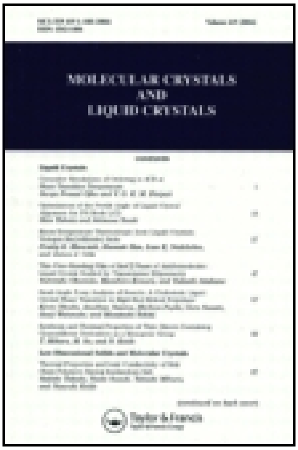

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Characteristics of Inorganic-Organic Hybrid Coating Films Synthesized from Nano Boehmite and Methyltrimethoxysilane

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We studied the properties of inorganic-organic hybrid coating films prepared by boehmite sol. Sols were synthesized by sol-gel process using nano boehmite and methyltrimethoxysilane in variation with the amount of methyltrimethoxysilane at different reaction time. In order to understand physical and chemical properties of sols prepared from boehmite and methyltrimethoxysilane, coating films were fabricated on glass substrates by dip-coating process. The crystalline pattern and morphology of sol powder of boehmite were observed. Contact angle, surface roughness, transmittance, chemical bond and thermal stability of coating films were investigated.

Keywords: boehmite; coating film; inorganic-organic hybrid; methyltrimethoxysilane

I. INTRODUCTION

In recent years the interest in inorganic-organic hybrid materials has increased at a fast rate. Inorganic-organic hybrid materials are increasingly important due to their extraordinary properties, which arise from the synergism between the properties of the components [1–3]. Inorganic components have excellent abrasion resistance, thermal resistance and high density, but are brittle and required high processing temperature. Conversely, typical advantages of organic components are mechanically flexible and tough, but

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organic components have poor abrasion and thermal resistance [4]. The sol-gel process is one of the most powerful techniques for tailoring excellent inorganic-organic hybrid materials. The sol-gel process involves the transition of a system from a liquid "sol" into a solid "gel" phase [5,6]. Sol is dispersion of colloidal particles in a liquid. Colloid is solid particles with diameters of 1–100 nm. Gel is interconnected, rigid network with pores of submicrometer dimensions and polymeric chains whose average length is greater than micrometer [7]. The sol-gel process is a novel procedure among solution reaction, which is based on the preparation of macromolecular network through the typical hydrolysis of alkoxide groups and the condensation reaction of hydroxide groups. Hydrolysis of the metallic alkoxide groups provides unstable and highly active metallic hydroxides under acid or base condition in alcohol solution. And metallic hydroxides become macromolecules subsequently due to the condensation reaction of themselves [8].

In this paper, we studied the properties of inorganic-organic hybrid coating films prepared by boehmite sol. In this respect, sols were synthesized by sol-gel process using nano boehmite [9] sol and methyltrimethoxysilane (MTMS) in variation with the amount of MTMS at different reaction time. Coating films were fabricated on glass substrates by dip-coating process. The crystalline pattern and morphology of sol powder of boehmite were observed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Surface hydrophobicity, roughness, transmittance, chemical bond and thermal resistance of coating films were investigated by contact angle meter, surface profiler, UV-Vis spectrophotometer, Fourier transform infrared (FT-IR) and thermogravimetric analyzer (TGA).

II. EXPERIMENTAL DETAILS

Boehmite sol (20 wt.% solid contents in water, pH 4) as inorganic material was purchased from Nissan chemical. MTMS as organic material was purchased from Toshiba Co. Ethyl alcohol (EtOH) and isopropyl alcohol (IPA) were used as diluent solvents. Coating sols were synthesized by 2-step sol-gel process. At the first step of the reaction, MTMS/EtOH solution was added to boehmite sol in the gravimetric ratio of 20/10 to 200 and the sol was stirred at 800 rpm, 25°C for 3 h. At the second step of the reaction, MTMS/IPA solution was added to boehmite/MTMS/EtOH sol in the gravimetric ratio of 50/50 and 80/80 to 230, respectively. The sols were stirred at 800 rpm, 25°C for 6, 12, 24 and 48 h. Table 1 shows synthetic condition of coating sols.

TABLE 1 Synthetic Condition of Coating Sols

Specimen	Boehmite sol (wt.%)	MTMS/EtOH (wt.%)	MTMS/IPA (wt.%)
S1	200	20/10	50/50
S2	200	20/10	80/80

Coating sols were coated on glass substrates using dip coater. Glass substrates were washed by IPA before coating. Dip coating was performed at a rate of 4 cm/min at room temperature. After drying in air for 30 min, the coated glasses were kept in an oven at 60°C for 1 h. Then coating films were cured at 300°C for 3 h. Properties of coating films on glass substrates were investigated as a function of reaction time of 48 h in the second step of the reaction.

Properties of boehmite sol and coating films prepared from boehmite sol and MTMS were investigated. Crystalline pattern of boehmite sol powder was observed by XRD (PANalytical, X' pert MPD 3040). Morphology of boehmite sol powder was observed by TEM (JEOL, JEM 2100 F). Dynamic contact angle meter (Surface and Electro-Optics) was used to measure the hydrophobic property of coating films. Surface roughness of coating films was measured by surface profiler (Tencor, alpha-step 500). Transmittance of coating films was investigated by UV-Vis spectrophotometer (Cary, 5000). Chemical bonds of boehmite sol, MTMS and coating films were identified by FT-IR (Brucker, IFS88). Thermal resistance was investigated by TGA (TA, Q600) up to 800°C at a heating rate of 20°C/min in N_2 atmosphere.

III. RESULTS AND DISCUSSION

Crystalline pattern and morphology for the powder of boehmite sol were observed by XRD and TEM, respectively. Figure 1 shows XRD results for the powder of boehmite sol after heat treating at 80°C. Crystalline pattern of boehmite was identified. TEM image of boehmite sol powder is shown in Figure 2.

Table 2 shows contact angle of coating films in variation with reaction time. Contact angle of coating films depends on the surface free energy of composition of materials. When MTMS encloses around the surface of boehmite particles, surface free energy of boehmite decreases. It means that surface of hydrophilic boehmite changes to hydrophobic property by treating hydrophobic MTMS. Therefore, the surface of coating films becomes hydrophobic and contact angle of

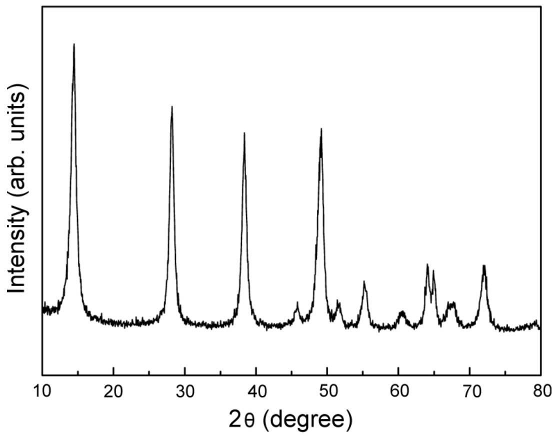

FIGURE 1 XRD pattern for the powder of boehmite sol.

coating films increases. In Table 2, contact angle of coating films increased with increasing reaction time. This indicates that hydrophobicity of coating films increases through sol-gel reaction between boehmite and MTMS. The contact angle of coating films rapidly increased in case of the reaction time for 48 h. The gelation of sols was observed in case of the reaction time of 48 h and the coating films formed hazy and rough surfaces. Therefore, their contact angles rapidly increased. Figure 3 shows typical drop of water on the surface

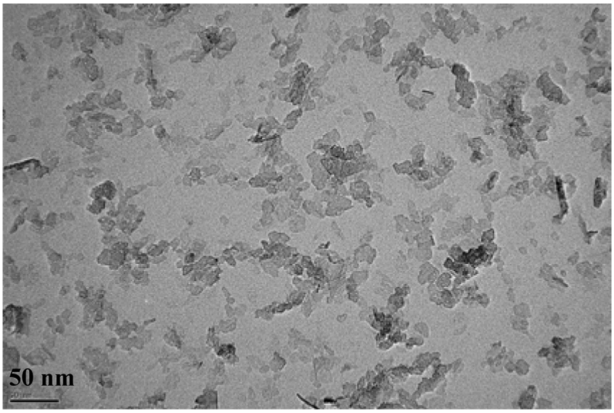

FIGURE 2 TEM image for the powder of boehmite sol (100 k).

TABLE 2 Contact Angle of Coating Films in Variation with Reaction Time

	Specimen (degree)	
Reaction time	S1	S2
6 h	84.12	84.13
12 h	86.11	87.19
24 h	86.18	87.87
48 h	106.72	93.26

of coating films to measure contact angle. This coating film was specimen S2 reacted for 12 h.

Surface roughness of coating films is affected by homogeneity of composition of materials and degree of gelation of sols. Figure 4 shows surface roughness of coating films in variation with reaction time. Surface roughness of coating films increased with decreasing the amount of MTMS and increasing reaction time. This indicates that heterogeneity and gelation of sol solution increases with decreasing the amount of MTMS and increasing reaction time. The roughness of coating films rapidly increased at the reaction time of 48 h due to rapid gelation of sols.

Figures 5 and 6 show transmittance of uncoated and coated glass substrate coated with sols of S1 and S2 in variation with reaction time. Transmittance of coated glass substrate coated with sols of S1 or S2 was measured after heat treatment at 300°C for 3 h. Transmittance was measured in the range between 400 and 780μm. Transmittance of glass substrate was approximately 89.5%. Transmittance of coated glass substrate coated with sols of S1 or S2 increased over 2% in comparison with uncoated glass substrate by 24 h reaction. However, the transmittance of glass substrates coated with sols of S1 and S2 were about 32.3 and 86.4%, respectively at the reaction time of 48 h.

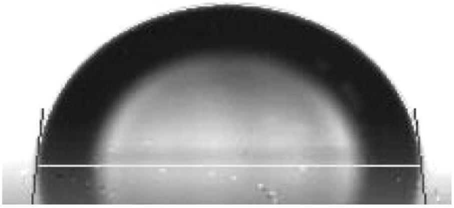

FIGURE 3 Photograph of water droplet on coating film to measure contact angle (coated with S2 sol reacted for 12 h).

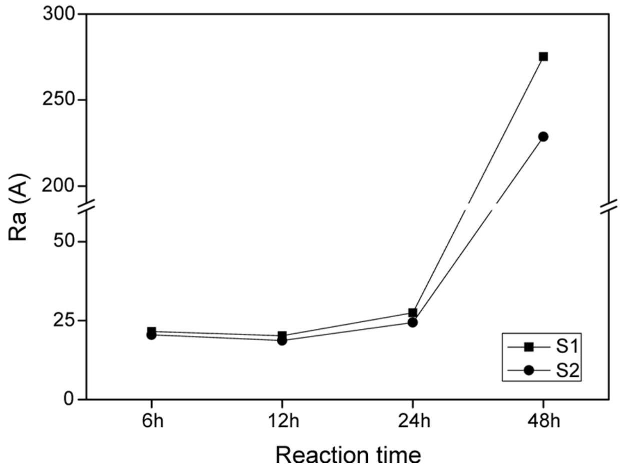

FIGURE 4 Surface roughness of coating films in variation with reaction time.

That is due to the gelation of sols and the formation of hazy and rough coating films at the reaction time of 48 h.

Figure 7 shows IR spectra for boehmite sol, MTMS and coating films heated in air at 50°C for 2 h. Figures 7(a) and 7(b) show the peaks

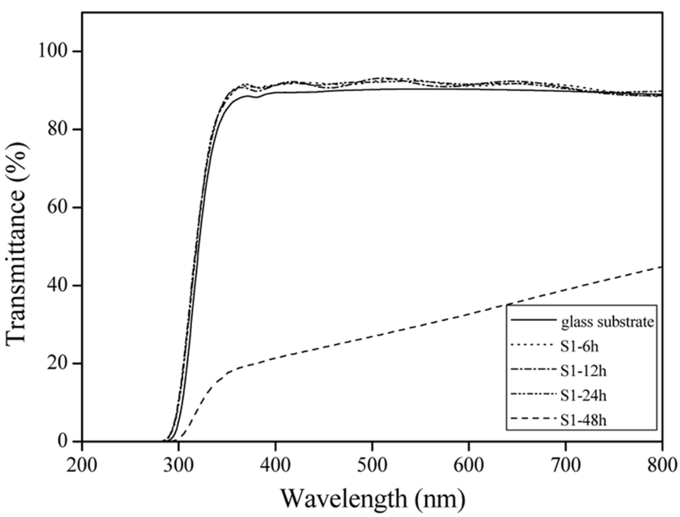

FIGURE 5 Transmittance of glass substrate uncoated and coated with S1 sol in variation with reaction time. Transmittance was measured after heat treatment at 300°C for 3 h.

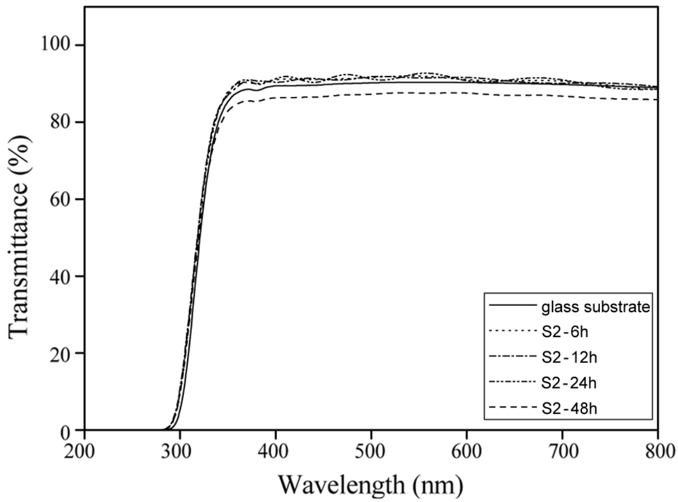

FIGURE 6 Transmittance of glass substrate uncoated and coated with S2 sol in variation with reaction time. Transmittance was measured after heat treatment at 300°C for 3 h.

of boehmite sol and MTMS, respectively. Figures 7(c) and 7(d) show the peaks of coating films of S1 and S2. As shown in Figure 7, the peaks corresponding to O–H and Al–OH bond of boehmite were observed

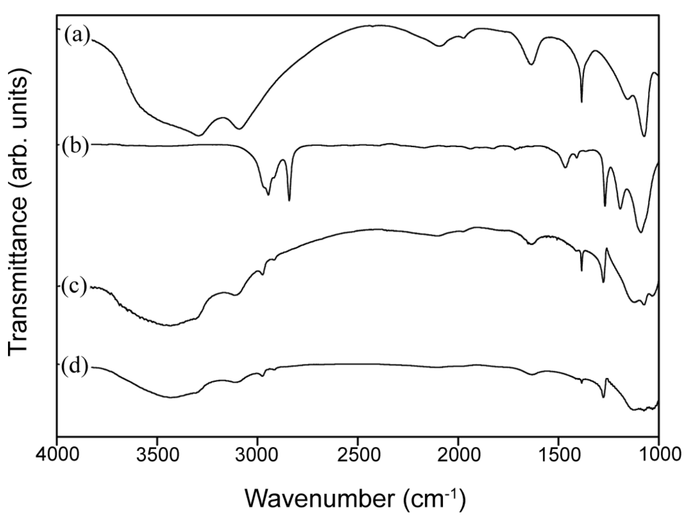

FIGURE 7 IR spectra for (a) boehmite sol, (b) MTMS, (c) S1 coating film, and (d) S2 coating film.

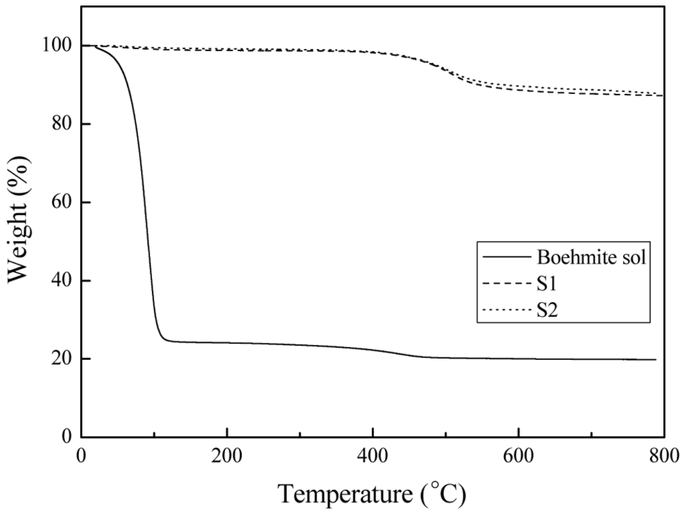

FIGURE 8 TGA curves of boehmite sol and coating films.

at around 3500 cm^{-1} and 1072 cm^{-1}, respectively. The peaks of MTMS at 2942 cm^{-1} and 1083 cm^{-1} corresponded to CH_3 and Si–OCH_3 bonds, respectively. The peaks of coating films at 1110 cm^{-1}, 1113 cm^{-1} and 1160 cm^{-1} corresponded to Si–O–Si, Al–O–Al and Si–O–Al bonds [10–12]. These peaks were the results of the condensation of MTMS and boehmite [13].

Figure 8 shows TGA curves of boehmite sol and coating films. For the boehmite sol, the weight decreased approximately 80 wt.% between room temperature and 100°C. The weight loss was due to the evaporation of water. In case of coating films of S1 and S2, the thermal degradation started at approximately 400°C. The weight loss was considered to be the degradation of methyl group of MTMS.

IV. CONCLUSIONS

Sols were synthesized by sol-gel process using nano boehmite sol and MTMS in variation with the amount of MTMS at different reaction time. Contact angle of coating films increased with increasing reaction time due to the increase of sol-gel reaction. Surface roughness of coating films increased with decreasing the amount of MTMS and increasing reaction time due to the increase of heterogeneity and gelation. Transmittance of coated glass substrate increased over 2% in comparison with uncoated glass substrate by 24 h reaction.

Transmittance and roughness of coating films changed rapidly when the reaction time was 48 h due to the gelation of sols and the formation of hazy coating films. Si–O–Si, Al–O–Al and Si–O–Al bonds for coating films were identified by FT-IR as the results of the condensation of MTMS and boehmite. The thermal degradation of coating films started at approximately 400°C.

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