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Characteristics of coating films synthesized by a sol-gel reaction using nanosized boehmite

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We investigated the properties of organic-inorganic hybrid coating films prepared by a sol-gel reaction using a nanosized boehmite sols. The sol was synthesized as a protective coating, functional coating, binder, etc. The sol was prepared from spherically shaped boehmite, and a mixture of spherical and fibrous shaped boehmite. Sol solutions were used to deposit onto substrates by way of a dip-coating process. In order to investigate the surface hydrophobicity, roughness and transmittance of coating films, a contact angle meter, a surface profiler and a UV-Vis spectrophotometer were used. In addition, surface modification of boehmite was investigated by a FT-IR spectrometer. Contact angle and surface roughness of coating films gradually increased with increasing reaction time due to the gelation of the sol by successive condensation reactions. The transmission rate of coating films within the visible-wavelength region was greater than 90% when the reaction time was less than 48 h. FT-IR measurement showed the spectra of condensation of MTMS and boehmite.

Keywords: Coating films, Sol-gel, Boehmite, Infrared spectroscopy, Surface properties.

Introduction

Organic-inorganic hybrid materials prepared via the sol-gel process may have enhanced mechanical and physical properties [1, 2]. Organic-inorganic hybrid materials have created very effective coating agents possessing the advantages of both inorganic and organic materials. Using the sol-gel method, it is possible to synthesize organic-inorganic hybrid materials as thin film coatings. These are based on the use of metal alkoxide and organoalkoxysilane [3-5]. In the sol-gel method, the synthesis of inorganic oxides starts from molecular precursors (metal alkoxides); the oxide network is obtained via hydrolysis and condensation reactions, which occur in the solution [6-8]. The metal hydroxide and organohydroxysilane become macromolecules due to the condensation reaction. The degree of polymerization can be controlled according to the reaction conditions such as concentration, temperature and catalyst [9-10].

In this paper we investigate the properties of organic-inorganic hybrid coating films prepared by a sol-gel reaction using a nanosized boehmite sol. The sol was synthesized as a protective coating, functional coating, binder, etc. A boehmite nano sol of spherical and fibrous shapes was used as inorganic material. Methyltrimethoxysilane (MTMS) was used as the organoalkoxysilane. Sols were prepared from boehmite sol and MTMS by a sol-gel reaction. Coating films were fabricated on glass substrates by a dip-coating process with sols prepared from boehmite and MTMS. The surface hydrophobicity and roughness of coating films were investigated by a contact angle meter and a surface profiler. The transmittance of coating films was measured by a UV-Vis spectrophotometer. Surface modification of boehmite was investigated by a Fourier transform infrared (FT-IR) spectrometer.

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Experimental

Sol preparation

Alumina-based organic-inorganic hybrid sols were prepared by a two-step hydrolysis-condensation process. Spherically shaped boehmite sol (20 wt% Al_2O_3 solid contents in water, pH 4) and fibrous shaped boehmite sol (10 wt% Al_2O_3 solid contents in water, pH 4.8) were obtained from Nissan Chemical Co. MTMS was obtained from Toshiba Co. EtOH (ethyl alcohol) and IPA (isopropyl alcohol) as diluent solvents were used. The morphology of boehmite sol powders was observed by a transmission

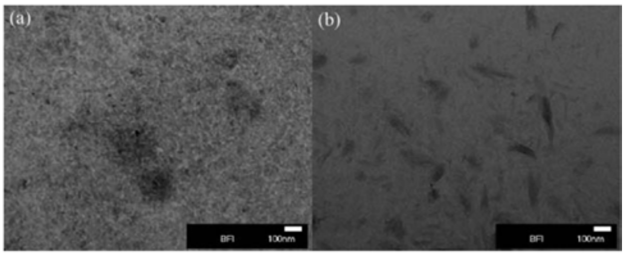

Fig. 1. TEM images of boehmite sol powders. (a) spherically shaped boehmite (b) fibrous shaped boehmite.

Table 1. Synthesis conditions and compositions of coating sols

Specimen	Boehmite sol (wt.%)	MTMS/EtOH (wt.%)	MTMS/IPA (wt.%)
BM70	Spherical boehmite (150)	20/10	50/50
BM100	Spherical boehmite (150)	20/10	80/80
MBM100	Spherical/fibrous boehmite (150/50)	20/10	80/80

electron microscope(TEM, JEOL, JEM 2100F) as shown in Fig. 1.

Table 1 shows synthesis conditions and compositions of coating sols. Three compositions of the sol were prepared. The sols were prepared with a spherically shaped boehmite, and a mixture of spherically and fibrous shaped boehmite in the gravimetric ratio of 150 to 50. The sol was controlled at pH 4.0 by adding acetic acid and phosphoric acid. Coating sols were synthesized by a 2-step sol-gel reaction. In the first step, MTMS/EtOH solution was added to a spherically shaped boehmite sol in the gravimetric ratio of 20/10 to 150. The MTMS/EtOH solution was added to the mixed sol of spherically and fibrous shaped boehmite in the gravimetric ratio of 20/10 to 200. The sol was stirred at a rate of 800 rpm for 3 h at a temperature of 25 °C. In the second step, a MTMS/IPA solution was added to the boehmite/MTMS/EtOH sol in the ratio of 50/50 and 80/80 to 180 and 230. The sols were stirred again at a rate of 800 rpm, for 6, 12, 24 and 48 h at a temperature of 25 °C.

Fabrication of thin film on substrate

The substrates used for the analysis of coating films were glass that had been washed with IPA. Three prepared sol solutions were used to deposit onto the substrates by way of a dip-coating process. Each substrate was dipped into the prepared sol at a constant speed of 40 mm minute^{-1} using a dip-coater and then withdrawn at the same constant speed previously mentioned. After drying in air for 30 minutes, the coated glasses were kept in an oven for 1 h at a temperature of 60 °C. Then the coated substrates were heated at a temperature of 300 °C for 3 h at a heating and cooling rate of 5 K minute^{-1}.

Characterization of coating films

The hydrophobic properties of coating films were measured by a dynamic contact angle meter (Surface and Electro-Optics, SEO300A). The surface roughness of coating films was measured by a surface profiler (Tencor, alpha-step 500). The transmittances of coating films were measured by a UV-Vis spectrophotometer (Cary 5000). The surface modification of boehmite was investigated by a FT-IR Spectrometer(Brucker, IFS 88).

Results and Discussion

Figure 2 shows the contact angle of coating films as a function of reaction time. Boehmite and MTMS form

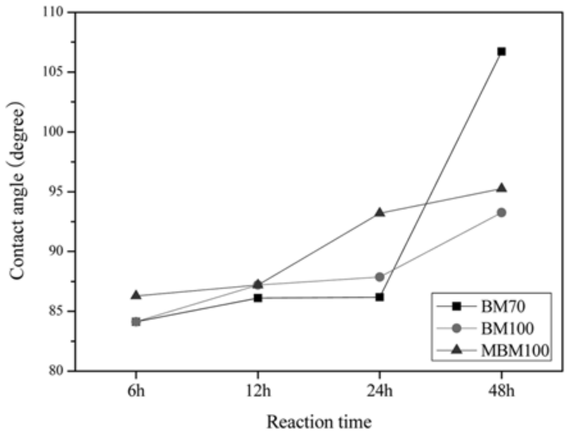

Fig. 2. Contact angle of coating films as a function of reaction time.

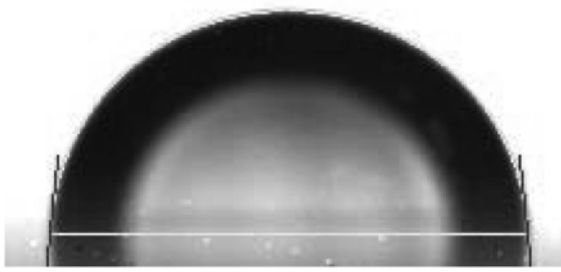

Fig. 3. Typical drop of water on a coating film(specimen MBM100 reacted for 12 h) for measuring contact angle. The amount of water dropped on a coating film was 10 μl.

networks as the reaction progresses, following an increase of solid contents of the hybrid sol. When MTMS encloses the surface of boehmite particles, the surface free energy of boehmite decreases. This indicates that the hydrophilic surface of boehmite changes to a hydrophobic character by treating it with hydrophobic MTMS. In Fig. 2, the contact angle of coating films is seen to increase with an increase in the reaction time. This is due to the gelation of the sol by successive condensation reactions. Therefore, the nature of the surface of the coating films was changed to hydrophobic with an increase in the reaction time.

Figure 3 shows a typical drop of water on a coating

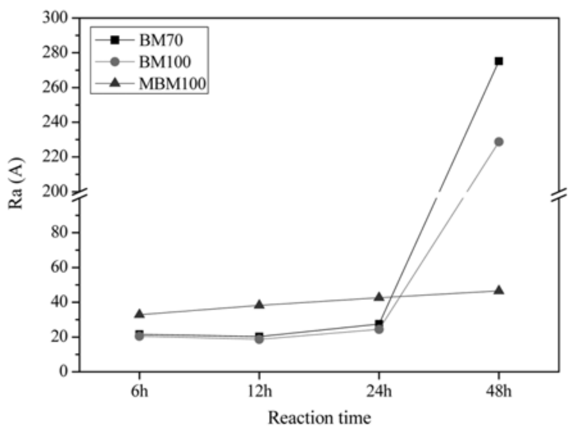

Fig. 4. Surface roughness of coating films as a function of reaction time.

film to measure contact angle. In this figure, the coating film was specimen MBM100 reacted for 12 h.

Figure 4 shows the surface roughness of coating films as a function of reaction time. The surface roughness of coating films increased with an increase in the reaction time. In Fig. 4, the surface roughness of coating films increased with an increase in the reaction time owing to excessive gelation by successive condensation reactions.

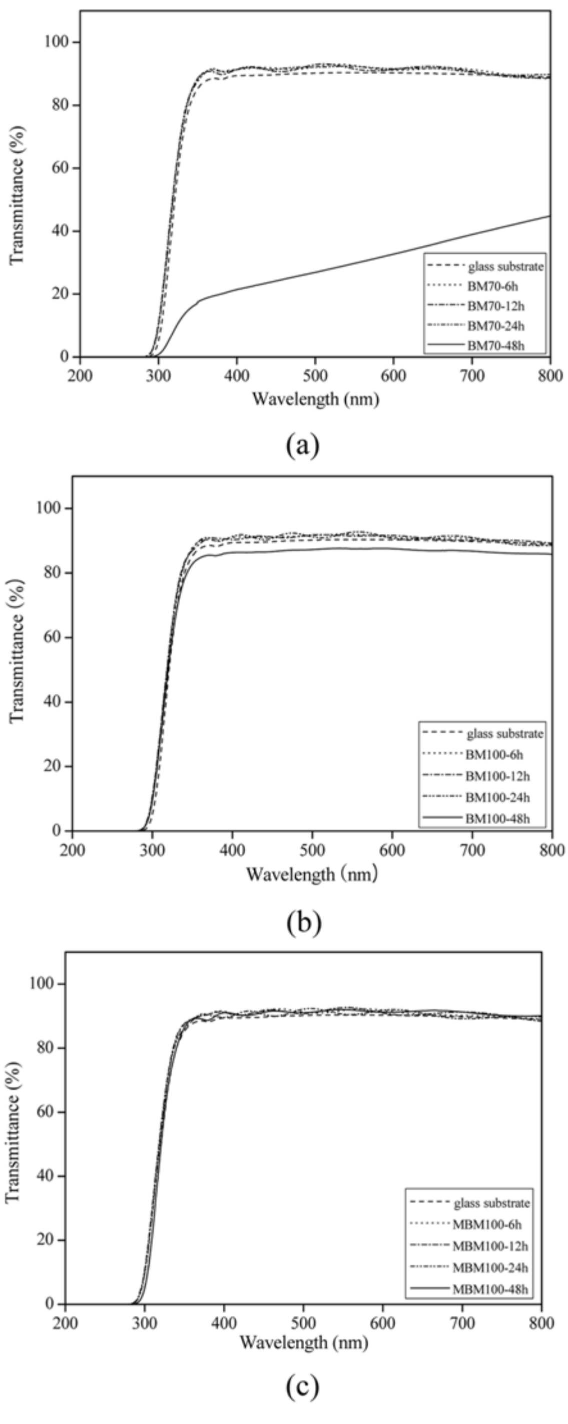

Fig. 5. Transmittance of coating films as a function of reaction time. (a) transmittance of specimen BM70 (b) transmittance of specimen BM100 (c) transmittance of specimen MBM100.

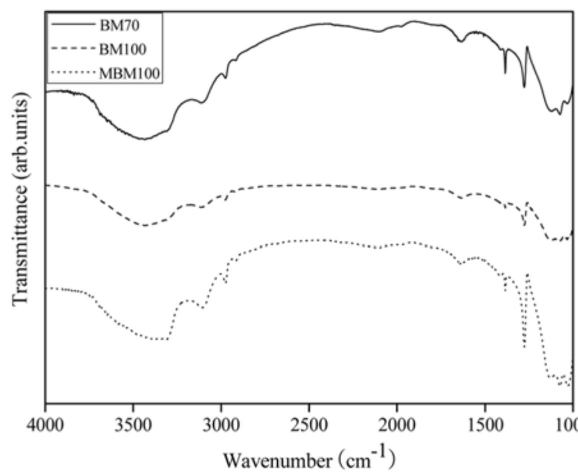

Fig. 6. FT-IR spectra of coating films reacted for 12 h.

The surface roughness of coating films prepared from the mixed boehmite sol of spherical and fibrous shapes increased slowly and was stable in comparison with the boehmite sol of only spherical shaped entities.

Figure 5 shows the curves of transmittance of coating films as a function of reaction time. In the case of specimens BM70 and BM100 reacted for 6, 12 and 24 h, the transmission within the visible-wavelength region was greater than 90%. However, the transmission of specimens BM70 and BM100 within the visible-wavelength region was approximately 32 and 86%, respectively, when the reaction time was 48 h. This decreased transmission was due to the excessive gelation. In the case of specimen MBM100 reacted for 6, 12, 24 and 48 h, the transmission within the visible-wavelength region was greater than 90%. This indicates that coating films prepared from a mixed sol of spherically and fibrous shaped boehmite is more stable than a sol of only spherically shaped boehmite.

Figure 6 shows FT-IR spectra of coating films (reacted for 12 h) dried for 3 h at a temperature of 50 °C. Si-O-Si, Si-O-Al and Al-O-Al bonds were shown at wavenumbers of 1,175 cm^{-1}, 1,160 cm^{-1} and 1,113 cm^{-1}, respectively. This shows that condensation of MTMS and boehmite occurred [11].

Conclusions

We investigated the properties of organic-inorganic hybrid coating films prepared by a sol-gel reaction using nanosized boehmite sols. The contact angle and surface roughness of coating films increased with an increase of the reaction time due to the gelation of the sol by successive condensation reactions. The surface of coating films was changed from hydrophilic to hydrophobic with an increase in the reaction time. The surface roughness of coating films prepared from a mixed sol of spherically and fibrous shaped boehmite increased slowly with an increase in the reaction time and was stable in comparison with a sol of only spherically shaped boehmite. In the case of specimens(BM70 and BM100) consisting of spherically shaped boehmite, the transmission within the visible-wavelength region was greater than 90% when the reaction time was 6, 12 and 24 h. However, the transmission was approximately 32 and 86%, respectively, when the reaction time was 48 h. In the case of a specimen consisting of spherically and fibrous shaped boehmite, the transmission within the visible-wavelength region was greater than 90% when the reaction time was 6, 12, 24 and 48 h. Coating films prepared from a sol of mixed spherical and fibrous shaped boehmite were more stable than a boehmite sol of only a spherical shape. FT-IR measurements showed that condensation of MTMS and boehmite occurred.

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