1	×	-
3	2	×	-
3	5	○	heterogeneous & porous
5	0	○	homogeneous
5	1	×	-
5	2	×	-
5	5	○	heterogeneous & porous

Without ammonia water, the particles did not electrophorese toward the anode since negative charge of the silica particles was too small. When more than 3 mass% ammonia water was added, solubility of the polyethylene maleate in the coating sols decreased because of the high water content. Excess amount of polyethylene maleate which could not dissolve in the mixture of acetone and ammonia water was easily be adsorbed on the organically modified silica particles by the hydrophobic interaction. When the amount of polyethylene maleate added in the coating sols was 1 or 2 mass%, organically modified silica particles were partly adsorbed by polyethylene maleate. While the polyethylene maleate-adsorbed sites are considered to be stable against further adsorption of polyethylene maleate, the sites without adsorption tend to attract polyethylene maleate which is adsorbed on the other particles. Such partially adsorbed particles were thus easily aggregated and precipitated. In contrast, the particles in the coating sols were well dispersed in the case that large amounts of polyethylene maleate were added because all particles were thoroughly adsorbed by polyethylene maleate and all the adsorbed polyethylene maleate acted as a dispersant. However, a lot of open spaces existed in the films and porous microstructure was observed. When both amounts of polyethylene maleate and ammonia water were as large as 5 mass%, particle arrangement in the films became irregular. This suggests that the amount of polyethylene maleate adsorbed on the particles was quite large. Such particles could not be rearranged when once deposited on the substrate because of high adhesion force between the adsorbed particles. As a result, the optimum amount of ammonia water was 1 mass% to give enough negative charge to the particles and to adsorb proper amount of polyethylene maleate on the particles. Consequently, thick inorganic-organic composite films which had no open spaces among the particles were prepared by adding 1 mass% ammonia water and 1 mass% polyethylene maleate. The vertical homogeneity of the films was also achieved at these conditions. The thickness of the films obtained was ca. 20 μm when the applied voltage was 200 V and deposition time was 1 min.

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