Characteristics of organic–inorganic hybrid coating films synthesized from colloidal silica-silane sol

Hoy Yul Park · Dong Pil Kang · Moon Kyong Na · Hee Woong Lee · Hyeon Hwa Lee · Dong Soo Shin

Abstract Colloidal silica/silane sol solutions were prepared in variation with the amount of silane and reaction time. Such sol solutions were synthesized from colloidal silica/tetramethoxysilane(TMOS)/methyltrimethoxysilane (MTMS). Sol solutions were prepared by sol-gel method through two step reactions. In order to understand their physical and chemical properties, dip coating of sol solutions was performed on the glass substrates. The effects of amount of MTMS and reaction time on the formation of coating films were studied. Coating films became transparent as the reaction time increased. Contact angle of coating films increased with increasing the amount of MTMS. Contact angle of coating films decreased with increasing reaction time. Surface free energy of coating films decreased with increasing the amount of MTMS. Surface roughness of coating films decreased with increasing the amount of MTMS when the reaction time was 6 h. When the reaction time was 24, 48 and 72 h, surface roughness of coating films decreased with increasing the amount of MTMS in the beginning, and then increased when further amount of MTMS was added. Plastic hardness increased with increasing the amount of MTMS. Elastic portion inversely decreased with increasing the amount of MTMS. Coating films were stable until 550°C. Thermal degradation temperature of coating films decreased with increasing the amount of MTMS.

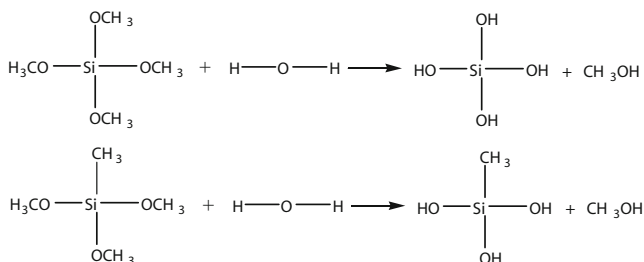**Keywords** Organic–inorganic hybrid · Coating films · Silane

1 Introduction

Organic–inorganic hybrid materials have applied to effective hard coating films possessing advantages of both organic and inorganic materials [1, 2]. There are many ways in which these materials may be synthesized. A typical one is the use of silica and silanes. The organic–inorganic hybrid materials can be synthesized by the use of trialkoxysilanes [3]. Organic–inorganic composite systems prepared by the sol-gel process have been investigated for several years [4]. The sol-gel process is a suitable means to synthesize this type of materials since the inorganic backbone can be built up by a low temperature process, and organics can survive processing. In order to avoid phase separation which is important for transparency and homogeneity, links for attaching the inorganic to organic units are necessary. Sol-gel method is one of the effective methods for the coating of colloidal silica at relatively low temperature on various organic polymer substrates [5–8]. Using sol-gel process, it is possible to synthesize the organic–inorganic hybrid materials in thin film coatings [9–11]. Sol solutions containing the desired alkoxide are prepared with a solvent and water. The sol-gel method is a novel procedure among solution reactions, which is based on the preparation of macromolecular network through the typical hydrolysis of alkoxide groups and the condensation reaction. Typical theoretical concept of hydrolysis and condensation reaction of alkoxysilane (TMOS and MTMS) is shown in Fig. 1.

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Hydrolysis of TMOS and MTMS

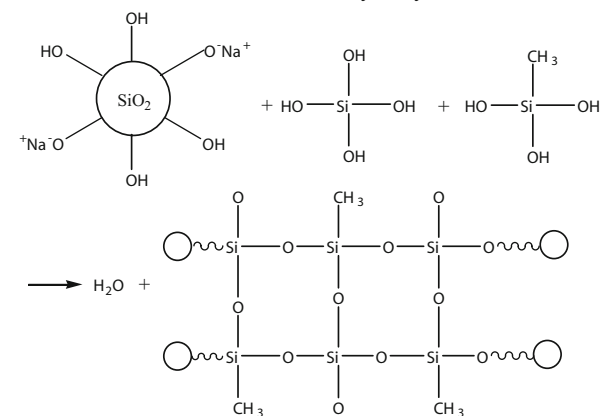Condensation of colloidal silica and hydroxysilane

Fig. 1 Theoretical concept of hydrolysis and condensation reaction of TMOS and MTMS

Organic–inorganic hybrid coatings on substrates like glasses have been mainly investigated for development of active optical systems [12–15]. In the scientific literature sol-gel dip coating techniques on glass have been investigated the most [16]. By use of organic–inorganic hybrid systems, thick layers up to several micrometers can be obtained without any problems, whereas pure inorganic layers are restricted in most cases to thickness up to around 1 μm. Using sol solutions, coating films on glass can be fabricated by spinning, dipping, or draining. After coating process, densification of so-gel coated films occurs during heat treatment. Densification means that the microporosity closes and eventually is eliminated. The degree of densification in sol-gel coating films is controlled by heat treatment, especially temperature. The properties of organic–inorganic hybrid coating films are affected by constitution, properties of composition, molecular structure and interaction of chemical bonds [17]. A major factor of coating film is chemical bond of organic materials with inorganic particles. Properties of organic–inorganic hybrid coating films improve with increasing chemical bond of organic materials and inorganic particles. Therefore, it is necessary to increase the attractive force between organic materials and inorganic particles.

In this paper, the effects of amount of MTMS and reaction time on the formation of coating films were studied. Colloidal silica/TMOS/MTMS sol solutions were prepared in variation with the amount of MTMS by sol-gel reaction through two step reactions. Coating films of sol solutions were performed on the glass substrates by dip-coater. State of coating films was investigated. Contact angle, surface free energy, surface roughness, plastic hardness and elastic portion of coating films were measured. In addition, thermal stability of coating films was studied.

2 Experiment

2.1 Fabrication of coating films

Colloidal silica (CS)/silane sol solutions were prepared in variation with the reaction time and the amount of silane. CS (Ludox HSA, 12 nm diameter, 30 wt% solids in water, pH 4.2) was obtained from W.R. Grace. Also, two kinds of silanes such as TMOS and MTMS were obtained from Toshiba Sol solutions were prepared by sol-gel reaction through two step reactions. At the first reaction step, TMOS and EtOH were added to CS in the ratio of 30 and 30 to 100, and reaction was carried out for 5 h at 30°C. At the second reaction step, MTMS was added to CS/TMOS/EtOH in the ratio of 60, 80, 100 and 120 to 160. The sol solutions were stirred at 300 rpm, 30°C for 6, 24, 48 and 72 h, respectively. Table 1 shows synthesis condition and composition of coating sols.

Glass substrates were washed and kept immersed in isopropanol. Dip coating was performed on the glass substrates using a rate of 4 cm/min, at room temperature. The coated glasses were kept in an oven for 1 h at 60°C for solvent removal. Then, they were heated to a temperature of 300°C and kept at this temperature for 3 h to obtain the final coated glasses.

The procedure for preparing sol-gel coating films is schematically shown in Fig. 2.

2.2 Measurement

Physical and chemical properties of coating films of sol solutions were investigated. Contact angle of the coating

Table 1 Synthesis condition and composition of coating sols.

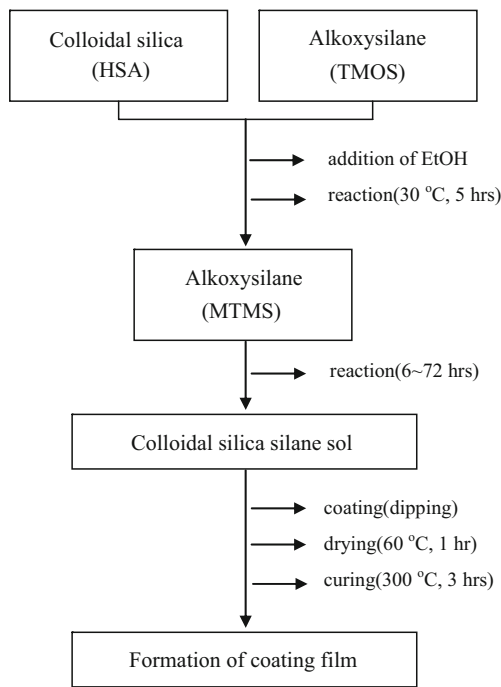| CS (wt%)	1st step reaction	2nd step reaction
	TMOS/EtOH (wt%)	MTMS (wt%)
100	30/30	60
100	30/30	80
100	30/30	100
100	30/30	120

Fig. 2 Procedure for preparing sol-gel coating films

films was measured using Dynamic Contact Angle Meter (Surface and Electro-Optics). Amount of water dropped on the coating films was 10 µl. Contact angle was measured in 10 s after dropping water on the coating films. Surface free energy of coating film was measured by Phoenix (Surface and Electro-Optics) using Lewis Acid/Base equation. Surface roughness (Ra) of coating films was measured by alpha-step 500 surface profiler. Ra was determined by averaging five measured values. Plastic hardness and elastic portion of coating films were measured using H100XYp Microhardness Tester (Fischerscope). Thermal stability of the coating films was analyzed using thermal gravimetric analysis (TGA, Q50, Dupont). Coating films were heated in air, at 20°C/min up to 800°C.

3 Results and discussion

3.1 Formation of coating films

Table 2 shows the state of coating films on the glass substrates. Coating films were transparent as the reaction time increased.

In the initial time of the reaction, hydrophilic CS and hydrophobic MTMS are not mixed appropriately and the states of coating films are unstable due to short reaction time. Coating films became transparent with increasing reaction time. It should be noted that the films with good transparency and low haze depends on the reaction time.

Table 2 State of coating films on the glass substrates.

Amount of MTMS versus CS 100	Reaction Time (h)	Formation of Coating Films
60	6	Hazy
	24	A little hazy
	48	Transparent
	72	Transparent
80	6	Hazy
	24	A little hazy
	48	Transparent
	72	Transparent
100	6	Hazy
	24	A little hazy
	48	Ttransparent
	72	Transparent
120	6	Hazy
	24	A little hazy
	48	Transparent
	72	Transparent

3.2 Contact angle

A water drop placed on solid surface is characterized by a contact angle. Contact angle of coating films depends on the surface energy of materials. CS has higher surface energy than water because of its ionic surface. Surface energy decreases when CS gets network with silanes. In case of using CS of Ludox HSA, contact angle was decreased much by using TMOS/MTMS than using MTMS only [18].
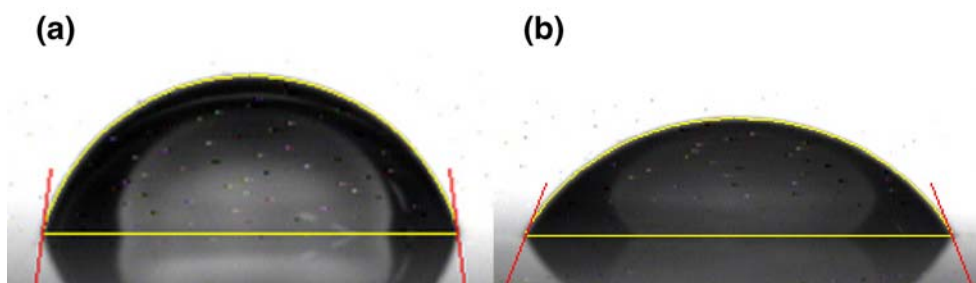
Table 3 shows contact angle of coating films in variation with the amount of MTMS and reaction time.

Contact angle of coating films increased with increasing the amount of MTMS when the reaction time was 6 h. This shows that hydrophilic property of CS changes into a form of hydrophobicity, since surface of CS particles are surrounded with MTMS. However, contact angle of coating films was not changed greatly with increasing the amount of MTMS when the reaction time was 24, 48 and 72 h. Contact angle of coating films decreased with increasing reaction time. That is due to the increased transparency with increasing reaction time, as shown in Table 2. Fig. 3 shows

Table 3 Contact angle of coating films in variation with the amount of MTMS and reaction time.

Reaction Time (h)	Amount of MTMS versus CS 100			
	60	80	100	120
6	76.21	80.25	81.21	81.45
24	69.02	70.55	70.01	70.50
48	68.50	69.21	69.55	69.30
72	68.48	68.85	68.45	69.02

the picture of contact angle of coating films when the ratio of CS to MTMS is 100 to 100.

3.3 Surface free energy

Surface free energy of coating films reacted for 48 h is shown in Fig. 4.

Surface free energy of coating films decreased with increasing the amount of MTMS. This indicates that CS are surrounded with methyl group in MTMS [18]. Surface free energy of CS is higher than that of methyl group.

3.4 Surface roughness

Figure 5 shows surface roughness of coating films in variation with the amount of MTMS and reaction time.

Surface roughness of coating films decreased with increasing the amount of MTMS when the reaction time was 6 h. This indicates that the addition of MTMS to CS particles effectively improved the formation of coating films by formation of siloxane chemical bonds between MTMS and CS particles. When the reaction time was 24 h, surface roughness of coating films decreased with increasing the amount of MTMS up to 100%, and then increased when further amount of MTMS was added. This indicates that surface of CS particles are surrounded with MTMS, followed by their condensation reaction with increasing the
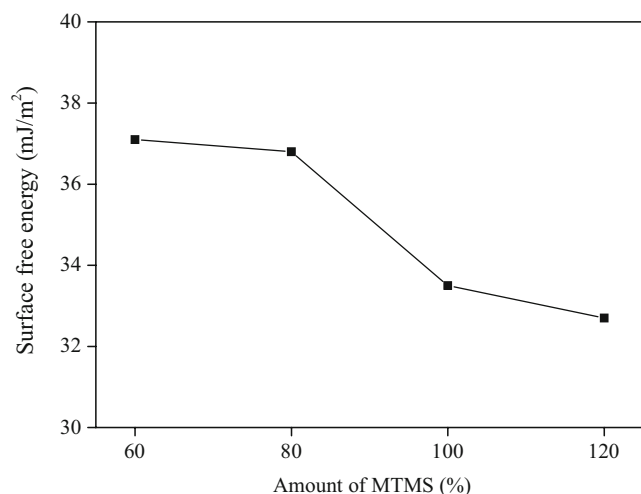
amount of MTMS. Surface roughness of coating films was lowest when the amount of MTMS was 100%. When the reaction time was 48 and 72 h, surface roughness of coating films decreased with increasing the amount of MTMS up to 80%, and then increased when further amount of MTMS was added, like the preceding.

3.5 Microhardness

Microhardness of coating films was measured by Vickers indenter [19, 20]. Plastic hardness (HU_{pl}) and elastic portion (η_{IT}) were determined through Eqs. 1 and 2 by measuring maximum depth (h_{max}) of indenter under constant loading and recovery depth (h_{corr}) under constant unloading, as shown in Fig. 6.

$$HU_{pl} = \frac{F_{max}}{26.43 \times (h_{corr})^2} \tag{1}$$

$$\eta_{IT} = \frac{W_{elast}}{W_{plast} + W_{elast}} \tag{2}$$

Plastic hardness and elastic portion of coating films reacted for 48 h are shown in Fig. 7.

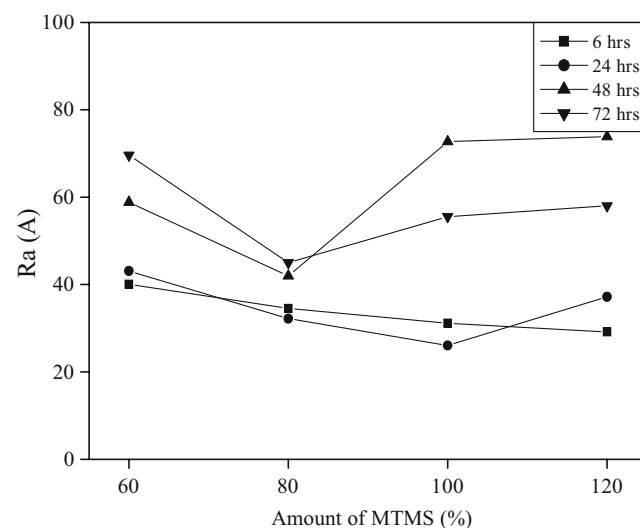**Fig. 4** Surface free energy of coating films reacted for 48 h

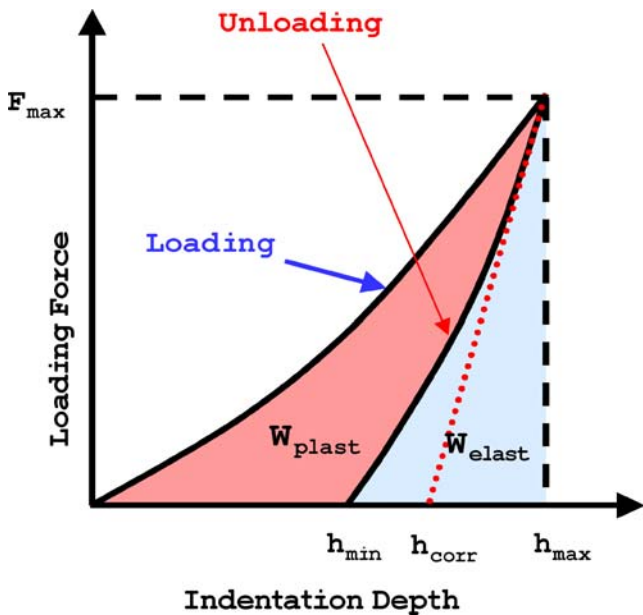**Fig. 5** Surface roughness of coating films in variation with the amount of MTMS and reaction time

Fig. 6 Schematics of indentation for measuring plastic hardness and elastic portion

Plastic hardness of coating film increased with increasing the amount of MTMS. This means that CS and MTMS get networks well with increasing the amount of MTMS. Elastic portion inversely decreased with increasing MTMS. This indicates that elastic segment causes to inverse behavior of plastic hardness and elastic portion of coating films decreased with increasing the amount of MTMS.

3.6 Thermal stability

Thermal gravimetric analysis provides an important tool for thermal stability studies of macromolecules. This technique allows to determining the temperature range at which a heated sample undergoes a major conformational change by means of monitoring the thermal weight loss profile.
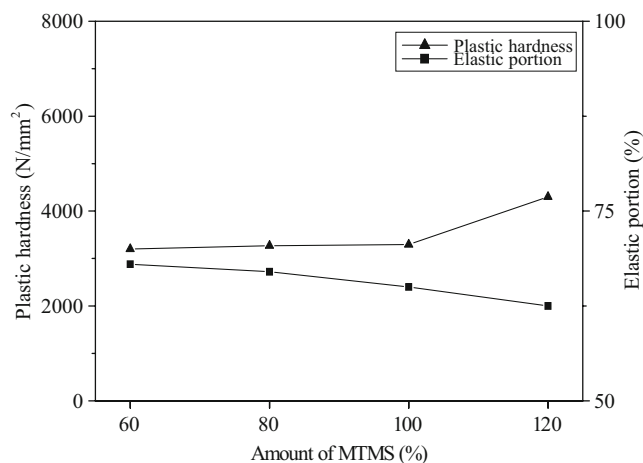

Fig. 7 Plastic hardness and elastic portion of coating films reacted for 48 h
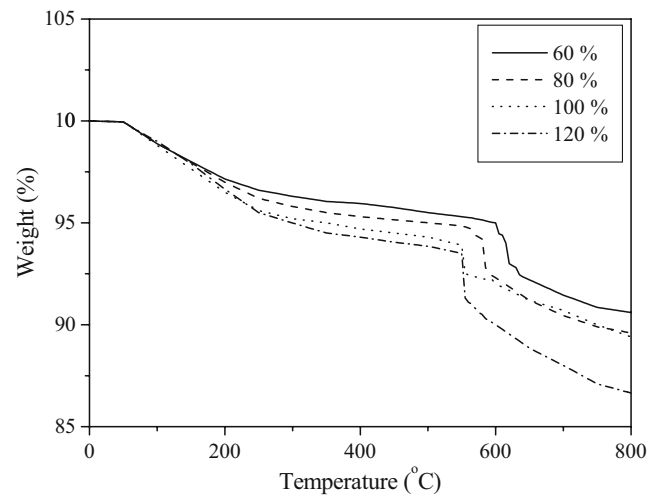

Fig. 8 TGA of coating films reacted for 48 h

Thermal gravimetric analyses of coating films in variation with the amount of MTMS were shown in Fig. 8.

The reaction time was 48 h. The decrease of weight until 550°C was due to the removal of produced water and alcohol during curing reaction. Weight reduction above 550°C was due to the thermal degradation of coating films. Coating films were stable until 550°C. Thermal degradation occurred above 600°C when the ratio of MTMS to CS was 60 to 100. Thermal degradation temperature decreased with increasing the amount of MTMS owing to the increase of organic components in MTMS.

4 Conclusion

CS/silane sol solutions were prepared in variation with the amount of MTMS and reaction time. Sol solutions were prepared by sol-gel method through two step reactions. Dip coating was performed on the glass substrates. Coating films became transparent as the reaction time increased. Contact angle of coating films increased with increasing the amount of MTMS when the reaction time was 6 h. However, contact angle of coating films was not changed greatly with increasing the amount of MTMS when the reaction time was 24, 48 and 72 h. Contact angle of coating films decreased with increasing reaction time. Surface free energy of coating films decreased with increasing the amount of MTMS. Surface roughness of coating films decreased with increasing the amount of MTMS when the reaction time was 6 h, due to the formation of siloxane chemical bonds between MTMS and CS particles. When the reaction time was 24 h, surface roughness of coating films decreased with increasing the amount of MTMS up to 100%, and then increased when further amount of MTMS was added, due to the surface of CS particles are surrounded with MTMS and following by their condensa-

tion reaction with increasing the amount of MTMS. When the reaction time was 48 and 72 h, surface roughness of coating films decreased with increasing the amount of MTMS up to 80%, and then increased when further amount of MTMS was added. Plastic hardness increased with increasing the amount of MTMS. Elastic portion inversely decreased with increasing the amount of MTMS. Coating films were stable until 550°C. Thermal degradation occurred above 600°C when the ratio of MTMS to CS was 60 to 100. Thermal degradation temperature decreased with increasing the amount of MTMS owing to the increase of organic components in MTMS.

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