

# Effect of the Miscibility between a Silane and a Sizing Agent on Silanol Condensation

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**ABSTRACT:** The miscibility between a hydrolyzed silane coupling agent, which had chemically nonreactive organofunctional groups such as propyl groups, and a film-forming polymer [poly(vinyl acetate) PVAc] and its effect on silanol condensation were studied. A mixture consisting of a silane hydrolyzate and PVAc obtained from an alcoholic aqueous solution was investigated with Fourier transform infrared spectroscopy and size exclusion chromatography. Hydrogen bonding between the SiOH groups of the silane and the C=O groups of PVAc and silanol condensation affected by PVAc were examined. The hydrogen bonding and condensation reaction were influenced by the miscibility between

the organofunctional group of the silane and PVAc. The miscibility of each system was estimated from the calculated Hildebrand solubility parameter of the organofunctional group. A correlation between the miscibility and the integrated absorbance of the hydrogen-bonded C=O, obtained by least-squares curve fitting, was established. On the basis of the molecular weight of the silane and the number of hydrogen-bonded C=O groups, a micellelike phase was proposed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 589–598, 2003

**Key words:** FT-IR; gel permeation chromatography (GPC)

## INTRODUCTION

Organofunctional silane coupling agents are commonly used to modify the surfaces of glass fibers and siliceous fillers for improved adhesion with polymer matrices. Numerous publications<sup>1–9</sup> have appeared in the past describing important molecular information concerning glass–matrix interfaces and interphases and improved composite properties. Industrially, glass fibers are generally treated with sizing agents consisting of a film-forming polymer, a lubricant, a coupling agent, and an antistatic agent. Therefore, in a sizing system with other components, the reaction behavior of the silane coupling agent is expected to be more complicated than that of the silane coupling agent alone.

Film formers are used for fiber coatings that mainly provide flexibility, drapeability, and surface protection. Typical examples of synthesized film formers are poly(ethylene glycol), poly(vinyl alcohol) (PVA), and poly(vinyl acetate) (PVAc). Because these polymers have hydroxyl or carbonyl groups, these agents interact with the silanol groups of hydrolyzed silanes through hydrogen bonding. Therefore, such film formers influence the condensation reaction of the hydrolyzed silane and the molecular structure of the subsequent polysilsesquioxane.

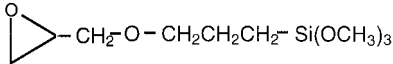
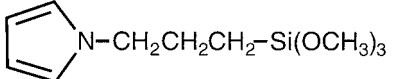
In comparison with the extensively studied interactions between silane coupling agents and matrix polymers, studies on the effects of film formers or lubricants on silanes are mostly phenomenological, and very little has been published. Therefore, the mechanism involved in their protection of glass–polymer interfaces and their interactions with silanes are not well understood. The structure and composition of the layer of the sizing system containing silane coupling agents are critical to understanding the properties of the composites, such as the mechanical strength and hydrothermal stability.

Although not directly related to the role of sizing agents, somewhat related studies in the field of coatings have been reported. The incorporation of methyltrimethoxysilane or its hydrolyzed species into ethylene/vinyl acetate (EVA) copolymer latices provided evidence of an interpenetrating polymer network (IPN) structure consisting of a hard polysilsesquioxane phase and an EVA phase.<sup>10</sup> Similarly, bonding through silane coupling agents with most polymers is explained by IPN formation and interdiffusion phenomena in the interphase.<sup>11</sup> The interdiffusion and crosslinking of silanes were identified as the mechanism of adhesion of poly(vinyl chloride) (PVC) plastisols to silane-treated glass.<sup>12</sup> Vinyltriethoxysilane (VTE) and  $\gamma$ -methacryloxypropyltrimethoxysilane ( $\gamma$ -MPS) modified acrylic,<sup>13</sup> PVAc,<sup>14,15</sup> and PVC<sup>16,17</sup> latices were prepared by emulsion copolymerization.

The purpose of this study was to elucidate the silanol condensation in the sizing system. A model sizing

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TABLE I  
Structural Formulas of Silanes

Name	Structural formula
Vinyltriethoxysilane (VTE)	$\text{CH}_2=\text{CH}-\text{Si}(\text{OC}_2\text{H}_5)_3$
Allyltriethoxysilane (ALE)	$\text{CH}_2=\text{CHCH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$
<i>n</i> -Propyltrimethoxysilane (PTM)	$\text{CH}_3\text{CH}_2\text{CH}_2-\text{Si}(\text{OCH}_3)_3$
2-Cyanoethyltriethoxysilane (CNE)	$\text{N}\equiv\text{C}-\text{CH}_2\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$
3-Cyanopropyltrimethoxysilane (CPE)	$\text{N}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OCH}_3)_3$
$\gamma$ -Methacryloxypropyltrimethoxysilane ( $\gamma$ -MPS)	$\text{CH}_2=\underset{\text{C}}{\overset{\text{CH}_3}{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OCH}_3)_3$
$\gamma$ -Glycidoxypropyltrimethoxysilane ( $\gamma$ -GPS)	
<i>N</i> -(3-Trimethoxysilylpropyl)pyrrole (PPY)	

system consisting of a silane hydrolyzate as a coupling agent and a low molecular weight PVAc as a film-forming polymer was used to study the effect of the miscibility and hydrogen bonding between the silane coupling agent and the film-forming polymer. Several kinds of silane coupling agents, having different miscibilities with PVAc, were used. Miscibility was estimated by the calculated Hildebrand solubility parameter of an organofunctional group of the silane and PVAc. The structural studies for some of the silane hydrolyzates and their oligomeric and polymeric species used in this study were extensively performed in our laboratory.<sup>18</sup> PVAc was used as a polymeric sizing agent. The carbonyl group of PVAc was expected to interact with the silanol group of the hydrolyzed silane coupling agent.

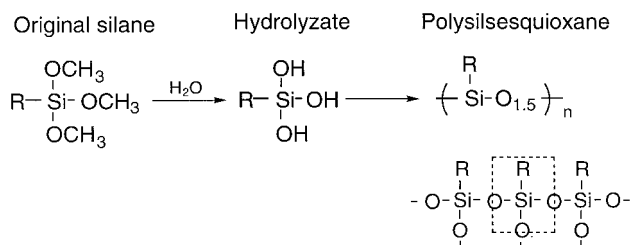
## EXPERIMENTAL

### Materials

Silane coupling agents were purchased from HULS Chemicals, Inc., and were used as received; their structural formulas are shown in Table I. An aqueous alcoholic solution (0.8 mL of H<sub>2</sub>O and 9.2 mL of ethanol) was used to hydrolyze the silanes. The pH of the solution was adjusted to 3.0 with a dilute aqueous solution of HCl. The polymeric sizing agent PVAc (0.6 g) was dissolved in the pH-adjusted solution by vigorous stirring for at least 30 min and was followed by the addition of 0.5 g of silane. The silanes were hydrolyzed in the aqueous alcoholic solution with PVAc for 1 h at room temperature.

After the silane was hydrolyzed for 1 h, 7 g of the sample solution was spread on a petri dish, and the solvent was driven off until the weight reached 2 g in

a desiccator under reduced pressure at room temperature. After the solvent was driven off, the petri dish was placed in a closed container in which the relative humidity was controlled at 84% with a saturated KCl aqueous solution at room temperature. Because a low molecular weight PVAc, which would be convenient for dissolution into a solvent and chromatographic separation from the silane, was not commercially available, PVA was acetylated under the following conditions. PVA, which was used for acetylation, was purchased from Scientific Polymer Products, Inc. (weight-average molecular weight = 2000 g/mol) and used as received. Twenty milliliters of acetic anhydride and 90 mL of pyridine were put in a 200-mL, round-bottom flask and were heated until 100°C in an oil bath over stirring. Then, ground PVA powder was added to the solvent. The mixture was refluxed at 100°C over stirring for 5 h. Then, the solution was cooled to room temperature and poured into an excess amount of *n*-hexane with vigorous agitation. A highly viscous material was precipitated, and this was followed by dissolution in tetrahydrofuran (THF). The THF solution was poured into an excess amount of *n*-hexane. The precipitation was repeated three times. The precipitate was filtered from the solvent, and the residual *n*-hexane was driven off in a desiccator under reduced pressure at room temperature for 24 h. The Fourier transform infrared (FTIR) spectrum of the PVAc obtained by the acetylation of the PVA previously mentioned indicated that the band at 1737 cm<sup>-1</sup> was attributable to the isolated C=O stretching mode of the acetyl group. Two bands at 1372 and 1237 cm<sup>-1</sup> were also due to the acetyl group. No hydroxyl bands were detected in the PVAc spectrum, indicating that the PVA was fully acetylated.



**Figure 1** Structural formulas of silane hydrolyzate and polysilsesquioxane.

### Measurements

An FTIR spectrophotometer (Bomem Michelson MB) with a liquid-nitrogen-cooled mercury-cadmium-telluride detector was used at a resolution of  $4 \text{ cm}^{-1}$  with the coaddition of 100 scans. The specific detectivity of the detector was  $1 \times 10^{10} \text{ cm Hz}^{1/2} \text{ W}^{-1}$ . The spectrometer was purged with dry nitrogen for the minimization of atmospheric water vapor and carbon dioxide. The mixture samples of hydrolyzates and PVAc were coated as a thin film on a potassium bromide disk. A Lorentzian/Gaussian curve-fitting procedure was used to resolve overlapped bands.

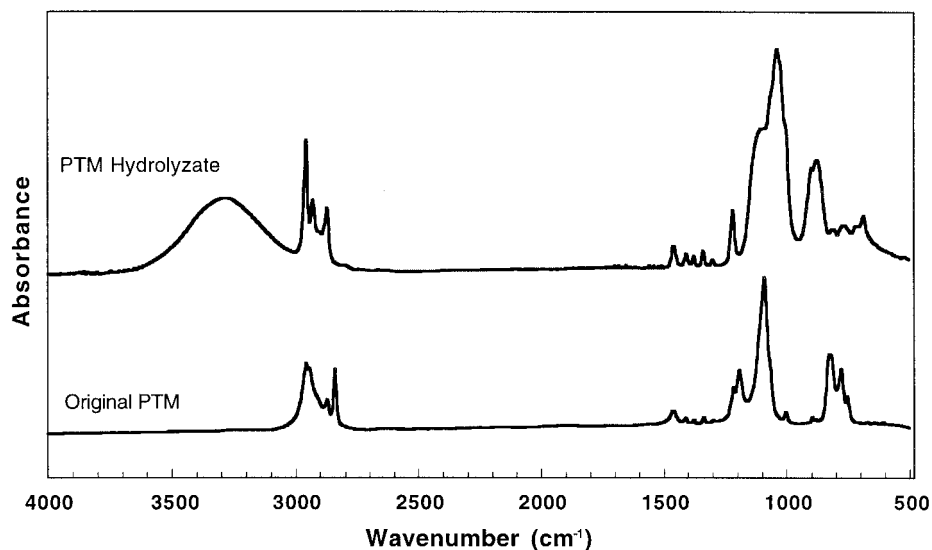
A size exclusion chromatograph, consisting of a metering pump (Waters model 510 HPLC pump), one series of packed columns, and an ultraviolet detector at 254 nm (Waters Associates model 484 tunable absorbance detector) was used to separate the oligomeric poly(methacryloxypropylsilsesquioxane) fractions and the polymeric sizing agent. One series of columns, which consisted of  $10^3$ -nm (Waters Associates),  $10^2$ -nm (Waters Associates), and 50.0-nm  $\mu$ Styragel columns (Waters Associates), was used. The mobile phase was HPLC-grade THF with a flow rate of 1 mL/min. The molecular weight distribution of the

silane fractions and sizing agent was measured with respect to near-monodisperse polystyrene standards (Tosoh Corp.).

### RESULTS AND DISCUSSION

Figure 1 illustrates the structural formulas of silane coupling agents and the schematic hydrolysis and silanol condensation reactions. Polysilsesquioxanes refer to monosubstituted siloxane polymers of the general form  $(\text{RSiO}_{1.5})_n$ . The carbonyl group ( $\text{C}=\text{O}$ ) of PVAc will hydrogen-bond with the silanol group ( $\text{SiOH}$ ) of the silane hydrolyzates. FTIR spectra of *n*-propyltrimethoxysilane (PTM) and its hydrolyzate are shown in Figure 2 as examples. The bands at 1193, 1090, and  $825 \text{ cm}^{-1}$  due to the methoxy group ( $\text{OCH}_3$ ) disappeared, whereas the siloxane bands from 1130 to  $1000 \text{ cm}^{-1}$  and the band corresponding to the  $\text{SiOH}$  group at  $900 \text{ cm}^{-1}$  appeared after hydrolysis.

In Figure 3, two main characteristics were observed in the model sizing system consisting of the PTM hydrolyzate and PVAc with respect to the PTM hydrolyzate, PVAc-free system. First, the acetyl  $\text{C}=\text{O}$  band was split into two bands. The band at  $1737 \text{ cm}^{-1}$  was due to the carbonyl stretching band of the free  $\text{C}=\text{O}$  of the acetyl group of PVAc (acetyl  $\text{C}=\text{O}$ ), and another band at  $1715 \text{ cm}^{-1}$  was due to hydrogen-bonded acetyl  $\text{C}=\text{O}$ .<sup>19</sup> According to the miscibility studies of EVA/poly(vinyl phenol) (PVPh) blends with FTIR by Coleman et al.,<sup>20</sup> the band at  $1737 \text{ cm}^{-1}$  of the acetyl  $\text{C}=\text{O}$  shifts to  $1708 \text{ cm}^{-1}$  by hydrogen bonding with the phenolic  $-\text{OH}$  group of PVPh. Second, the shape of the siloxane bands of the region from 1130 to  $1000 \text{ cm}^{-1}$  was drastically changed. The intensity of the silanol band also changed. Judging from these spectra, we conclude that silanol condensation



**Figure 2** FTIR spectra of propyl-functional silane and its hydrolyzate.

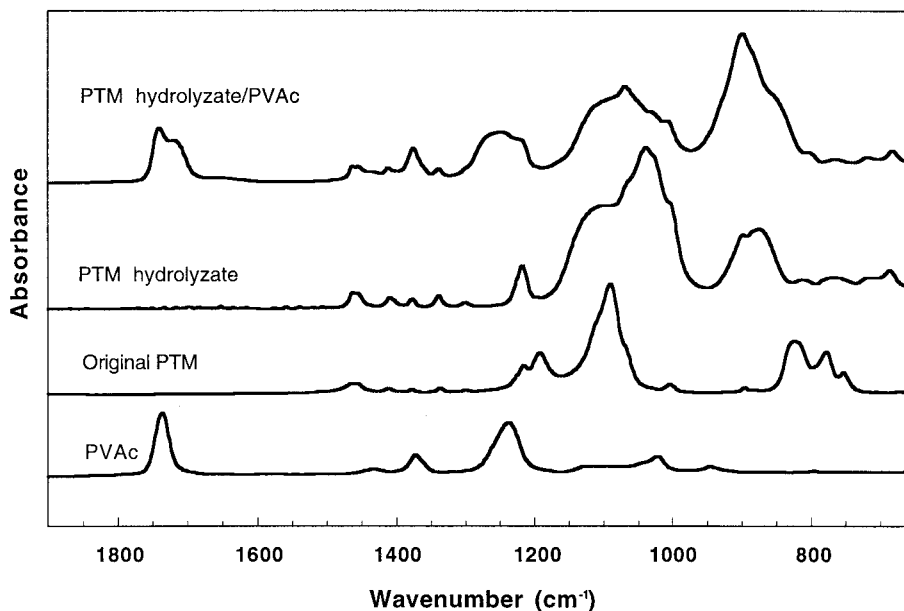


Figure 3 FTIR spectra of the mixture of hydrolyzed propyl-functional silane and PVAc.

must be affected by the presence of the film-forming polymer PVAc.

FTIR spectra of the carbonyl stretching band of the region from 1790 to 1650  $\text{cm}^{-1}$  of the several model sizing systems are shown in Figure 4. The intensities of the hydrogen-bonded acetyl  $\text{C}=\text{O}$  bands around 1715  $\text{cm}^{-1}$  were different. The siloxane bands of each model sizing system also showed characteristic

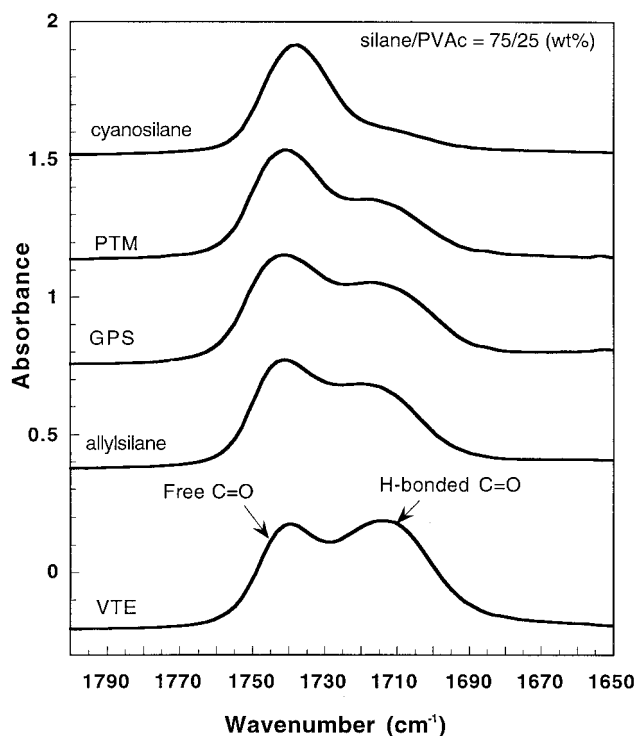


Figure 4 FTIR spectra of the mixtures of silane hydrolyzate and PVAc.

shapes, indicating that the extent of hydrogen bonding was influenced by the organofunctional group of the silane. It is thought that a different extent of hydrogen bonding between  $\text{SiOH}$  and acetyl  $\text{C}=\text{O}$  indicates a different environment for  $\text{SiOH}$  of each model sizing system, resulting in different silanol condensations. Therefore, the organofunctional group of the silane may influence the hydrogen bonding and silanol condensation.

Time-dependent IR measurements were made for each model sizing system and silane coupling agent, and IR spectra of the region from 1900 to 650  $\text{cm}^{-1}$  of typical examples are shown in Figures 5–7. IR spectra of an unhydrolyzed original silane coupling agent and PVAc are also shown in each figure as references. In these figures, the dotted lines are the spectra of the corresponding silane hydrolyzate at each corresponding drying time without the sizing agent present. In the spectrum of PVAc, the bands at 1737, 1450, 1370, 1230, and 1050  $\text{cm}^{-1}$  were due to the free  $\text{C}=\text{O}$  stretching mode, the  $-\text{OCH}_3$  group, the  $\text{CH}_3\text{C}=\text{O}$  symmetric deformation, the asymmetric  $\text{COC}$ , and the  $\text{OC}$  group, respectively.<sup>21</sup>

Shown in Figure 5 are the FTIR spectra of (1) the model sizing system consisting of the VTE hydrolyzate and PVAc and (2) the VTE hydrolyzate. In the spectrum of the original VTE, the bands at 1168, 1104, and 1082  $\text{cm}^{-1}$  and the shoulder around 937  $\text{cm}^{-1}$  were due to the ethoxy groups. A weak band at 1600  $\text{cm}^{-1}$  was due to the  $\text{C}=\text{C}$  group. The band at 1011  $\text{cm}^{-1}$  was due to the trans  $\text{CH}$  wagging of the vinyl group. Some characteristic features can be observed in the IR spectra of the model sizing system as follows. The  $\text{C}=\text{O}$  band was split into two distinct bands

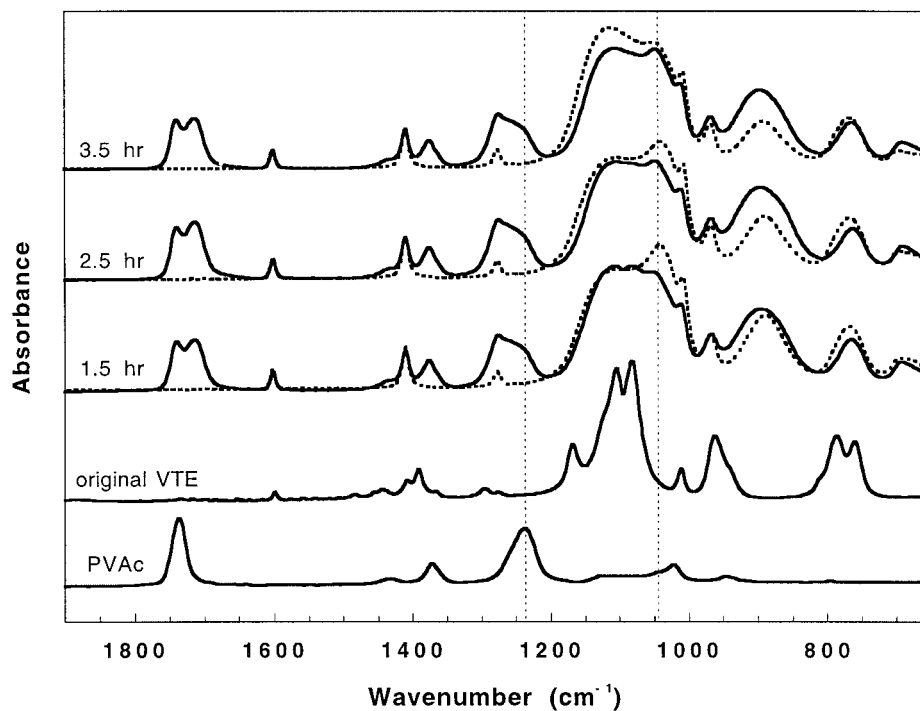


Figure 5 FTIR spectra of vinyl silane hydrolyzate and its mixture with PVAc as a function of time.

because of hydrogen-bond formation with the silanol and appeared around  $1740$  and  $1715\text{ cm}^{-1}$ . The intensity of the hydrogen-bonded  $\text{C}=\text{O}$  remained almost constant throughout the experimental periods. The absorbance at  $1230\text{ cm}^{-1}$  due to the  $\text{COC}$  symmetric stretching became broad toward the region of higher

frequencies because the positively charged carbon atom of the  $\text{C}=\text{O}$  group, which was forming a hydrogen bond, caused the  $\text{C}-\text{O}$  single bond to be strengthened. The shape of the siloxane bands and the intensity of the  $\text{SiOH}$  band remained mostly unchanged. However, the absorbance at  $1130\text{ cm}^{-1}$  increased and

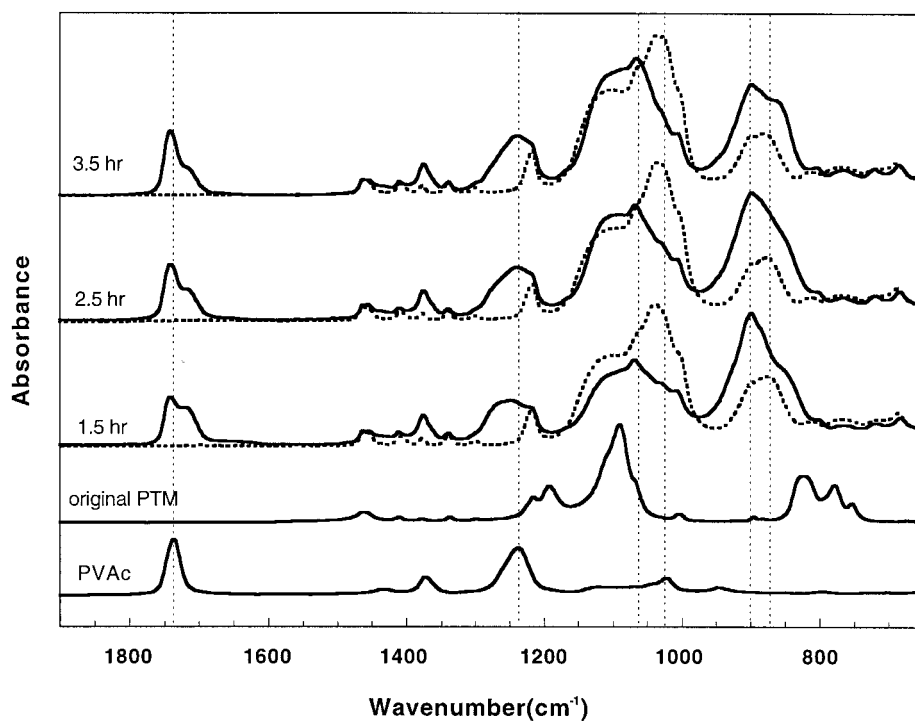


Figure 6 FTIR spectra of propyl silane hydrolyzate and its mixture with PVAc as a function of time.

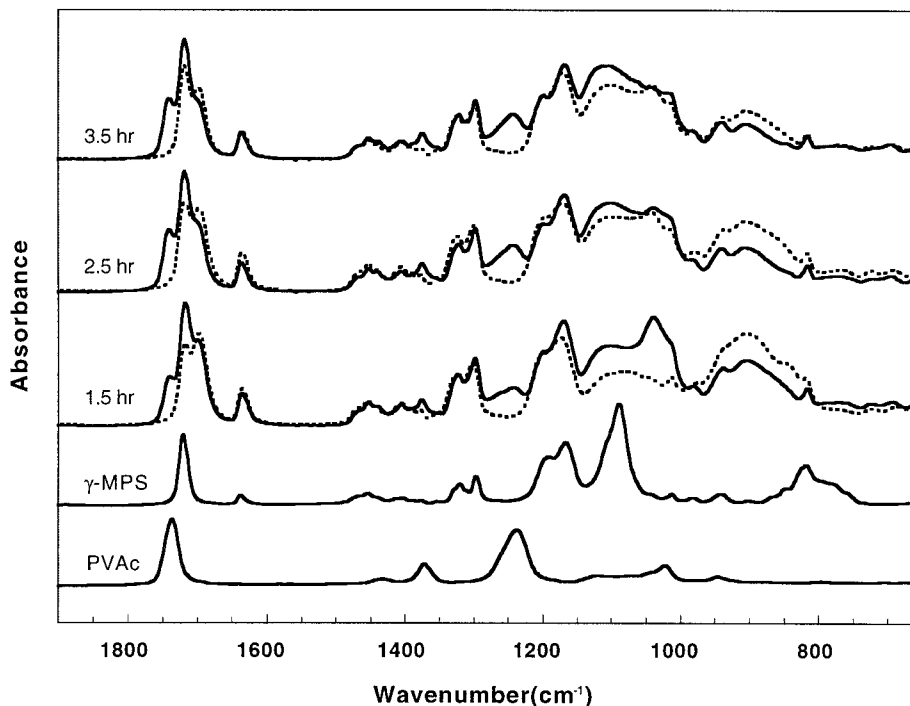


Figure 7 FTIR spectra of methacryl silane hydrolyzate and its mixture with PVAc as a function of time.

the SiOH band decreased with time for the VTE hydrolyzate alone. From these results, it is concluded that the silanol condensation in the model sizing system was depressed by the hydrogen bond between acetyl C=O and SiOH.

Next, FTIR spectra of (1) the model sizing system consisting of the PTM hydrolyzate and PVAc and (2) the PTM hydrolyzate are shown in Figure 6. Three bands at 1192, 1090, and 825  $\text{cm}^{-1}$  of the original PTM were due to the methoxy groups. For the model sizing system, the C=O band was also split into two bands. However, the absorption intensity of the hydrogen-bonded C=O was weaker than that of the VTE model sizing system. As shown in Figure 6, the intensity of the hydrogen-bonded acetyl C=O decreased with time in the PTM model sizing system, indicating that the interaction between acetyl C=O and SiOH decreased. The band shape at 1230  $\text{cm}^{-1}$  also changed as the hydrogen-bonded C=O band decreased. In the spectrum for 1.5 h of drying time, no peak could be seen around 1230  $\text{cm}^{-1}$ . The siloxane bands of the model sizing system were quite different from those of the PTM hydrolyzate alone. First, the intensity increased with time, although silanol condensation seemed to proceed much more slowly than that of the silane without PVAc. Furthermore, the oligomeric silane was peculiar in its structure because the shape of the siloxane bands was obviously different. Because the intensity at 1020–1010  $\text{cm}^{-1}$  was evidently lower than that in PTM and the intensity around 1120  $\text{cm}^{-1}$  increased, the depression of the cyclic trimer and the

formation of polysiloxane, which was greater than the octamer, could be expected. The intensity of the silanol band at 870  $\text{cm}^{-1}$  in the silane hydrolyzate alone was weak in comparison with that of the model sizing system and remained almost constant. Also, the shape of the siloxane bands did not change throughout the experimental periods. Therefore, the silanol condensation of the silane without PVAc seemed to proceed to a considerable extent even at drying time of 1.5 h.

FTIR spectra of (1) the model sizing system consisting of the  $\gamma$ -MPS hydrolyzate and PVAc and (2) the  $\gamma$ -MPS hydrolyzate alone are shown in Figure 7. The acetyl C=O band and the carbonyl stretching band of  $\gamma$ -MPS (ester C=O) heavily overlapped, and the hydrogen-bonded acetyl C=O was hidden by the ester C=O. Therefore, we used the band at 1230  $\text{cm}^{-1}$  to estimate the amount of hydrogen-bonded C=O qualitatively. Because a peak at 1230  $\text{cm}^{-1}$  was seen, it could be estimated that the hydrogen bond in the  $\gamma$ -MPS model sizing system was weaker than that in the other model sizing system. The band at 1130  $\text{cm}^{-1}$  attributed to the oligomeric  $\gamma$ -MPS increased and was stronger than that of the silane without PVAc.

The effect of miscibility between the organofunctional group of the silane and PVAc on the silanol condensation previously mentioned was evaluated. We used both parameters, the Hildebrand solubility parameter<sup>22</sup> and the integrated absorbance of the acetyl C=O at 1745  $\text{cm}^{-1}$ , for the estimation of the miscibility. Taking into account the structural formula and the weight-average molecular weight of the or-

TABLE II  
Calculated Hildebrand Solubility Parameter of the Silane Coupling Agents

Silane	$\delta_r$	$\delta_{\text{PVAc}} - \delta_r$	$\chi_c (\times 10^{-2})$	$\Delta\delta_c (\times 10^{-2})$	$ \Delta\delta - \Delta\delta_c $	Ratio of H-bonded C=O
VTE	5.59	3.72	2.09	8.75	3.63	59.0
ALE	6.36	2.95	1.44	6.60	2.88	46.8
$\gamma$ -GPS	7.08	2.23	0.59	3.39	2.20	45.0
PTM	7.44	1.87	1.38	6.70	1.80	43.5
$\gamma$ -MPS	8.78	0.53	0.54	3.05	0.50	23.8
PPY	8.86	0.45	0.62	3.51	0.41	22.1
CPE	10.2	-0.91	0.93	5.10	0.96	25.3
CNE	10.8	-1.43	1.13	6.27	1.49	27.0

$\delta$ :  $(\text{cal}/\text{cm}^3)^{1/2}$ .

ganofunctional groups ( $r$ ) of the silane, we calculated the solubility parameter ( $\delta$ ) as follows. Hildebrand suggested the estimation method for the solubility of a low molecular weight solvent. Many researchers applied this method to systems containing polymers to calculate the solubility parameter. We used the structural formula method and the group molar attraction constants ( $G$ ) derived from the measurement of the heat of evaporation by Small.<sup>23</sup> Small published  $G$ , which allowed the estimation of the solubility parameter from the structural formula of the compound and its density. The  $G$  values are additive over the formula and are related to the solubility parameter by the following equation:

$$\delta = d \sum G / M_w$$

where  $\sum G$  is the sum of all the atoms and groups in the molecule,  $d$  is the density, and  $M_w$  is the weight-average molecular weight. The miscibility can be expressed by the difference of  $\delta$ , expressed by  $\Delta\delta$ , between the organofunctionality and PVAc. However, in general, the solubility also depends on the components' molecular weights, as shown in the next equation:

$$\chi_{\text{crit}} = \frac{1}{2} \left[ \frac{1}{\sqrt{M_r}} + \frac{1}{\sqrt{M_{\text{PVAc}}}} \right]^2$$

where  $\chi_{\text{crit}}$  is the critical value of the Flory–Huggins  $\chi$  parameter and  $M_r$  and  $M_{\text{PVAc}}$  are the molecular weights of the organofunctionality of the silane coupling agent and PVAc (3200 g/mol), respectively. Therefore, the molecular weight must be considered. The Flory–Huggins  $\chi$  parameter can be approximated to the difference between the Hildebrand solubility parameter ( $\delta$ ) of organofunctional groups ( $\delta_r$ ) and  $\delta$  of PVAc ( $\delta_{\text{PVAc}}$ ) by the following equation:

$$\chi = \frac{V_r}{RT} [\delta_x - \delta_{\text{PVAc}}]^2 = \frac{V_r}{RT} \Delta\delta^2$$

where  $V_r$  is the molar volume of the organofunctional group,  $R$  is the gas constant, and  $T$  is the temperature. Therefore, the critical value of  $\Delta\delta$  ( $\Delta\delta_{\text{crit}}$ ), which is the maximum value for a blend to be miscible and takes into account the molecular weight of each component, can be obtained with the following equation:

$$\Delta\delta_{\text{crit}} = \sqrt{\frac{RT \times \chi_{\text{crit}}}{V_r}} = \left( \frac{1}{\sqrt{M_r}} + \frac{1}{\sqrt{M_{\text{PVAc}}}} \right) \times \sqrt{\frac{RT}{2V_r}}$$

Therefore,  $\Delta\delta - \Delta\delta_{\text{crit}}$  was used to estimate the miscibility between the organofunctional group of the silane and PVAc. Each parameter ( $\delta$ ,  $\Delta\delta$ ,  $\Delta\delta_{\text{crit}}$ , and  $\Delta\delta - \Delta\delta_{\text{crit}}$ ) of each silane is shown in Table II.

To resolve the individual C=O bands, we performed least-squares curve fitting on the experimental

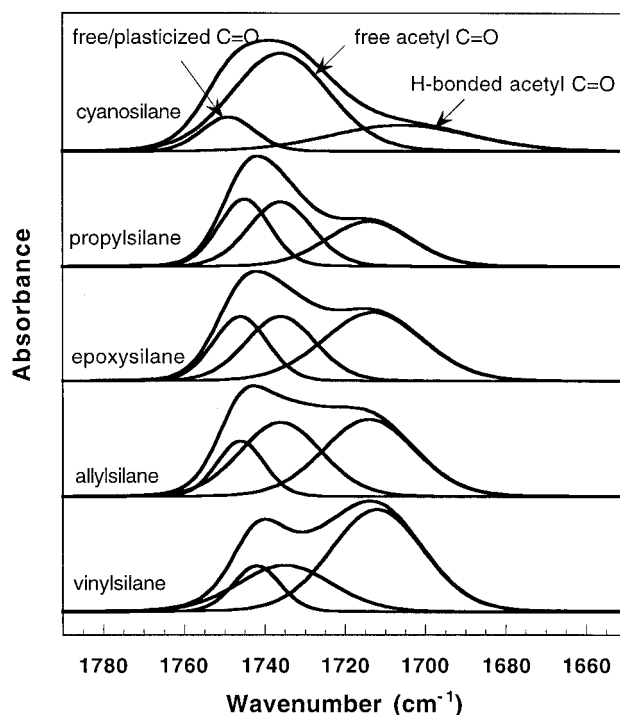
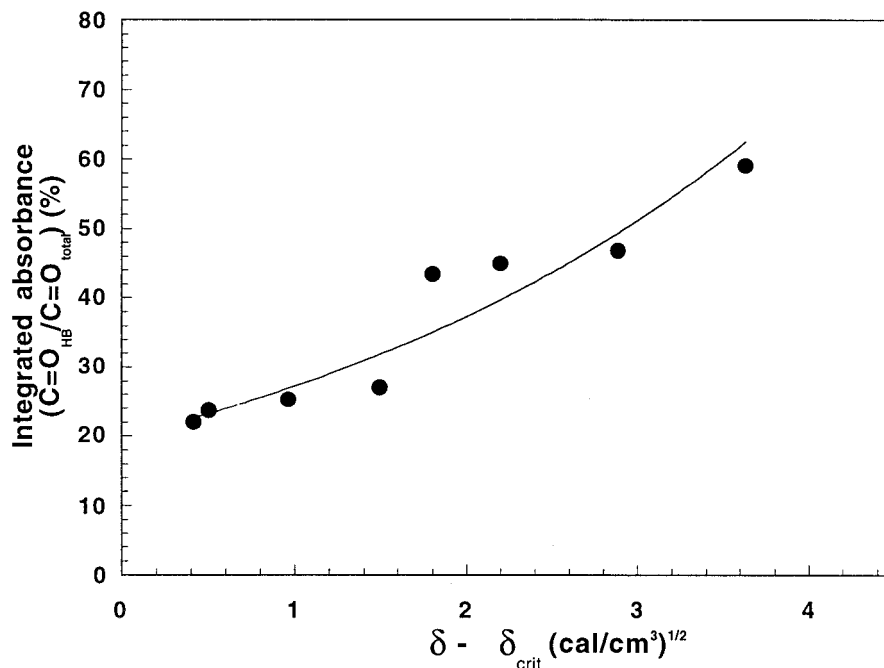


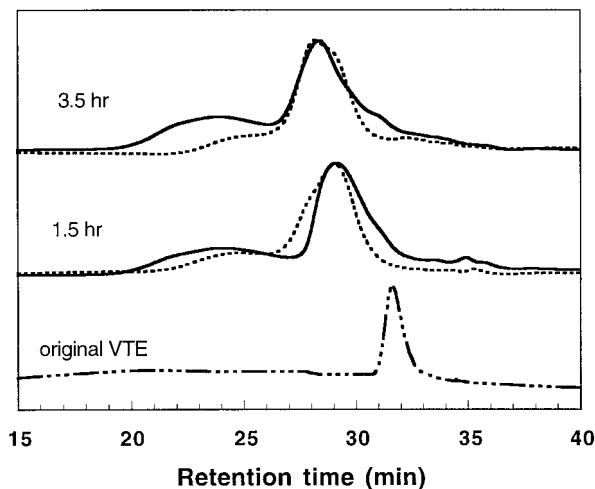
Figure 8 Least-squares curve fitting for the C=O region of the mixture of silane and PVAc.



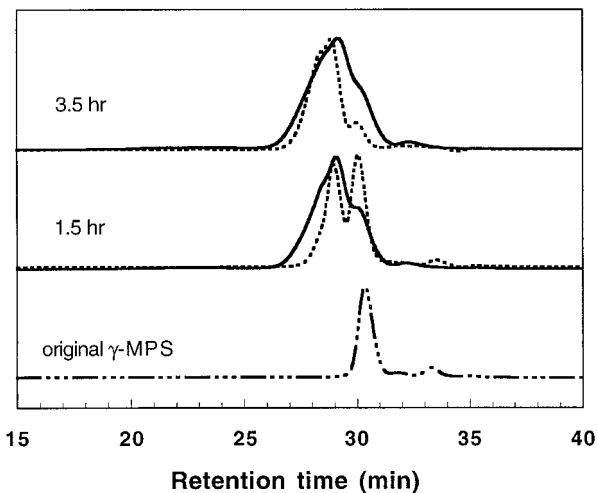
**Figure 9** Change in the integrated absorbance of hydrogen-bonded C=O as a function of the difference in the solubility parameter.

spectra of the acetyl C=O stretching bands in the region from 1790 to 1650  $\text{cm}^{-1}$ . We adopted the restrictive curve-fitting procedures rather than permitting the computer to obtain the best fit by changing variables freely to obtain physically meaningful fits. The carbonyl region was assumed to be composed of a maximum of the aforementioned three carbonyl bands, whose shape was assumed to be a combination of Gaussian and Lorentzian distributions. The curve-fitting approach and the experimental determination of the peak position and curve shape of individual bands will be described elsewhere.<sup>24</sup>

The results of the curve-fitting analysis for the acetyl C=O stretching region from 1790 to 1650  $\text{cm}^{-1}$  are shown in Figure 8. The C=O band was resolved into three individual bands. The bands at 1745 and 1737  $\text{cm}^{-1}$  were due to the non-hydrogen-bonded acetyl C=O, and the band at 1714  $\text{cm}^{-1}$  was due to the hydrogen-bonded acetyl C=O. The change of the integrated absorbance of the hydrogen-bonded acetyl C=O as a function of  $\Delta\delta - \Delta\delta_{\text{crit}}$  is shown in Figure 9. It is obvious that the integrated absorbance of the hydrogen-bonded acetyl C=O in the model sizing system was stronger when the value of  $\Delta\delta - \Delta\delta_{\text{crit}}$  was



**Figure 10** GPC chromatograms of the mixture of vinyl silane and PVAc as a function of time.



**Figure 11** GPC chromatograms of the mixture of methacryl silane and PVAc as a function of time.



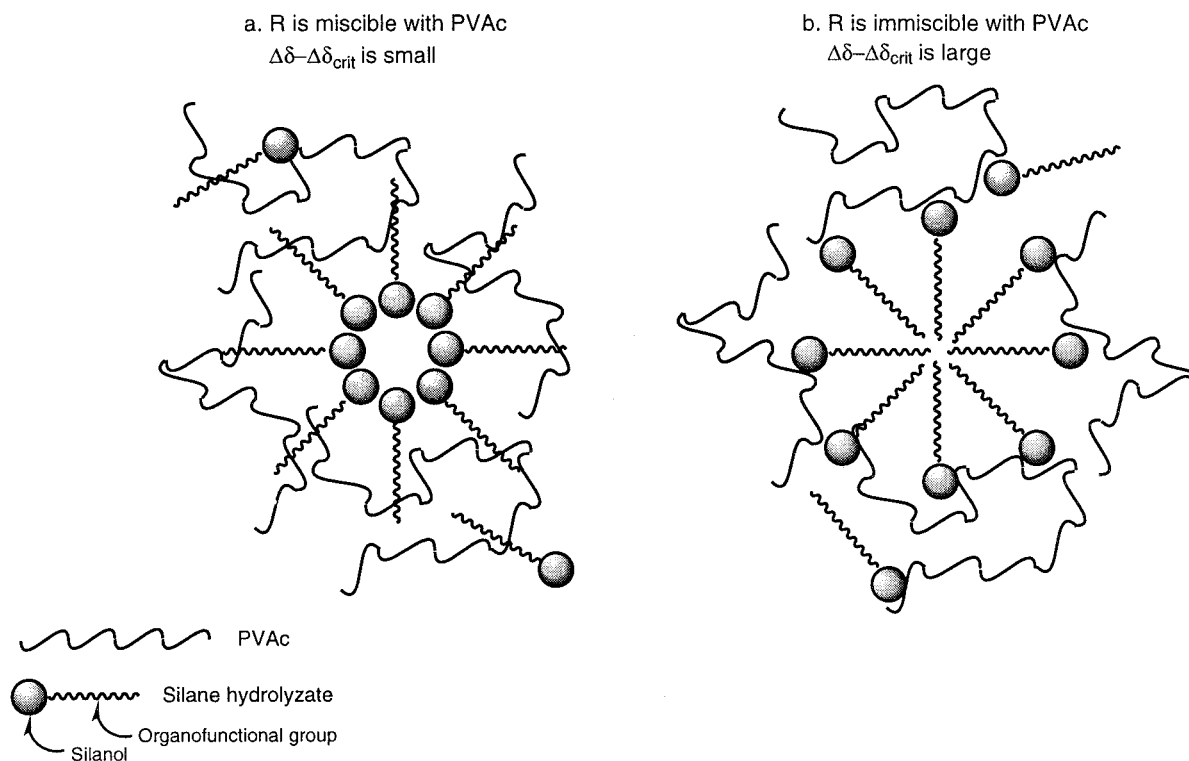


Figure 12 Schematic diagrams of silane hydrolyzate and PVAc.

greater. It is thought that the SiOH group interacts with the acetyl C=O group through hydrogen bonding when the organofunctional group is immiscible with PVAc.

The non-hydrogen-bonded C=O band was resolved into two bands at 1745 and 1737  $\text{cm}^{-1}$ .<sup>24</sup> The free C=O band due to the entangled PVAc molecules appeared at 1737  $\text{cm}^{-1}$ . However, the C=O band due to plasticized PVAc molecules from the permeation of the organofunctional group of silane appeared at 1745  $\text{cm}^{-1}$  (free/plasticized C=O).<sup>24</sup> The free/plasticized C=O indicates the miscibility between silane and PVAc. It is hypothesized that the fraction of the integrated absorbance of the free/plasticized C=O at 1745  $\text{cm}^{-1}$  may be used as the criterion of miscibility. As shown in Figure 8, the integrated intensity of the free/plasticized C=O became greater; in other words, the fraction of the integrated absorbance ( $\text{C}=\text{O}_{\text{HB}}/\text{C}=\text{O}_{\text{total}}$ ) became smaller for the system with a smaller value of  $\Delta\delta - \Delta\delta_{crit}$ .

These results regarding the Hildebrand solubility parameter and the integrated absorbance of free/plasticized C=O may be summarized as follows. If the silane molecules are almost linear, silane will have two main directions toward the acetate group of PVAc molecules. The organofunctional groups will be oriented toward the PVAc phase because of miscibility in one case, and in the other case, SiOH will interact with PVAc because of hydrogen bonding. These directions may be influenced by the miscibility between the or-

ganofunctional group and PVAc, which is expressed by  $\Delta\delta - \delta_{crit}$ , as shown in Figure 9.

Size exclusion chromatography (SEC) chromatograms of a model sizing system, the VTE hydrolyzate and the  $\gamma$ -MPS hydrolyzate, are shown in Figures 10 and 11. The molecular weight of the  $\gamma$ -MPS hydrolyzate in the model sizing system was higher and the molecular weight distribution was broader than those of the  $\gamma$ -MPS hydrolyzate alone, even in the initial stage, as shown in Figure 11. The molecular weight distribution changed only a little at a drying time of 3.5 h in comparison with the chromatogram of the  $\gamma$ -MPS hydrolyzate alone, in which the molecular weight increased in a stepwise fashion. However, the molecular weight of the VTE hydrolyzate in the model sizing system was lower in the initial stage than that of the VTE hydrolyzate alone. From these SEC results, it can be concluded that the evolution of the  $\gamma$ -MPS oligomer may be accelerated in the initial stage of silanol condensation in the model sizing system; however, a further condensation reaction is not expected.

From the IR and SEC results, we propose a hypothesis for a phase structure of the model sizing system as follows. Silane hydrolyzates will form a micellelike phase as shown in Figure 12. Schematic diagrams of the phase structures of the model sizing system for both cases, for which  $\Delta\delta - \Delta\delta_{crit}$  is large or small, are depicted in Figure 12. When the organofunctional group interacts with PVAc, the SiOH groups tend to form hydrogen bonds with one another, and silanol

condensation easily occurs even in the initial stage of the condensation. Once polysiloxane is formed in such a phase, further condensation cannot be expected because of protection by the outer shell of the organofunctional groups. On the contrary, when the SiOH group interacts with PVAc, the silanol condensation will be different from that of the previous case.

Such a phase structure can be thought to affect silanol condensation and can be controlled by the miscibility between the organofunctional groups of silane and PVAc.

### CONCLUSIONS

The miscibility between several silane coupling agents and PVAc and its effect on silanol condensation were studied with FTIR spectroscopy and SEC. The formation of hydrogen bonds between the SiOH group of the silane and the C=O group of PVAc was shown with FTIR. The extent of hydrogen bonding was determined with the integrated absorbance of the hydrogen-bonded C=O group of PVAc obtained by the least-squares curve-fitting procedure. A correlation between the extent of hydrogen bonding and the miscibility between the organofunctionality of silane and PVAc was obtained. The molecular weight and distribution of  $\gamma$ -MPS in PVAc were higher and broader, respectively, than those of the PVAc-free system in the initial stage of the silanol condensation. However, the molecular weight of VTE of the model size was lower than that of the PVAc-free system. The vinyl group was estimated to be immiscible with PVAc. The silanol condensation of  $\gamma$ -MPS in the model sizing system may be accelerated. It is proposed that silane hydrolyzates form a micellelike phase in the mixture system, and the orientation of each silane molecule is controlled by the miscibility between the organofunctionality and PVAc. This characteristic phase structure is

expected to affect the silanol condensation and siloxane structure.

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