

Water Permeation Properties of $\text{SiO}_2\text{-RSiO}_{3/2}$ (R = Methyl, Vinyl, Phenyl) Thin Films Prepared by the Sol-Gel Method on Nylon-6 Substrate

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SYNOPSIS

Nylon-6 substrates were coated with $\text{SiO}_2\text{-RSiO}_{3/2}$ (R = methyl, vinyl, phenyl) thin films by the sol-gel method, and their water permeability was evaluated. Tetraethoxysilane (TEOS) and trifunctional alkoxides such as methyltriethoxysilane (MTES), vinyltriethoxysilane (VTES), and phenyltriethoxysilane (PhTES) were used as starting materials. Water permeability coefficients of the nylon-6 substrates coated with these $\text{SiO}_2\text{-RSiO}_{3/2}$ thin films were increased with an increase in the content of these trialkoxysilanes in the films. The water permeability coefficients of these coated nylon-6 substrates were smaller in the order of the systems $\text{TEOS-PhTES} < \text{TEOS-VTES} < \text{TEOS-MTES}$ in the relatively low content of the trialkoxysilanes. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The sol-gel method is now widely accepted as the useful method for preparing inorganic materials and organic-inorganic composite materials from metal alkoxides [M(OR)_x ; M = Si, Ti, Zr, Al, R = methyl through butyl]. Hydrolysis and condensation polymerization of these alkoxides result in the formation of a three-dimensional metal oxide network. This method has several features such as the low-temperature process, the easy preparation of high-purity materials, and the variety of the shapes of the products. Recently, new organic-inorganic composite materials have been prepared by the sol-gel method because of advantages such as low-temperature process and high homogeneity.^{1,2}

The sol-gel method is also known to be one of the practical methods for the coating of oxide thin films on various substrates such as glasses,³ metals,⁴ and organic polymers.⁵⁻⁸ This method is suitable for the coating of thin films on organic polymer substrates since the metal oxide network is formed at relatively low temperatures. However, it is difficult to make crack-free thin films on organic polymers when only

Si(OR)_4 , Ti(OR)_4 , Zr(OR)_4 , or Al(OR)_3 [R = methyl through butyl] is used as a starting material. Schmidt et al. succeeded in ORMOCER (Organic Modified Ceramics) coating on polycarbonate or poly(ethylene terephthalate),^{5,6} and Wang and Wilkes succeeded in organic-inorganic hybrid coatings on polycarbonate.⁷ Such organic-inorganic composites are useful for the coating of thin films on organic polymer substrates.

We have recently found that crack-free thin films can be formed on polyimide and nylon-6 substrates using the mixtures of tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) as starting materials and that the coating on these organic polymers is effective to suppress the water permeability of the films.^{9,10} It is expected that water permeability changes with the kind of organic group if we use other organically modified trialkoxysilanes instead of MTES.

In this study, $\text{SiO}_2\text{-RSiO}_{3/2}$ (R = methyl, vinyl, phenyl) thin films are coated on nylon-6 substrates of 25 μm thickness by the sol-gel method; the substrates kept flexibility after the coating. Water permeability coefficients of the coated films are evaluated, and the effects of the composition of the coating solution and variety of the organic groups, R, on the coefficients are examined on the basis of

Table I State of Nylon-6 Substrates Coated with SiO₂-RSiO_{3/2} Thin Films^a

	x in $[100 - x] \text{ Si(OEt)}_4 \cdot x \text{ RSi(OEt)}_3$ (mol %)											
	$x =$	0	10	20	30	40	50	60	70	80	90	100
MTES	×	○ (1.0)	○ (0.7)	○ (0.8)	○ (0.9)	○ (0.8)	○ (1.1)	○ (1.0)	○ (1.2)	△	△	
VTES	×	○ (0.8)	○ (0.9)	○ (1.0)	○ (1.0)	○ (1.2)	○ (1.4)	○ (1.3)	△	△	△	
PhTES	×	○ (1.1)	○ (1.2)	○ (1.4)	○ (1.8)	○ (1.7)	○ (2.0)	○ (2.0)	○ (2.3)	△	△	

^a Compositions are represented as $[100 - x] \text{ Si(OEt)}_4 \cdot x \text{ RSi(OEt)}_3$, where x shows mol % of trialkoxysilane (MTES, VTES, PhTES) to the total alkoxides in the starting solutions. Thicknesses of the coating films are shown in parentheses in micrometers. Open circles, homogeneous (crack free); crosses, cracked; open triangles, heterogeneous.

infrared spectra and contact angle for water of the thin films.

EXPERIMENTAL

TEOS, MTES, vinyltriethoxysilane (VTES), and phenyltriethoxysilane (PhTES) were used as starting materials. TEOS was dissolved in ethanol, and then H₂O containing 0.06 wt % HNO₃ was added to the solution. The solution was stirred for 1 h at room temperature to hydrolyze TEOS. Proper amounts of MTES, VTES, or PhTES were then poured into the solution. After hydrolysis and condensation polymerization were done for about 24 h at room temperature in a closed container, the solution obtained was used for coating. The molar ratios of ethanol and H₂O to the total alkoxides (TEOS + MTES, VTES, or PhTES) were kept at 5 and 4, respectively.

The nylon-6 substrates with a thickness of 25 μm were used for coating. Silicon wafers and soda-lime glass plates were also used as substrates for coating to measure infrared spectra and contact angle for water, respectively. The coating was carried out on the substrates in a dipping-withdrawing manner (withdrawing speed, 7 mm/s) in a dry box with relative humidity less than 30%. The coating films obtained were heat treated at 50°C for 4 h and kept in a desiccator before the measurements of water permeability, contact angle, and infrared spectrum. The thickness of the coating films on the nylon-6 substrates was evaluated by a scanning electron microscopic (SEM) micrograph of the cross-section of the coating films.

Water permeability measurements for these coated nylon-6 substrates were performed with a hand-made permeation apparatus.^{9,10} The permeation apparatus was evacuated to 10⁻³ mm Hg, and

the saturated vapor of water at 0°C (4.58 mm Hg) was introduced to the upstream side. The permeated pressure on the downstream side was monitored by an MKS-Baratron transducer (MKS-220B).

Infrared spectra of SiO₂-RSiO_{3/2} thin films deposited on silicon wafers were measured with an FT-IR spectrophotometer (Perkin-Elmer 1650). Contact angles for these thin films on soda-lime glass substrates were measured with a horizontal microscope with a protractor eyepiece equipped with cross-hairs at room temperature. H₂O droplets were placed at five positions for one sample, and the averaged value was adopted as the contact angle.

RESULTS AND DISCUSSION

When only TEOS was used as a starting material, microcracks were observed in the thin films coated on nylon-6 substrates because of the lack of flexibility of the coating films. The addition of trialkoxysilane (MTES, VTES, or PhTES) to the sol solution has enabled the formation of crack-free coating films. Table I shows the state of the coating films on nylon-6 substrates. The thickness of each film is shown in parentheses. Compositions are represented as $[100 - x] \text{ Si(OEt)}_4 \cdot x \text{ RSi(OEt)}_3$, where x indicates mol % of trialkoxysilane (MTES, VTES, or PhTES) to the total alkoxides in the starting solution. Open circles, open triangles, and crosses indicate that the coating film is homogeneous, heterogeneous, or cracked, respectively. When MTES or PhTES was used as the starting material, homogeneous and crack-free thin films were obtained in the composition range from 10 to 80 mol % of MTES or PhTES to the total alkoxides. In the case of VTES, homogeneous thin films are obtained in the range from 10 to 70 mol % of VTES. The film thickness ranges

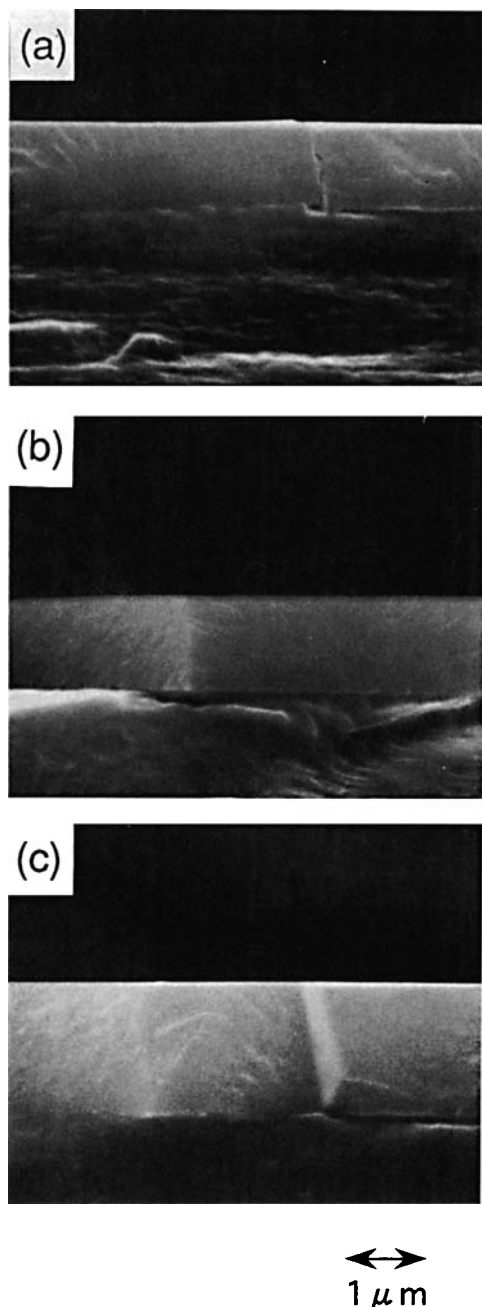


Figure 1 SEM micrograph of the cross-section of the coating films. (a) 50TEOS·50MTES, (b) 50TEOS·50VTES, (c) 50TEOS·50PhTES (in mol %).

from 0.7 to 1.2 μm for the TEOS-MTES system, from 0.8 to 1.3 μm for the TEOS-VTES system, and from 1.1 to 2.3 μm for the TEOS-PhTES system. The thickness increases with an increase of VTES or PhTES in the TEOS-VTES or the TEOS-PhTES system, while no systematic variation is observed in the TEOS-MTES system. Moreover, the thickness of the films in the TEOS-PhTES system is larger

than that of the TEOS-MTES and the TEOS-VTES systems.

Figure 1 shows SEM micrographs of the cross-section of the coating films: (a) for 50TEOS·50MTES, (b) for 50TEOS·50VTES, and (c) for 50TEOS·50PhTES, respectively. The coating films adhere strongly to the nylon-6 substrates. The thickness of the coating film of 50TEOS·50PhTES is larger than that of 50TEOS·50MTES and 50TEOS·50VTES. It can be seen from Table I and Figure 1 that the thickness of the coating films was changed with varying the organic groups, R.

Figure 2 shows the composition dependence of the water permeability coefficient of the nylon-6 substrates coated with the thin films. Open circles, open squares, and solid triangles indicate the TEOS-MTES, TEOS-VTES, and TEOS-PhTES systems, respectively. In the TEOS-MTES system, the coefficients are increased with an increase of MTES. In the TEOS-VTES and the TEOS-PhTES systems, the coefficients are increased with an increase of VTES or PhTES in the composition range from 10 to 60 mol % of VTES or PhTES and decreased with an increase of VTES or PhTES in the composition range over 60 mol % of VTES or PhTES. The coefficients are smaller in the order of the system TEOS-

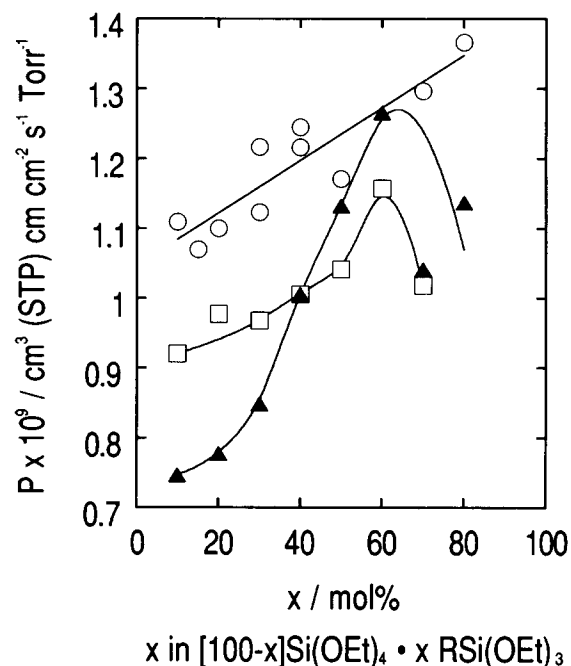


Figure 2 Composition dependence of the water permeability coefficient of the nylon-6 substrates coated with $\text{SiO}_2\text{-RSiO}_{3/2}$ thin films. (O) TEOS-MTES system, (\square) TEOS-VTES system, (\blacktriangle) TEOS-PhTES system. The lines are drawn as a guide.

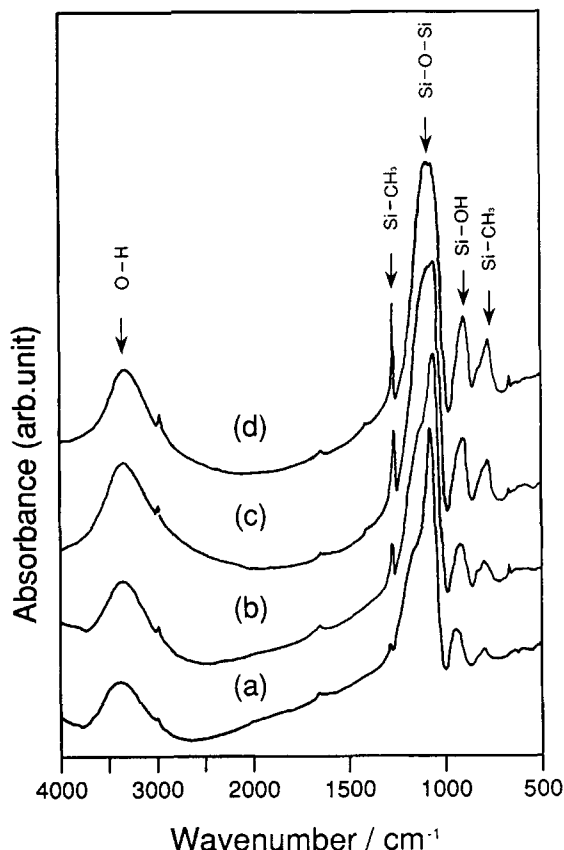


Figure 3 FT-IR spectra of $\text{SiO}_2\text{-CH}_3\text{SiO}_{3/2}$ thin films deposited on silicon wafers. (a) 90TEOS · 10MTES, (b) 70TEOS · 30MTES, (c) 50TEOS · 50MTES, (d) 30TEOS · 70MTES (in mol %).

PhTES < TEOS-VTES < TEOS-MTES in the relatively low content of the trialkoxysilanes.

Figure 3 shows infrared spectra of the coating films prepared from the TEOS-MTES system: (a) for 90TEOS · 10MTES, (b) for 70TEOS · 30MTES, (c) for 50TEOS · 50MTES, and (d) for 30TEOS · 70MTES, respectively. The peaks at about 1,100 and 800 cm^{-1} are assigned to Si-O-Si bonds, those at 1,260 and 760 cm^{-1} to Si-CH₃ bonds, and those at around 3,400 and 910 cm^{-1} to Si-OH bonds. The intensity of the peaks related to Si-CH₃ bonds and to Si-OH bonds is increased with an increase of MTES. In the TEOS-VTES and the TEOS-PhTES systems, the increase in the intensity of the peaks related to Si-OH bonds was also observed with an increase of VTES and PhTES. It is known that the Si-CH₃ groups decrease the connectivity of the oxide network.¹¹⁻¹³ Since the Si-R (R = methyl, vinyl, phenyl) groups set the distance apart between the silanol groups present around the organic groups, the Si-R (R = methyl, vinyl, phenyl) groups may inhibit the formation of siloxane bonds resulting

from condensation between the silanol groups, which causes the stronger intensity of the silanol groups with increasing trialkoxysilane content.

Figure 4 shows the composition dependence of the contact angle of the coating films for water. Open circles, open squares, and solid triangles indicate the TEOS-MTES, TEOS-VTES, and TEOS-PhTES systems, respectively. The solid circle shows the angle of the films prepared from only TEOS. In all of the systems, the contact angle is increased with an increase in the content of trialkoxysilane (MTES, VTES, PhTES) in the range from 10 to 30 mol %. These increases are due to an increase of the organic substituents (methyl, vinyl, and phenyl groups), which are the hydrophobic groups. In the TEOS-MTES system, the contact angle is decreased with an increase of MTES in the composition range over 50 mol %. This is due to the increase of silanol group, as shown in Figure 3. However, in the TEOS-VTES and TEOS-PhTES systems, the contact angle is not decreased with an increase of trialkoxysilane in the composition range over 50 mol % of VTES and PhTES. It can be recognized that the vinyl- and the phenyl-modified silica thin films are more hydrophobic than the methyl-modified ones,¹¹ and therefore, the contact angle is not decreased, even though the amount of silanol groups increased with an increase of trialkoxysilane.

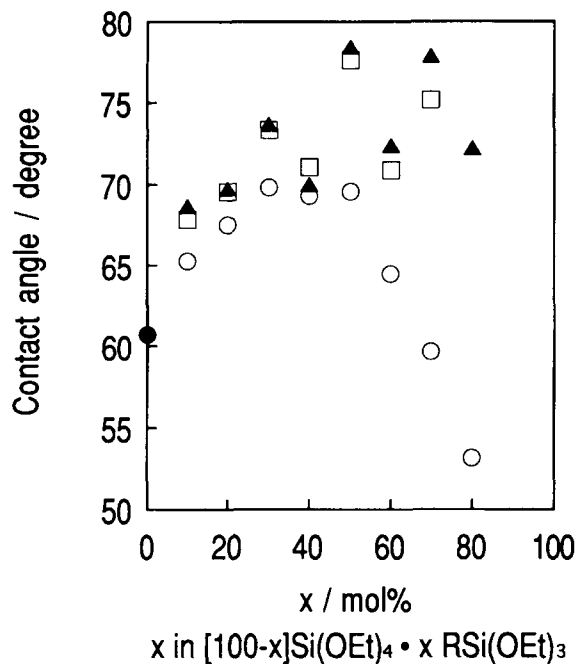


Figure 4 Composition dependence of contact angle for $\text{SiO}_2\text{-RSiO}_{3/2}$ thin films. (○) TEOS-MTES system, (□) TEOS-VTES system, (▲) TEOS-PhTES system, (●) 100TEOS (prepared from only TEOS).

It has been revealed from the results above that the water permeation property of nylon-6 substrates coated with $\text{SiO}_2\text{-RSiO}_{3/2}$ (R = methyl, vinyl, phenyl) thin film is dependent on the composition and the kind of organic groups, R, since the structure and properties of coating films are changed with varying the composition and organic groups, R. As shown in Figure 2, the water permeability coefficient was increased with an increase of trialkoxysilane (MTES, VTES, PhTES) in the composition range from 10 to 60 mol %. Figure 3 showed that the intensity of peaks due to silanol groups was also increased with an increase of MTES. These indicate that the increase of water permeability coefficient in this composition range is due to the increase of silanol groups in the coating films, because the silanol group is hydrophilic. In this range, an increase of hydrophilic silanol groups preferentially influences water permeation properties.

It is also expected that the difference in hydrophobicity caused by the introduction of various organic groups influenced water permeability. In Figure 2, the water permeability coefficient is increased with an increase of MTES in all of the composition ranges studied and, by contrast, is decreased with an increase of VTES and PhTES in the range over 60 mol %. As shown Figure 4, in the TEOS-VTES and TEOS-PhTES systems, the contact angle is not decreased with an increase of trialkoxysilane in the range over 50 mol %. These results can be attributed to an increase of the vinyl and phenyl groups, which make silica thin films more hydrophobic than the methyl-modified ones. Water permeability coefficients are smaller in the order of the system TEOS-PhTES < TEOS-VTES < TEOS-MTES in the low content of trialkoxysilane because the silica thin films are more hydrophobic in the order of the phenyl- > vinyl- > methyl-modified silica thin films.

CONCLUSION

In the composition range from 10 to 60 mol % of trialkoxysilane (MTES, VTES, PhTES), water permeation coefficients are increased with an increase of trialkoxysilane. In this range, an increase of hydrophilic silanol group preferentially influences water permeation properties. In the composition range over 60 mol %, the coefficients of the TEOS-

MTES system are increased with an increase of MTES. In the TEOS-VTES and TEOS-PhTES systems, however, these coefficients decreased with an increase of VTES and PhTES in this composition range. These results are attributed to an increase of the vinyl and phenyl groups, which make silica thin films more hydrophobic than do the methyl-modified ones. In this composition range, the difference in hydrophobicity caused by the introduction of various organic groups of trialkoxysilane preferentially influences water permeability. Water permeability coefficients are smaller in the order of the system TEOS-PhTES < TEOS-VTES < TEOS-MTES in the low content of trialkoxysilane because the silica thin films are more hydrophobic in the order of the phenyl- > vinyl- > methyl-modified silica thin films.

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