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# Properties of nano-hybrid sol-gel coating films synthesized with colloidal silica and organoalkoxy silanes

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Colloidal silica (CS)-silane sols were synthesized as a dispersion medium of dispersoid, ceramic powders. Functionalizing silanes for nano-hybrid sols were methyltrimethoxysilane (MTMS) and  $\gamma$ -glycidoxypropyltrimethoxysilane (GTMS). GTMS was added to sols in different amounts. The stability of the sol was evaluated as a function of reaction time up to 10 days through the variation of the viscosity and the transmittance. The viscosity of the sols increased only slightly with reaction time before 10 days. When the sols were reacted for 10 days, the viscosity increased and the transmittance decreased markedly, as well. The coating films were formed on a glass substrate using a spin coating procedure. The coating films were flat and transparent without cracks. Also, the properties of the coating films such as contact angle, roughness, and thermal property were characterized. The CS/MTMS coating films showed a large contact angle. When a large amount of GTMS was added, the contact angle decreased due to the epoxy group. The roughness of the coating films was found to be very low, less than 20 nm. However the roughness of the coating films reacted for 10 days increased due to degradation of the stability of the sol. No thermal degradation of the CS/MTMS coating film occurred up to 600 °C. The CS/MTMS/GTMS coating films degraded at 400 °C due to decomposition of the epoxy group which has a long organic chain easily degraded by the thermal shock.

Keywords: Organic/inorganic nano-hybrid materials, Sol-gel process, Colloidal silica, Silane.

#### Introduction

Organic/inorganic nano-hybrid materials prepared using a sol-gel process have received considerable attention in the past decade [1]. Using the sol-gel process one can relatively easily obtain homogeneous nano-hybrid materials with a good dispersion of nanoparticles when compared with a direct dispersion method. As a result, the mechanical and physical properties of the organic/inorganic nano-hybrid materials can be easily improved by the introduction of a low content of inorganic nano fillers using a sol-gel process [2, 3]. In particular, nano-hybrid materials give low environmental pollution. They have high transparency, hardness, toughness, thermal dissociation temperature, and hydrophobicity using nano-sized inorganic material. There are many ways in which these materials may be synthesized, a typical one being the use of silica and silane. Using a sol-gel process, it is possible to fabricate organic/inorganic nano-hybrid materials in various forms, e.g. ultra-fine or spherically-shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, and extremely porous aerogel materials. The sol-gel reactions are catalyzed by both acids and bases and produce silica sols [4]. The gelation of silica-silane sol occurs with curing time, also, a networked structure of sol-gel silica evolves as a result of successive hydrolysis and

condensation, following the subsequent drying and curing [5, 6]:

Hydrolysis:  
Si - (OR)<sub>4</sub> + H<sub>2</sub>O 
$$\rightarrow$$
 Si - (OH)<sub>4</sub> + 4R - OH (1)

Condensation:  $2Si - (OH)_4 \rightarrow 2(Si - O - Si) + 4H_2O$  (2)

The silica particles are dispersed in water. The surfaces of silica particle are surrounded by ions to maintain a colloidal solution using the ionic repulsions among the ions. So the surface of colloidal silica (CS) is hydrophilic. When silanes are added to CS, they surround the surface of CS through the hydrolysis and condensation reactions (1) and (2). This is the surface treatment of CS using silane. The surface of silane-treated CS is hydrophobic. The hydrophobic sol can be applied to many fields as a surface protection coating agent and for optical applications.

In this paper, nano-hybrid sols were synthesized. The sols are involved with type of silane such as methyltrimethoxysilane (MTMS) and  $\gamma$ -glycidoxypropyltrimethoxysilane (GTMS) using CS. MTMS has three methoxy groups and a methyl group. GTMS has three methoxy groups and a bulky epoxy group. GTMS was added to sols in different amounts. The GTMS was added to improve the adhesive strength and softness of films, but it decreases the thermal stability of films due to its low thermal degradation temperature [7]. The stability of the sol was evaluated as a function of reaction time up to 10 days in terms of

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the variation of the viscosity and the transmittance. The coating films were formed on a glass substrate using a spin coating procedure with the reaction time varied. Also, the properties of the coating films such as contact angle, roughness, and thermal property were characterized in order to understand the behavior of the sols for forming coating films from them. The sol is used as a dispersion medium of dispersoid, ceramic powders. When the sol is stable, it can form a good dispersion with the dispersoid and a uniform transparent film. If the stability of the sol is degraded, it is difficult to apply as a dispersion medium due to its high viscosity and heterogeneous dispersion.

# **Experimental Details**

# Synthesis of the sol and formation of the coating film

The sols were synthesized from CS, MTMS, and GTMS. LS CS (particle size, 12 nm; pH 8.2; solid content: 30%) and 2327 CS (particle size, 20 nm; pH 9.3; solid content: 40%) obtained from Ludox Co. MTMS and GTMS were purchased from Toshiba Co. The sols were prepared using 2-step sol-gel reactions. LS and 2327 CS were mixed in equal amounts. The CS/MTMS sol was made from the CS mixture and MTMS. In the beginning of such sol fabrication, the acid, as catalyst, was added to the CS mixture to pH 4.0, following the addition of MTMS to the CS mixture at a gravimetric ratio of 20 to 100. The solution was reacted by stirring at 400 rpm for 1 day at room temperature. In the second step of the sol-gel reaction, MTMS was again added to the CS/ MTMS solution at a gravimetric ratio of 50 to 110. The solution was stirred at 300 rpm for 10 days at room temperature. Two CS/MTMS/GTMS sols were made from CS, MTMS, and GTMS. The first step was the same as that of the CS/MTMS solution. In the second step, MTMS and GTMS were added to the CS/MTMS solution at a gravimetric ratio of 40/10 and 30/20 to 120. GTMS has the bulky epoxy group so it is difficult to dissolve in water. So a small amount of GTMS was added to the sol. The synthesis conditions of the sol are described in Table 1.

The coating films were prepared using diluted sols with alcohol to decrease the viscosity, enhance the sol stability, and improve the wettability on a glass substrate. Diluted sols were coated on a glass substrate using a spin coating procedure. The coating films were dried

Table 1. Synthesis condition of nano-hybrid sol

Materials	acidity	1st step reaction	2 <sup>nd</sup> step reaction
LS/2327 50/50	Acetic acid /Phosphoric acid pH 4.0	MTMS/EtOH 20/20	MTMS/IPA 50/30
			MTMS/GTMS/IPA 40/10/30
			MTMS/GTMS/IPA 30/20/30

for 1 h at 90  $^{\rm o}{\rm C}$  for solvent removal and then cured for 2 h at 150  $^{\rm o}{\rm C}.$ 

### Characteristics of the sol and the coating film

To observe the stability of the sol, the viscosity and the transmittance of the sol were measured. The viscosity of the sol was measured with a BROOKFIELD digital rheometer DV- programmable viscometer at 20 °C. The transmittance of the sol was measured by a VARIAN cary 5000 UV-vis-NIR spectrophotometer.

The contact angle of the coating films was measured by a Surface and Electro Optics Phoenix 300. The roughness of the coating films was measured by a TENCOR alphastep 500 surface profiler. The thermal stability was identified using a TA instruments SDT Q600 at 10 K minute<sup>-1</sup> to 1,200 °C and under a nitrogen atmosphere.

# **Results and Discussion**

The viscosity of the sols with the reaction time varied is given in Fig. 1. As the reaction progresses low molecular silane and CS form silica form a three-dimensional network so the solid content of the sol increases. Further condensation of the remaining silanol groups leads to the gelation of the sol and eventually the completion of the sol-gel reaction. The viscosity of the sols slightly increased with the reaction time varied. When the sol reacted for 10 days, the viscosity increased markedly. This indicated the stability of the sol degraded. Sols reacted for more than 10 days were difficult to apply as a dispersion medium due to their high viscosity.

Figure 2 shows the transmittance of the sols with the reaction time varied. When silane was introduced into the reaction system after the hydrolysis the sol tended to be opaque regardless of the silane type. The loss of transparency indicates the occurrence of a large scale (i.e., > 400 nm) phase separation [8]. The hydrolysis replaces the methoxy group of MTMS and GTMS with hydroxyl



Fig. 1. Variation of the viscosity measured at  $20 \,^{\circ}$ C of sol synthesized from (a) CS/MTMS, CS and MTMS/GTMS contents of (b) 60/10 and (c) 50/20 with the reaction time varied.



**Fig. 2.** The transmittance of (a) CS/MTMS, CS and MTMS/ GTMS contents of (b) 60/10 and (c) 50/20 sol with the reaction time varied in the visible light region (wave length : 380-800 nm).



Fig. 3. The contact angle of the coating films from (a) CS/ MTMS, CS and MTMS/GTMS contents of (b) 60/10 and (c) 50/20 sol with the reaction time varied.

groups. Condensations involved the silanol groups produce siloxane groups (Si-O-Si), byproducts, alcohol, and water. Subsequent condensations between silanol groups and alcohol produced large silica particles and macroscopic organic-inorganic phase separation in the hybrid materials, leading to loss of transparency of the sols. The bulky epoxy group of GTMS hinders the condensation due to its long chain group, this hinders the transparency of the CS/MTMS/GTMS sol. The transmittance of the sols reacted for 10 days decreased markedly due to further condensation of remaining silanol groups, leading to the gelation of the sol.

The coating films were formed on a glass substrate using a spin coating procedure as a function of reaction time up to 10 days. The coating films were flat and transparent without cracks. The contact angle of the coating films is given in Fig. 3. The surface of CS has an ionic charge for dispersion in water. The hydrophobic sols were synthesized through hydrolysis and condensation, a threedimensional silica network formed. The CS/MTMS coating



**Fig. 4.** The roughness of the coating films from (a) CS/MTMS, CS and MTMS/GTMS contents of (b) 60/10 and (c) 50/20 sol with the reaction time varied.



**Fig. 5.** The thermogravimetric analysis (TGA) of the coating films from (a) CS/MTMS, CS and MTMS/GTMS contents of (b) 60/10 and (c) 50/20 sol reacted for 7 days under a nitrogen atmosphere.

films showed a large contact angle of 85°. When a large amount of GTMS was added the contact angle decreased due to its epoxy group. A hydroxyl group is formed when the epoxy group undergoes a ring-open reaction, leading to a high surface energy. But addition of a small amount of GTMS has no influence on the contact angle.

Figure 4 shows the roughness of the coating films with the reaction time varied. The roughness of the coating films was found to be very low, less than 20 nm. The sol formed smooth and flat coating films. In the beginning of the reaction the bulk epoxy group of GTMS had little influence on the surface property of the coating film. The roughness of the coating film using the sol reacted for 10 days increased due to degradation of the sol stability. The roughness of the CS/MTMS/GTMS coating film reacted for 10 days showed a larger roughness than the CS/MTMS coating film. As the reaction proceeded with GTMS condensation became difficult with the hydrolysis group due to its bulky epoxy group, this lead to an increase of the roughness.

A set of representative thermogravimetric analysis (TGA) thermograms of the coating films reacted for 7 days measured under a nitrogen atmosphere are shown in Fig. 5. The initial weight loss of 2-3% in all the samples is considered to be the result of desorption of the moisture adsorbed onto the surface of CS and the dehydration between CS and silanol. The CS/MTMS coating film shows one major weight loss at an elevated onset temperature of 600 °C, which is attributed to the thermal decomposition of the methyl group of MTMS. The CS/MTMS/GTMS coating films have one more major weight loss at 400 °C attributed to the decomposition of the epoxy group which has a long organic chain and so is easily degraded by thermal shock. After these decompositions, the TGA thermograms become flat again up to 1,200 °C because the organic component has been completely removed, leaving behind only the inorganic SiO<sub>2</sub> component. The silica networks between CS and silane increased the thermal stability but were affected by the type and the amount of silane.

#### Conclusions

Nano-hybrid sols were synthesized using a sol-gel process. Two types of silanes were used. GTMS was added to sols in different amounts. The stability of the sol synthesized at room temperature was maintained for 7 days regardless of the type of silane. The sol reacted for more than 7 days was difficult to apply as a dispersion medium as the viscosity of the sol increased and the transmittance decreased. The coating films were formed on a glass substrate using a spin coating procedure as a function of

reaction time up to 10 days. The coating films were flat and transparent without cracks. The CS/MTMS coating films showed a large contact angle. When a large amount of GTMS added, the contact angle decreased due to its epoxy group. The roughness of the coating films was found to be very low, less than 20 nm. But the roughness of the coating film using the sol reacted for 10 days increased due to degradation of the sol stability. No thermal degradation of the CS/MTMS coating film occurred up to 600 °C. The CS/MTMS/GTMS coating film degraded at 400 °C by the decomposition of the epoxy group which has long organic chain so is easily degraded by thermal shock.

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