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Citation	Journal of the Ceramic Society of Japan, 105(1223), 555-558 https://doi.org/10.2109/jcersj.105.555
Issue Date	1997-07-01
Doc URL	https://hdl.handle.net/2115/73941
Rights(URL)	https://creativecommons.org/licenses/by-nd/4.0/
Type	journal article
File Information	JCS105.555-558.pdf



Preparation of Organic-Inorganic Hybrid Coating Films from Vinyltriethoxysilane-Tetraethoxysilane by the Sol-Gel Method

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ゾル-ゲル法によるビニルトリエトキシシラン-テトラエトキシシラン系からの有機-無機複合コーティング薄膜の作製

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Organic-inorganic hybrid coating films were prepared using vinyltriethoxysilane and tetraethoxysilane by the sol-gel method on polyimide substrates. Tetraethoxysilane (TEOS) and vinyltriethoxysilane (VTES) or polyvinyltriethoxysilane (PVTES), which was obtained by the radical polymerization of VTES, were used as starting materials. In the TEOS-PVTES system, the organic-inorganic hybrid films with both carbon-carbon and siloxane bonds were obtained, and PVTES gave crack-free and flexible films over a wide composition range. It was found that the Si-O-Si bonds in the organic-inorganic hybrid films contributed to the increase in the dynamic hardness, while the smoothness of the coating films prepared using PVTES contributed to the increase in the pencil hardness.

[Received December 24, 1996; Accepted May 9, 1997]

Key-words : Sol-gel method, Organic-inorganic hybrid, Coating film, Hardness, Radical polymerization

1. Introduction

Recently, organic-inorganic hybrid materials have attracted much attention because they have both organic and inorganic characters.¹⁾ Preparation of the organic-inorganic hybrid through the sol-gel process, where organic and inorganic constituents are bonded to each other, has been reported.²⁾⁻⁸⁾ For example, Wojcik and Klein^{6),7)} reported that highly transparent organic-inorganic hybrids were prepared by copolymerization of vinyltriethoxysilane and meth (acrylate) monomers.

Polymer films are widely used for wrapping materials in our daily life because of their transparency, softness, lightness, and so on. In contrast, the disadvantages of these films are, for example, lack of abrasion resistance and of thermal stability, and high permeability of gases like water vapor and oxygen. On the other hand, inorganic materials have high mechanical strength, high thermal stability, and low gas permeability. It is thus possible to create new kinds of materials that have advantages of both organic and inorganic materials if polymer films and inorganic materials are combined.

We have already reported that SiO₂-based coating films can be formed on polyimide and nylon-6 substrates and these coatings are effective to suppress the water permeability.⁹⁾⁻¹¹⁾ In these studies, the thin films formed on polymer substrates were cracked when only tetraethoxysilane (TEOS) was used as a starting material, and the formation of cracks was avoided with addition of three-functional alkoxides. The addition of organic components is expected to give flexibility to the thin films and to avoid the formation of crack or to improve the adhesion of the thin films with polymer substrates.

In this study, organic-inorganic hybrid coating films were prepared by the sol-gel method on polyimide substrates from TEOS and vinyltriethoxysilane (VTES) or polyvinyltriethoxysilane (PVTES), which was obtained by the radical polymerization of VTES. Polyimide films were used as polymer substrates in this study since polyimides have high glass-transition temperature and heat-resistance. The thin films obtained by hydrolysis and condensation-polymerization of PVTES have carbon-carbon and siloxane

bonds, and are expected to have both flexibility and hardness. Microhardness and contact angle for water of these thin films were measured, and the influences of organic constituents on the properties of the thin films are discussed.

2. Experimental

Vinyltriethoxysilane (VTES) and di-*t*-butylperoxide were heated at 120°C for 1h in an argon filled flask to obtain polyvinyltriethoxysilane (PVTES) by the radical polymerization of VTES. The formation of PVTES was examined by ¹H, ¹³C and ²⁹Si NMR spectroscopies, which were measured using a JEOL JNM-GX500 spectrometer. CDCl₃ was used as a solvent for the measurement.

Tetraethoxysilane (TEOS) and VTES or PVTES were used as the starting materials. TEOS was dissolved in ethanol, and then H₂O containing 0.06 mass% HNO₃ was added to the solution. The solution was stirred for 1h at room temperature to hydrolyze TEOS. Proper amount of VTES or PVTES was then poured into the solution. After hydrolysis and condensation-polymerization were performed for about 24h, the solution obtained was used for coating. The molar ratios of ethanol and H₂O to the total alkoxide were kept to be 5 and 4, respectively.

Polyimide substrates with a thickness of 25 μm were used for coating. Silicon wafers were also used as substrates for coating to measure infrared spectra, the contact angle and microhardness of the films. The coating was carried out on the substrates in a dipping-withdrawing manner (withdrawing speed of 7 mm/s) in a dry box with relative humidity less than 30%. The coating films obtained were dried at 50°C for 4h, and then heat-treated at 150°C for 1h.

The cross section of the coating films on the polyimide substrates was observed using a scanning electron microscope (SEM) and the thickness of the films was evaluated. Infrared spectra of the coating films were measured with an FT-IR spectrophotometer. Contact angles for water on these thin films were measured with a horizontal microscope with a protractor eyepiece at room temperature. H₂O droplets were placed at five positions for one sample and the averaged value was adopted as the contact angle.

For the evaluation of hardness of the coating films, the

pencil hardness and the dynamic hardness were measured. The pencil hardness was measured according to JIS K5400. The dynamic hardness of the coating films on the silicon substrate was measured with a dynamic ultra-micro-hardness tester (Shimadzu, DUH-200). The penetration depth of an indenter during loading the indenter for 1 s was measured so that the dynamic hardness, DH , can be obtained from the following equation;

$$DH = \alpha(P/D^2) \quad (1)$$

where P (N) is the load of the indenter, D (mm) is the penetration depth, and α is the constant value for an indenter (in this study, $\alpha = 3.710 \times 10^5$).¹²⁾

The surface morphology was observed with an atomic force microscope (AFM) using a contact mode.

3. Results and discussion

The product obtained by the radical polymerization of VTES was viscous liquid. Figure 1 shows the ^{29}Si NMR spectra of VTES monomer and PVTES. In the spectrum of VTES, a sharp peak at -58 ppm is observed. In the spectrum of PVTES, a broad peak at -44 ppm is observed and no peaks are observed at around -58 ppm, where the peak due to VTES monomer was observed. IR, ^1H and ^{13}C NMR spectra of PVTES showed the absence of vinyl groups. These indicate that almost all the vinyl groups in VTES are polymerized by the radical polymerization. Gel permeation chromatography measurements showed that the degree of polymerization was about 10. The molecular structure of VTES and PVTES is shown in Scheme 1. PVTES prepared in this study was soluble in ethanol and ethanol/water mixture, and thus coating can be performed with the usual dipping-withdrawing manner.

Table 1 shows the state of the coating films on polyimide substrates in the TEOS-VTES and TEOS-PVTES systems. Compositions are represented as $x\text{TEOS} \cdot (100-x)$ (VTES or PVTES), where x shows the mol% of TEOS to the total alkoxides in the starting solutions. The open circles, open triangles and crosses represent that the coating film is homogeneous, heterogeneous and cracked, respectively. As mentioned in the experimental section, the coat-

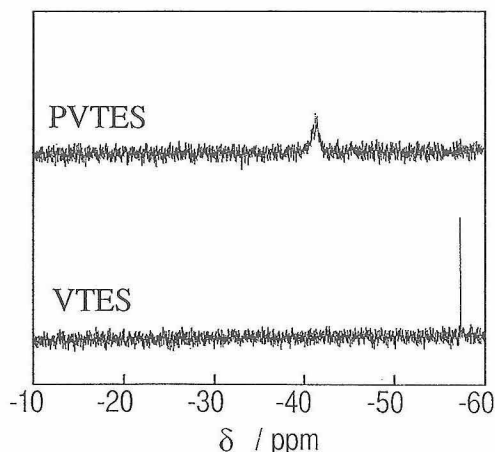
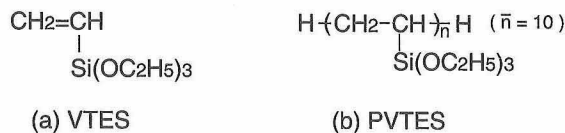


Fig. 1. ^{29}Si NMR spectra of VTES monomer and PVTES.



Scheme 1

Table 1. State of the Coating Films on Polyimide Substrates in the TEOS-VTES and TEOS-PVTES Systems. Compositions are Represented as $x\text{TEOS} \cdot (100-x)$ (VTES or PVTES), where x Shows the mol% of TEOS to the Total Alkoxides in the Starting Solutions

x / mol%	$x =$	0	25	50	75	100
$x\text{TEOS} \cdot (100-x)\text{VTES}$		Δ	Δ	$\circ$	$\circ$	$\times$
$x\text{TEOS} \cdot (100-x)\text{PVTES}$		$\circ$	$\circ$	$\circ$	$\circ$	$\times$

$\circ$; homogeneous Δ ; heterogeneous $\times$; cracked

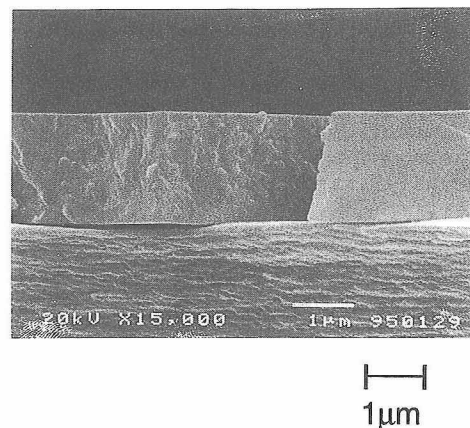


Fig. 2. SEM photograph of the cross section of the coating film prepared using only PVTES as the starting material.

ing films were dried at 50°C for 4h and heat-treated at 150°C for 1h. When only TEOS was used as a starting material, the thin films formed on polyimide substrates were cracked while drying the coating films. The addition of VTES or PVTES to the starting materials yielded crack-free and flexible films. In the case of VTES, homogeneous and uniform thin films without crack are obtained in the composition range from 50 to 75 mol% of TEOS. In the case of PVTES, the homogeneous films can be obtained in the range from 0 to 75 mol% of TEOS. All the coating films with homogeneous structure are transparent. It should be noted that the thin films can be obtained when only PVTES was used as a starting material.

Figure 2 shows an SEM photograph of the cross section of the coating film prepared using only PVTES as a starting material. The upper side is the coating film and the lower side is the polyimide substrate. Thickness of the coating film is about $1.8\text{ }\mu\text{m}$. This photograph shows that homogeneous, uniform coating film with very smooth surface is obtained. Despite the polyimide substrate being broken to observe the cross section of the coating films with SEM, the films do not peel off from the substrate but the polyimide substrate itself is broken. This means that the coating films strongly adhered to the substrate. A peel adhesion tape test to the coating films also showed that the coating films strongly adhered to the substrate. In the case of the usual sol-gel method, repeated coating procedures are needed to obtain the coating films with thickness larger than $1\text{ }\mu\text{m}$ without cracks. In the case of PVTES, the crack-free coating film with thickness of $1.8\text{ }\mu\text{m}$ was obtained with only one coating procedure. This shows that the formation of C-C bonds makes the coatings flexible and is effective for obtaining crack-free coatings.

Figure 3 shows infrared spectra of the coating films prepared from (a) $50\text{TEOS} \cdot 50\text{PVTES}$, (b) $50\text{TEOS} \cdot 50\text{VTES}$, (c) $75\text{TEOS} \cdot 25\text{PVTES}$ and (d) $75\text{TEOS} \cdot$

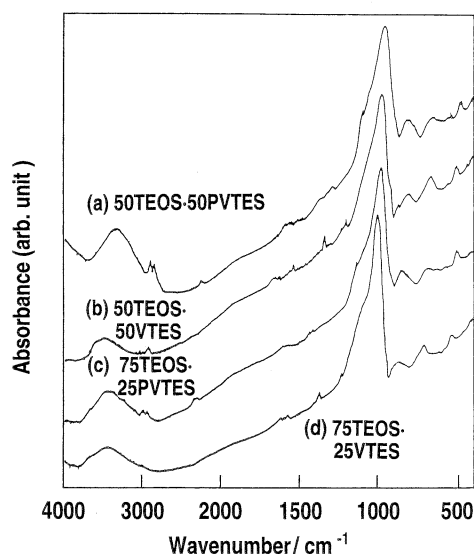


Fig. 3. FT-IR spectra of the coating films prepared from (a) 50TEOS · 50PVTES, (b) 50TEOS · 50VTES, (c) 75TEOS · 25PVTES and (d) 75TEOS · 25VTES.

25VTES. The peak at about 1100 cm^{-1} is assigned to Si-O-Si bonds, those at around 3000 cm^{-1} to C-H bonds, and those at around 3400 and 900 cm^{-1} to Si-OH bonds. The intensity of the peaks related to C-H bonds and to Si-OH bonds is increased with an increase of PVTES or VTES. The intensity of the peaks related to Si-OH bonds in the TEOS-VTES system is stronger than that in the TEOS-PVTES system. It is known that the Si-R groups decrease the connectivity of the oxide network of the gels prepared from TEOS-RSi(OR)₃ system.¹¹⁾ The C-C bonds in PVTES may become steric hindrance for the hydrolysis-condensation reaction of PVTES, and the bonds may inhibit the formation of siloxane bonds resulting from condensation between the silanol groups, which causes the strong intensity of the silanol groups in the TEOS-PVTES system.

Figure 4 shows the composition dependence of the contact angle of the coating films for water. Open triangles and solid circles indicate the TEOS-VTES and TEOS-PVTES systems, respectively. In both systems, the contact angle is increased with a decrease in the content of TEOS. These increases are due to an increase of the organic constituents that are hydrophobic groups. In the composition range from 25 to 50 mol% of TEOS, the contact angle of the coating films from the TEOS-VTES system is larger than that from

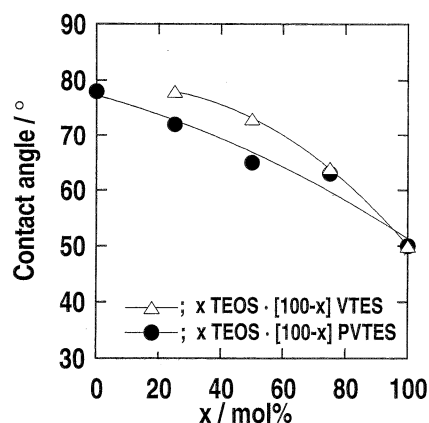


Fig. 4. Composition dependence of the contact angle for water of the coating films.

the TEOS-PVTES system. As shown in IR spectra (Fig. 3), the intensity of the peaks related to Si-OH bonds in the TEOS-PVTES system is stronger than that in the TEOS-VTES system. Thus, the large amount of silanol groups in the films from the TEOS-PVTES system caused the small contact angles.

Figure 5 shows the dynamic hardness of the coating films on Si substrates. Open triangles and solid circles indicate the TEOS-VTES and TEOS-PVTES systems, respectively. In both systems, the dynamic hardness is decreased with an increase in the content of VTES or PVTES in the starting materials. Since VTES and PVTES are three functional alkoxides, these indicate that the increase of VTES or PVTES results in the decrease of connectivity of the oxide network that has large contribution to the magnitude of the dynamic hardness. The dynamic hardness of the coating films from the TEOS-VTES system is larger than that of the TEOS-PVTES system in the whole composition range. This shows that the C-C bonds in the PVTES cause the decrease of connectivity of the Si-O-Si bonds. This is consistent with the results of IR spectra as shown in Fig. 3, in which the intensity of the peaks related to Si-OH bonds in the TEOS-PVTES system is stronger than that in the TEOS-VTES system.

Table 2 shows the pencil hardness of coating films on Si substrate. In the TEOS-VTES system, the pencil hardness becomes larger with an increase in the content of TEOS. However, in the TEOS-PVTES system, the pencil hardness is 9H in the whole composition range, while the dynamic hardness, shown in Fig. 4, was decreased with a decrease in the TEOS content. In the TEOS-VTES system, Si-O-Si bonds are assumed to be increased with an increase in the content of TEOS, and the formation of the bonds contributes to the increase in the pencil hardness as well as the dynamic hardness. Although Si-O-Si bonds in the TEOS-PVTES films are assumed to be decreased with a decrease in the content of TEOS, the pencil hardness is 9H in all the composition range. This indicates that not only the Si-O-Si bonds contribute to the increase in the pencil hardness but PVTES plays an important role in the increase of the pencil hardness.

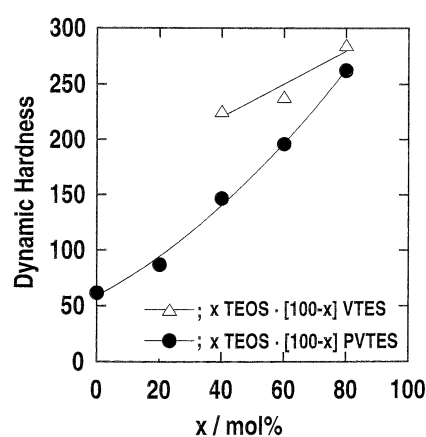


Fig. 5. Dynamic hardness of the coating films on Si substrate.

Table 2. Pencil Hardness of the Coating Films on Si Substrate

x / mol%	x = 0	25	50	75	100
x TEOS · (100 - x)VTES	—	—	3H	5H	9H*
x TEOS · (100 - x)PVTES	9H	9H	9H	9H	9H*

(* ; cracked)

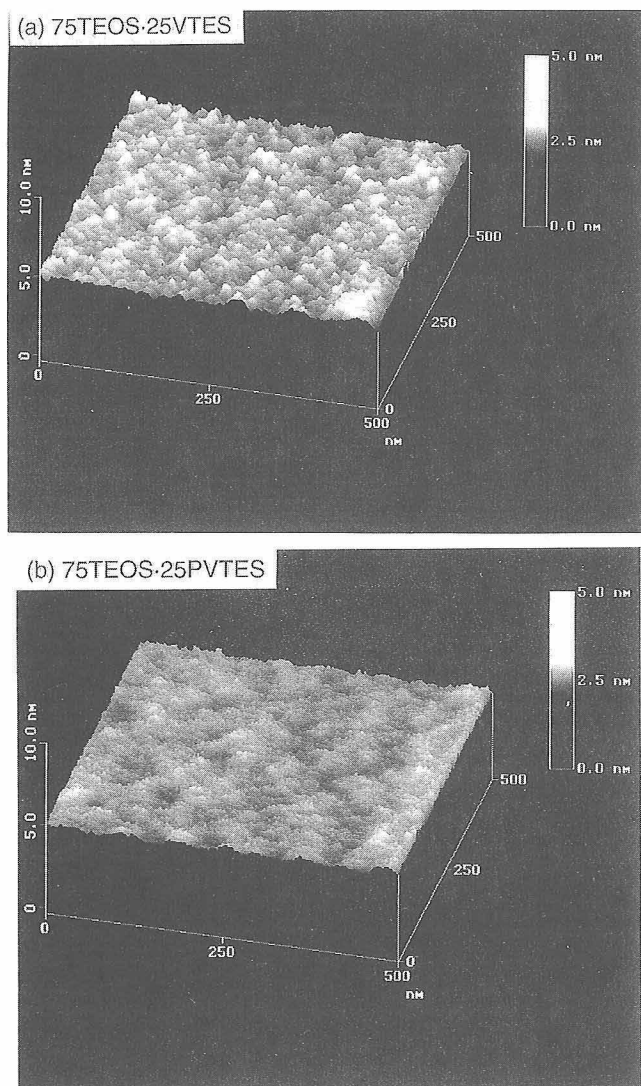


Fig. 6. AFM image of the coating films prepared from (a) 75TEOS · 25VTES and (b) 75TEOS · 25PVTES.

Figure 6 shows AFM images of the coating film prepared from (a) 75TEOS · 25VTES and (b) 75TEOS · 25PVTES. Smooth surface with unevenness of less than 1 nm is observed in (b), while rough surface with unevenness of larger than a few nanometers and with small grains of 20 to 50 nm in diameter is observed in (a). Since surfaces are scratched with pencils to examine the pencil hardness, the surface morphology is one of the reasons affecting the pencil hardness; the smooth surface may give large pencil hardness. These indicate that PVTES is effective to increase the pencil hardness since the coating films using PVTES have very smooth surface. The pencil hardness is assumed to be closely related to abrasion resistance. The coating films

from PVTES are thus expected to have high abrasion resistance.

By using TEOS and PVTES, it was found that the coating films can be formed on nylon-6 and PET substrates. The films were transparent and flexible, and strongly adhered to the substrates. As shown in Fig. 4 and Table 2, the coating films have large hardness and may have high abrasion resistance. The coatings must have high potentiality for practical applications such as protective and gas barrier coatings for organic polymers.

4. Conclusion

Organic-inorganic hybrid coating films were prepared by the sol-gel method on polyimide and Si substrates from TEOS and VTES or PVTES. The addition of VTES or PVTES to the starting materials gave crack-free and flexible films. The dynamic hardness was decreased with an increase in the content of VTES or PVTES in the starting materials, since the increase of VTES or PVTES resulted in the decrease of connectivity of the oxide network that has large contribution to the magnitude of the dynamic hardness. In the case of the TEOS-PVTES system, the pencil hardness was 9H in all the composition range, while the dynamic hardness was decreased with a decrease in the TEOS content. It was suggested that the smoothness of the coating films prepared using PVTES contributed to the increase of the pencil hardness.

Acknowledgment The authors thank Mr. Akira Yuasa and Mr. Hideki Yamamoto of Central Glass Co., Ltd., for the dynamic hardness measurement. The present study was supported by a Grant-in-Aid (No. 09450328) from the Ministry of Education, Science, Sports and Culture of Japan.

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