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## Substrate Effects on the Chemisorbed and Physisorbed Layers of Methacryl Silane Modified Particulate Minerals

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**ABSTRACT:** The substrate effects on the chemisorbed and physisorbed layers of [ $\gamma$ -(methacryloxy)-propyl]trimethoxysilane ( $\gamma$ -MPS) modified particulate minerals were studied by diffuse reflectance Fourier transform infrared spectroscopy and gel permeation chromatography. The infrared measurements show that the adsorbed  $\gamma$ -MPS molecules exist as two well-defined layers on the substrate surface and that the relative proportion of these is influenced by the acid/base nature of the surface as well as the surface chemical functionality and the adsorbate loading. The acid/base nature of the particulate surface was characterized by measuring the pH of an aqueous slurry of each particulate, and the specimens examined gave values ranging from pH 1.9 through pH 12.4. The near-neutral pH substrates demonstrate the greatest proportion of chemisorbed silane. Gel permeation chromatography demonstrates that the physisorbed layers consist of unhydrolyzed or partially hydrolyzed monomers and polysiloxane oligomers or polymers with a molecular weight up to several thousand. The molecular weight of the oligomeric species is dependent on the long-range acid/base influence of the substrate surface and descends in the order neutral > basic  $\geq$  acidic. This effect can be modeled by adjusting the pH of the treating solution and depositing oligomers in bulk form. The substrate characteristics determine the molecular structure of deposited trifunctional silanes by providing suitable or unsuitable sites for chemical reaction with the substrate, influencing the intramolecular condensation reaction, and determining the effective concentration and mobility of the adsorbate.

### Introduction

Organofunctional silane coupling agents are used to modify the adhesive, chemical, rheological, and other properties of particulate polymer composites. Much of the early coupling agent technology centered on applications involving glass fibers or siliceous-type surfaces. More recently, considerable interest has developed in the use of coupling agents on other inorganic mineral substrates. While some of these are siliceous (e.g., clay) and analogies may be made with the glass-related research, others are not (e.g., calcium carbonate and alumina trihydrate).<sup>1</sup>

Deposition of organofunctional silanes is not similar to the modification of surfaces by most small organic molecules or monomers. Neither is it similar to the adsorption of polymeric materials. The organofunctional silanes used as coupling agents are trifunctional molecules capable of both reaction with the substrate surface and formation of complex polymeric networks upon deposition. A number of factors are known to influence the structure of adsorbed silanes on glass surfaces. These include the silane type, hydrolysis and drying conditions, heat treatment, and solution pH.<sup>1</sup> When the nature of surface-treated particulate substrates is studied, the most important independent variables are the substrate characteristics. Par-

ticulate minerals vary in chemical composition, surface charge, acid/base character, shape, size, surface area, and porosity.

Silane coupling agents are known to form chemisorbed and physisorbed layers on the surface of glass fibers.<sup>2-4</sup> The existence of physisorbed silane layers is not unique to the glass fiber surface. Dry-blended particulate minerals treated with silanes from either organic or aqueous solutions also give large amounts of physisorbed silane.<sup>4,5</sup> The physisorbed silanes play important roles as modifiers of the matrix interphase, influencing both the mechanical and rheological properties of the composite system. Recently, experimental observations have been made that can be attributed to the function of physisorbed silanes. An (aminopropyl)silane ( $\gamma$ -APS) treated aluminum oxide substrate with a polyethylene coating failed adhesively or cohesively depending on the heat treatment of the silane layers.<sup>6</sup> The failure mechanism was proposed to be a function of the degree of silane/matrix interpenetration and more recently, Kaul et al.<sup>7</sup> demonstrated direct evidence for interdiffusion between  $\gamma$ -APS and polyethylene in the same system. Improved peel strength was reported in all cases for this  $\text{Al}_2\text{O}_3/\gamma\text{-APS/PE}$  system<sup>6</sup> over the untreated substrate in spite of the lack of substantial

chemical reactions between  $\gamma$ -APS and polyethylene.

It has been shown that a monolayer-thick silane coating does not yield an optimum strength but rather thick layers give the best mechanical properties.<sup>2,6,8</sup> This suggests that reinforcement may be enhanced through interpenetration, and this subject has been reviewed recently by Plueddemann et al.<sup>9</sup> Gahde<sup>10</sup> studied the effect of silane-modified kaolin on the orientation of high-density polyethylene in the interphase and found that the mechanical properties of the composite seemed more dependent upon the polyethylene structure and morphology at the interface than upon chemical grafting between the coupling agent and the matrix. Nakatsuka et al.<sup>4</sup> demonstrated that modification of calcium carbonate to increase the molecular weight of the extractable methacryl silane resulted in significant tensile strength and modulus improvement. They concluded that the polymeric silane coupling agent, prepared through condensation of the monomeric agent on the filler surface and extracted with styrene, acts as a primary cross-linking agent rather than the silane-modified filler particles.

Rheological properties are also strongly influenced by the application of silane coupling agents. Han et al.<sup>11</sup> demonstrated that when calcium carbonate and glass beads are treated with ( $\gamma$ -aminopropyl)triethoxysilane and *N*-octyltriethoxysilane for use in highly filled polypropylenes, the melt viscosity shows opposite trends depending on the specific interaction of the coupling agent in each system.

From a chemical and polymerization viewpoint these systems present a relatively unexplored area, the polymerization of trifunctional monomers on chemically active substrates. We have utilized diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and gel permeation chromatography (GPC) to examine the chemically and physically adsorbed layers of [ $\gamma$ -(methacryloxy)propyl]trimethoxysilane ( $\gamma$ -MPS) on a variety of particulate mineral substrates. A large number of particulates have been studied to illustrate the substrate effects on the structure of the adsorbed silanes.

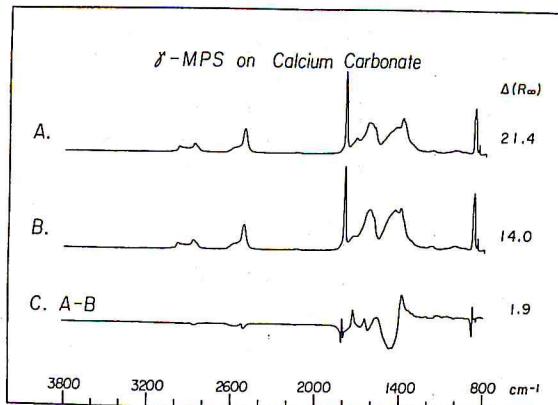
## Experimental Section

A Fourier transform infrared spectrophotometer (Digilab FTS-20E) with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector and a hemispherical diffuse reflectance attachment (Digilab DRA-100) was used at a resolution of  $2\text{ cm}^{-1}$  with coaddition of 100 scans. The spectrophotometer was purged with dry nitrogen to reduce atmospheric water vapor. Single-beam reflectance data were ratioed against high-purity KBr, and the Kubelka-Munk<sup>12,13</sup> function was plotted to obtain linear diffuse reflectance spectra.

Gel permeation chromatography was performed using a metering pump (Altex Model 110) and the following packed columns:  $\mu$ Styragel  $10^5\text{ \AA}$ ,  $\mu$ Styragel  $100\text{ \AA}$ , Ultrastyragel  $10^3\text{ \AA}$ , and Ultrastyragel  $100\text{ \AA}$  (Waters Associates, Inc.) and  $\mu$ Spheroel  $10^4\text{ \AA}$  and  $\mu$ Spheroel  $500\text{ \AA}$  (Altex Scientific Inc.). An ultraviolet detector (Beckman Model 153) was used at 254 nm, and the mobile phase was tetrahydrofuran (THF) at an elution rate of  $1\text{ mL/min}$ . The molecular weight distribution of the polymeric silane was measured relative to near-monodisperse polystyrene standards (Pressure Chemical Co.). The 250 molecular weight calibration corresponds to the elution volume of monomeric  $\gamma$ -MPS.

Particulate mineral samples were generously supplied by a number of firms. The clay sample is Hydrite R (Georgia Kaolin Co.) with a median particle size of  $0.77\text{ }\mu\text{m}$  and a BET surface area of  $13.1\text{ m}^2/\text{g}$ . The calcium carbonate sample is Camel-CARB (Flintkote Stone Products Co.) with an average particle size of  $7\text{ }\mu\text{m}$ . Silane coupling agent, [ $\gamma$ -(methacryloxy)propyl]trimethoxysilane, was purchased from Petrarch Systems Inc. and used as received.

Aqueous slurry pH was measured as the pH of a mixture of 5 g of particulate in 100 mL of twice-distilled, deionized water after a 5-min boil of the slurry. Silane modification of the par-



**Figure 1.** DRIFT spectra of  $\gamma$ -MPS-modified calcium carbonate (pH 9.4): (A) calcium carbonate dry-blended with 1%  $\gamma$ -MPS from an aqueous alcoholic solution and heated in air at  $80^\circ\text{C}$  for 3 h; (B) untreated calcium carbonate; (C) difference spectrum of poly([methacryloxy)propyl]silsesquioxane) on the calcium carbonate surface.

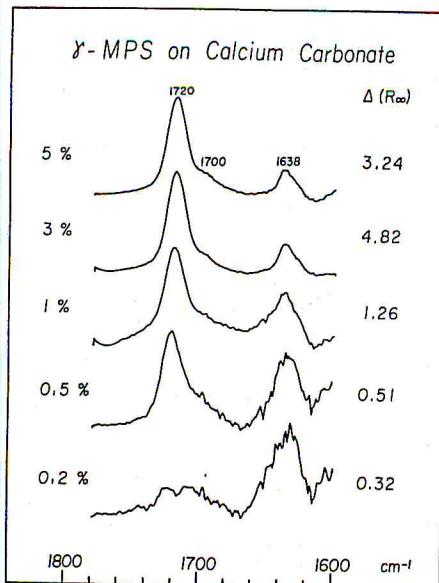
ticulate substrates was accomplished by a dry-blending method.  $\gamma$ -MPS was hydrolyzed prior to surface treatment for 1 h in an aqueous alcoholic solution (8 mL of  $\gamma$ -MPS, 6 mL of  $\text{H}_2\text{O}$ , and 72 mL of 1-butanol). The solution was sprayed onto the substrate surfaces in appropriate concentrations from an atomizer, and the samples were thoroughly mixed. Calcium carbonate and clay samples were treated in the concentration range 0.2–6% methacryl silane based on the particulate weight. All other particulates were treated with 1% methacryl silane. The silane-modified particulates were sealed for 12 h at room temperature and exposed to the atmosphere for an additional 12 h to drive off the alcohol. The particulate samples were then heated in air at  $80^\circ\text{C}$  for 3 h.

The physisorbed silane was removed from the surface with a gentle THF with (0.2 g of particulate and 3 mL of THF) for 30 min at room temperature. The mixture was centrifuged and the supernatant was collected for GPC analysis. Samples of both unwashed and washed silane-modified particulates were examined by DRIFT without further sample preparation. Bulk pH-adjusted poly([methacryloxy)propyl]silsesquioxane) was cast from solution in a manner simulating the surface treatment. The prehydrolyzed treating solution was pH adjusted with dilute aqueous solutions of either NaOH or HCl. The pH-adjusted samples were covered for 12 h at room temperature and exposed to the atmosphere for an additional 12 h to drive off the alcohol. Spectral subtraction and least-squares curve fitting routines<sup>14–16</sup> were used to aid in the data analysis. All spectra were scale expanded without any smoothing function and plotted in Kubelka-Munk reflectance units  $f(R_\infty)$ .  $\Delta(R_\infty)$  is used to designate the difference between the maximum and minimum reflectance of the spectrum.

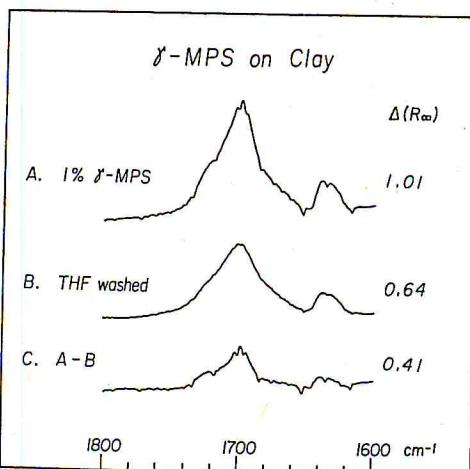
## Results and Discussion

**A. Surface Chemical Functionality.** Figure 1 demonstrates the applicability of DRIFT and the corresponding spectral subtraction based on a least-squares curve fit to observe the adsorbate methacryl silane coupling agent molecules deposited on calcium carbonate. The ability to observe and analyze adsorbate species at near-monolayer concentrations on useful substrates is a formidable task which has limited the availability of chemical information concerning these systems. Although only a few adsorbate bands are easily recognizable in the difference spectrum, spectrum C, the diffuse reflectance technique has substantially advanced the ability to study the chemistry of adsorbate molecules.<sup>17,18</sup>

Clay (pH 4.1) and calcium carbonate (pH 9.4) samples were dry-blended with varying amounts of  $\gamma$ -MPS. The dry-blending technique for particulate minerals requires that an absolute amount of coupling agent be deposited on the substrate surface while a typical treatment for glass fibers allows for adsorption from dilute aqueous solution.



**Figure 2.** DRIFT difference spectra of calcium carbonate (pH 9.4) dry-blended with increasing amounts of  $\gamma$ -MPS.

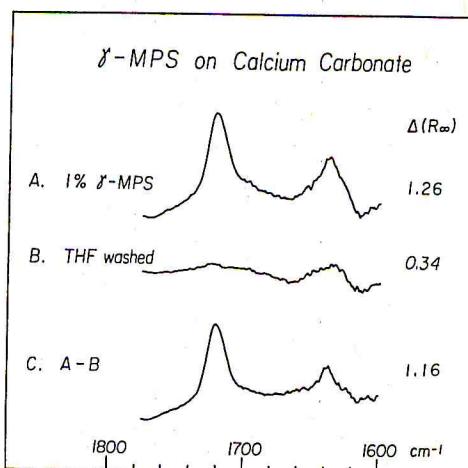


**Figure 3.** DRIFT difference spectra of  $\gamma$ -MPS modified clay (pH 4.1): (A) 1%  $\gamma$ -MPS surface treatment; (B) after 30-min THF wash at room temperature; (C) subtraction of (B) from (A), representing the silane species extracted from the clay surface.

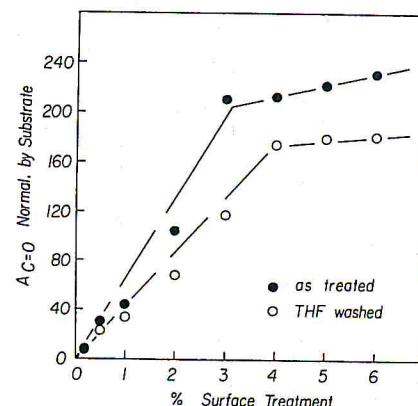
Therefore, coupling agent modification of mineral particulates is based on the weight of the particulate, and a 1% treatment implies 1 g silane per 100 g of particulate or one part per hundred.

Figure 2 shows the DRIFT spectral subtractions for increasing amounts (0.2–5%) of  $\gamma$ -MPS dry-blended with calcium carbonate in the infrared C=O and C=C stretching regions between 1800 and 1600  $\text{cm}^{-1}$ . This mid-infrared region is both quantitatively and qualitatively useful for the analysis of adsorbed  $\gamma$ -MPS on mineral particulates. The C=O band in  $\gamma$ -MPS has a large specific absorptivity, allowing for high-sensitivity measurements. The C=O band can also provide information with respect to the orientation of the adsorbed silane molecules.<sup>18</sup> The bands at 1720 and 1638  $\text{cm}^{-1}$  result from the C=O and C=C stretching modes in methacryl silane, respectively. The band near 1640  $\text{cm}^{-1}$  at low percent surface treatments is due to imperfect subtractions of adsorbed water on the calcium carbonate surface and not the C=C stretching mode of  $\gamma$ -MPS.

The degree of chemical and physical adsorption of the silane can be examined by extraction in an anhydrous organic solvent. The chemisorbed layers may be defined



**Figure 4.** DRIFT difference spectra of  $\gamma$ -MPS-modified calcium carbonate (pH 9.4): (A) 1%  $\gamma$ -MPS surface treatment; (B) after 30-min THF wash at room temperature; (C) subtraction of (B) from (A), representing the silane species extracted from the calcium carbonate surface.

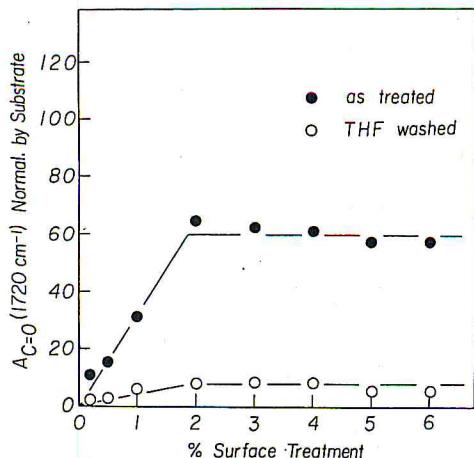


**Figure 5.** Integrated area of the carbonyl band normalized by the substrate reflectance as a function of the percent surface treatment on  $\gamma$ -MPS-modified clay (pH 4.1). The closed circles represent the dry-blended samples after heat treatment and the open circles are the same samples after a 30-min THF wash at room temperature.

as those that cannot be removed by the solvent. The physisorbed layers can be removed by the solvent, indicating that no extensive siloxane networks exist in these layers. This analysis using anhydrous tetrahydrofuran (THF) was applied to the silane-modified particulates as seen in Figures 3 and 4. Figure 3 demonstrates that at a 1% loading, 66% of the deposited silane is chemisorbed on clay. The clay surface is composed of both Si-OH and Al-OH functionalities which are capable of covalent bond formation with the coupling agent silanols. The carbonyl band of  $\gamma$ -MPS in Figure 3 appears at 1700  $\text{cm}^{-1}$  due to hydrogen bonding.<sup>18,19</sup> Additional work in this laboratory has shown that at the 1% loading on clay depicted in Figure 3,  $\gamma$ -MPS exists as an equivalent monomer.<sup>18</sup> This indicates that not all of the surface-interacting molecules chemically adsorb.

Calcium carbonate has a surface functionality void of hydroxyl groups and therefore, little methacryl silane is expected to chemisorb. This observation is experimentally observed in Figure 4. The methacryl silane on calcium carbonate that was not removed (19%) may be bound as a result of small amounts of calcium hydroxide sites<sup>20</sup> or oxide and hydroxide impurities.

**B. Adsorbate Loading.** The amount of adsorbed silane in both the chemisorbed and physisorbed forms is a function of the degree of surface treatment. For silane



**Table I**  
**Aqueous Slurry pH Values for Various Particulate  
 Mineral Substrates**

	Acidic	Basic	
Iron (III) Oxide	1 . 9	Calcium Oxide	12 . 4
Titanium Oxide	2 . 9	Calcium Hydroxide	12 . 3
Zirconium Oxide	3 . 1	Magnesium Oxide	11 . 1
Aluminum Oxide	3 . 3	Glass Spheres	10 . 7
Clay	4 . 1	Barium Hydroxide	10 . 5
Tin (IV) Oxide	4 . 1	Lead Oxide	10 . 0
Aluminum Oxide	4 . 8	Wollastonite	9 . 9
Tungsten Oxide	4 . 8	E - Glass	9 . 5
Tin Oxide	5 . 3	Calcium Carbonate	9 . 4
Iron (III) Oxide	5 . 7	Calcium Metasilicate	9 . 3
Copper (II) Oxide	6 . 1	Mica	9 . 3
Aluminum Silicate	6 . 6	Mica	9 . 0
Titanium Oxide	6 . 6	Zinc Oxide	7 . 6
Amorphous Silica	6 . 9	Kaolin	7 . 1
Nickle Oxide	7 . 0		

**Figure 6.** Integrated area of the carbonyl band normalized by the substrate reflectance as a function of the percent surface treatment on  $\gamma$ -MPS-modified calcium carbonate (pH 9.4).

adsorption on clay (pH 4.1), this dependence is illustrated in Figure 5. The integrated intensity of the carbonyl band was normalized by the substrate absorbance and plotted as a function of the percent surface treatment. The data for the unwashed samples reflect the infrared absorption from a combination of the chemisorbed and physisorbed layers while the data for the THF-washed samples reflect the infrared absorption from only the chemisorbed layers. The plot shows a linear dependence of the amount of silane adsorption on the percent treatment or quantity deposited. Above 3% treatment the amount of adsorbed coupling agent is relatively independent of the percent surface treatment. The breakpoint and flattening of the curve is a result of the evaporation of a significant portion of the deposited methacryl silane as previously noticed by Nakatsuka et al.<sup>4</sup> The evaporation occurs while the carrier alcohol is being driven off in air at room temperature.

The quantitative relation between the amount of adsorbed coupling agent and the percent surface treatment on calcium carbonate is depicted in Figure 6. Again, there is a linear dependence and breakpoint near 2%. This indicates that surface treatments above 2% on this sample of calcium carbonate are ineffective in depositing additional silane due to the evaporation of the agent upon drying. The position of the breakpoint is considerably lower than that observed for clay and might be explained by differences in surface area of the particulate as well as other chemical factors. The evaporation behavior suggests that the evaporated species is substantially different from the adsorbed species, and further analysis may provide insight concerning the adsorption mechanism. The small amount of chemisorbed silane on calcium carbonate at all loadings is reflected by the low integrated intensity of the THF-washed samples.

The chemisorbed/physisorbed phenomenon is a complex chemical subject. The calcium carbonate example in Figure 6 suggests that chemical linkage with the substrate surface functionality is necessary to produce a large degree of chemical adsorption. The clay example indicates that even when compatible surface functionality exists, the chemisorbed silane involves much more than the molecules bonded directly to the surface.

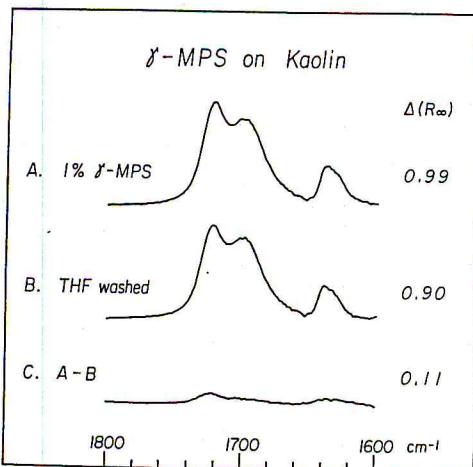
**C. Surface Acid/Base Properties.** The relative amount of chemisorbed to physisorbed layers depends on a number of complex interacting phenomena, each of which must be examined separately. The surfaces of the various mineral particulates examined are vastly different and this is especially true with respect to their acid/base

nature. Many studies have shown the existence of both Lewis and Brønsted acid sites on surfaces and even preferential adsorption at these sites. Additionally, the surface area of the particles will determine the effective concentration of these sites that are available to the adsorbing coupling agent molecules. As a result, it would be helpful to specify a single variable that might be correlated with the coupling agent structure on the substrate surface. Isoelectric points have been defined for metal oxides, yet the isoelectric point is an intrinsic property of the surface which is determined solely by the surface chemical composition. The pH of an aqueous slurry of the particulate is a combined property of the concentration of the surface acid centers and the surface area. The aqueous slurry pH is a more realistic value with respect to the long-range acid/base influence of the substrate.

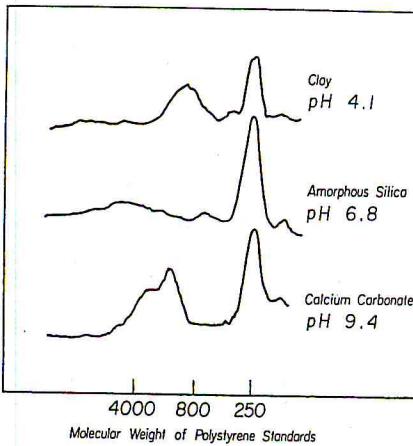
The aqueous slurry pH values measured for the mineral particulates examined encompass the entire pH range (1.9–12.4) as listed in Table I. The clay sample has an acidic surface at pH 4.1 and the calcium carbonate sample has a basic surface at pH 9.4. There are also rather neutral aqueous slurry pH particulates like kaolin at pH 7.1. The same type of mineral particulate can have different aqueous slurry pH values, depending on the nature of production techniques and surface preparations, as exemplified by the pH values for different samples of aluminum oxide (pH 3.3 and pH 4.8) and titanium oxide (pH 2.9 and pH 6.6).

Figure 7 illustrates the solvent extraction analysis for methacryl silane modified kaolin. Bands at 1720 and 1700  $\text{cm}^{-1}$  are due to the carbonyl stretching modes of the methacryl silane. The kaolin sample is a calcined clay and is very similar in chemical composition to the clay sample examined previously in Figure 3. After THF extraction at room temperature, 96% of the originally adsorbed silane remains. This degree of chemisorption is substantially higher than was observed on the clay surface. Other work in our laboratory<sup>18</sup> demonstrates that at a 1% loading the silane coverage on this kaolin surface is thicker than on the clay surface. This evidence refutes any notion that chemisorption of trifunctional silanes is entirely dependent on the surface chemical functionality or that it involves only surface-interactive molecules.

The major observable difference between these two samples is the values of their aqueous slurry pH. Clay (pH 4.1) has an acidic surface and kaolin (pH 7.1) has a neutral



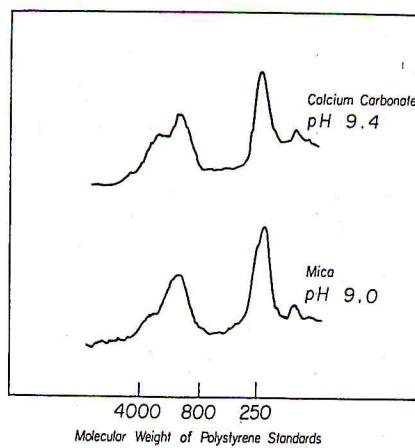
**Figure 7.** DRIFT difference spectra of  $\gamma$ -MPS-modified kaolin (pH 7.1): (A) 1%  $\gamma$ -MPS surface treatment; (B) after 30-min THF wash at room temperature; (C) subtraction of (B) from (A), representing the silane species extracted from the kaolin surface.



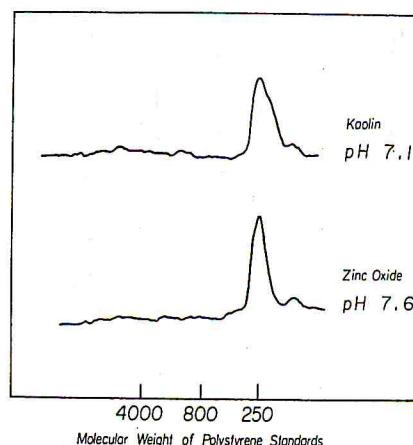
**Figure 8.** GPC chromatograms of the THF extracts from the surfaces of 1%  $\gamma$ -MPS-modified clay (pH 4.1), amorphous silica (pH 6.8), and calcium carbonate (pH 9.4).

surface. The ratio of chemisorbed and physisorbed methacryl silane on particulate substrates encompassing a large range in aqueous slurry pH values was examined, and the values are listed in Table II. At near-neutral pH, the retention of coupling agent after the THF wash is consistently high, indicating a large degree of chemisorbed material. On the acidic and basic surfaces the amount of chemisorbed material is not consistently as high, suggesting that the surface chemical functionality of these surfaces plays a major role in determining their degree of chemical adsorption.

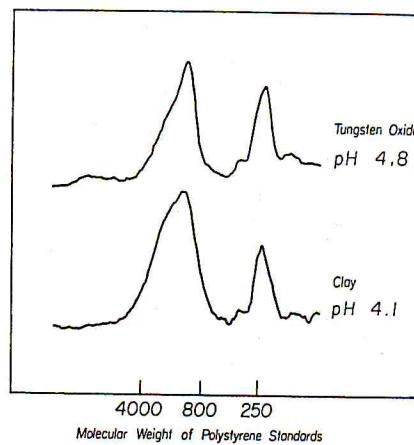
pH is known to influence the rate of condensation of organofunctional silanes in aqueous solution.<sup>21,22</sup> Similarly, the acid/base nature of the particulate modifies the environment of the deposited hydrolyzed silanes and should have a large effect on their ultimate structure. Gel permeation chromatography is ideal for analyzing the differences in the physisorbed silane structures resulting from the pH influence of the substrate. Typical examples on various particulates having different aqueous slurry pH values are depicted in Figure 8. The physisorbed silane molecules extracted from the surface exist as unhydrolyzed or partially hydrolyzed monomers and polysiloxane oligomers or polymers with a molecular weight up to several thousand. At a silane loading of 1% the basic surface of calcium carbonate (pH 9.4) produces two distinct oligomeric structures. The neutral surface of amorphous silica (pH 6.8) shows a rather high molecular weight oligomer



**Figure 9.** GPC chromatograms of the THF extracts from the surfaces of calcium carbonate (pH 9.4) and mica (pH 9.0) treated with 1%  $\gamma$ -MPS.



**Figure 10.** GPC chromatograms of the THF extracts from the surfaces of kaolin (pH 7.1) and zinc oxide (pH 7.6) treated with 1%  $\gamma$ -MPS.



**Figure 11.** GPC chromatograms of the THF extracts from the surfaces of 1%  $\gamma$ -MPS-modified tungsten oxide (pH 4.8) and 3%  $\gamma$ -MPS-modified clay (pH 4.1).

but in a very small quantity. The acidic surface of clay (pH 4.1) gives an oligomeric structure slightly lower in molecular weight than the calcium carbonate surface. The extent of the homocondensation reaction on the particulate surface is reflected by the molecular weight of the oligomeric species and is the greatest in neutral environments.

Confirmation that the acid/base nature of the surface is the controlling influence on the physisorbed silane structure is provided by comparing the GPC chromato-

Table II  
Degree of Chemisorbed Methacryl Silane on Particulate Mineral Substrates

## Acidic

## Neutral

## Basic

Iron (III) Oxide	(pH 1.9)	82 %
Zirconium Oxide	(pH 3.1)	78 %
Aluminum Oxide	(pH 3.3)	100%
Clay	(pH 4.1)	66 %
Tin (IV) Oxide	(pH 4.1)	77 %
Tungsten Oxide	(pH 4.8)	45 %
Tin Oxide	(pH 5.3)	100 %
Iron (III) Oxide	(pH 5.7)	100 %
Copper (II) Oxide	(pH 6.1)	18 %

Aluminum Silicate	(pH 6.6)	87 %
Titanium Oxide	(pH 6.6)	84 %
Amorphous Silica	(pH 6.9)	83 %
Nickel Oxide	(pH 7.0)	86 %
Kaolin	(pH 7.1)	96 %
Zinc Oxide	(pH 7.6)	100%

Calcium Hydroxide	(pH 12.3)	57 %
Magnesium Oxide	(pH 11.1)	98 %
Glass Spheres	(pH 10.7)	32 %
Barium Hydroxide	(pH 10.5)	46 %
Lead Oxide	(pH 10.0)	80 %
Wollastonite	(pH 9.9)	21 %
E - Glass	(pH 9.5)	50 %
Calcium Carbonate	(pH 9.4)	19 %
Calcium Metasilicate	(pH 9.4)	34 %
Mica	(pH 9.3)	55 %
Mica	(pH 9.0)	55 %

grams from a number of chemically different substrates having similar aqueous slurry pH values. Specific examples at a 1% silane loading are shown in Figures 9–11. Calcium carbonate (pH 9.4) and mica (pH 9.0) have substantially different chemical and surface properties, yet their aqueous slurry pH values are similar. The corresponding GPC chromatograms in Figure 9 illustrate that the physisorbed silane structure on the basic surfaces of mica (pH 9.0) and calcium carbonate (pH 9.4) are the same, producing the two overlapping oligomeric peaks at the same molecular weight in addition to the residual monomeric species. Both kaolin (pH 7.1) and zinc oxide (pH 7.5) demonstrate that, at near-neutral aqueous slurry pH, the physisorbed layer contains very small amounts of significantly higher molecular weight polymer as seen in Figure 10. The previously described DRIFT results showed that on neutral surfaces very small amounts of the coupling agent existed as physisorbed layers at a 1% loading. The GPC chromatograms confirm this and suggest that a neutral environment produces a very high molecular weight polysiloxane structure which is more resistant to the THF wash than are the silane species at acidic or basic pH. When the substrate surface imparts an acidic environment to the physisorbed silane layers, the polysiloxane structure is slightly lower in molecular weight than under basic conditions as seen in Figure 11. Tungsten oxide (pH 4.8) and clay (pH 4.1) obviously have different surface functionalities, yet their similar acidic nature produces physisorbed silanes with the same structure. The GPC chromatogram from the 3% treated clay sample is illustrated in Figure 11 to account for the difference in surface areas of the two particles since clay having a much higher surface area produces little physisorbed material at a 1% loading.

It is possible to model the acid/base influence imparted by the substrate surface by adjusting the pH of the treating solution and precipitating methacryl silane oligomers in a manner similar to the surface treatment of the particulate minerals. The GPC chromatograms in Figure 12 illustrate the comparison which can be made between the poly([(methacryloxy)propyl]silsesquioxane) structures observed on the particulate surface and deposited from the pH-adjusted treating solution. When the pH of the treating solution was adjusted with NaOH to a pH near the aqueous slurry pH of calcium carbonate (pH 9.4), the structures appear to be identical, both showing the two overlapping oligomeric species at the same molecular weight. The only difference seems to be in the relative amount of monomeric species present, which is probably due to the presence of a higher effective concentration of the resulting silanols in the treating solution than on the particulate surface. This shifts the condensation reaction

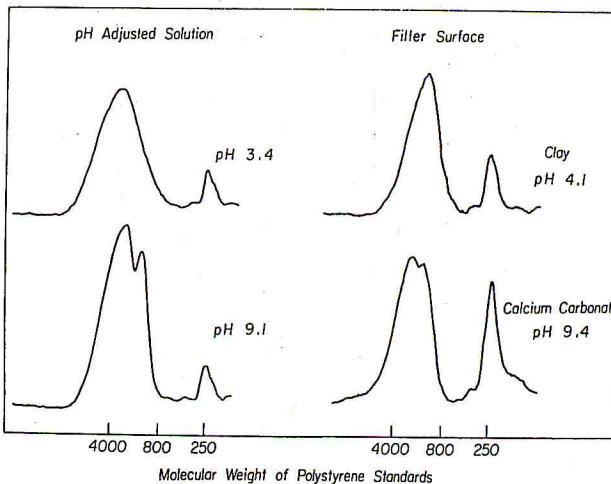
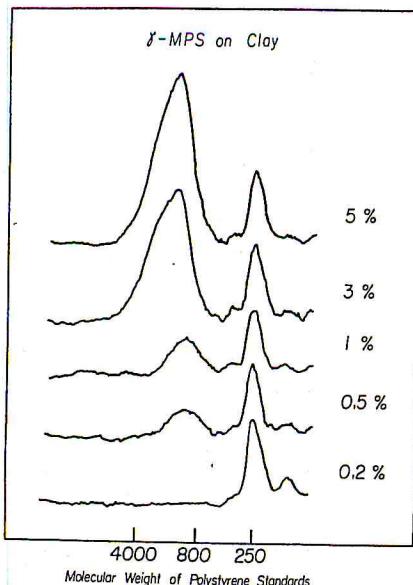


Figure 12. GPC chromatograms of the pH-adjusted  $\gamma$ -MPS solution at pH 3.4 and pH 9.1 and the THF extracts from the surfaces of clay (pH 4.1) and calcium carbonate (pH 9.4).

in favor of the oligomeric species. The same observation is made for the clay (pH 4.1) surface and bulk oligomers adjusted to an acidic pH of 3.4.

The pH influence determines the extent of the polycondensation reaction, which in turn determines the molecular weight of the siloxane oligomers in the physisorbed layer. We would also expect the acid/base nature of the substrate surface to play a large role in the chemisorbed silane. Under a mild THF extraction these layers cannot be removed from the substrate surface and therefore cannot be submitted to GPC analysis. However, the effect is observable in other ways. Kaolin (pH 7.1), having a near-neutral aqueous slurry pH, contains almost 100% chemisorbed layers at a 1% silane loading and showed only a small portion of very high molecular weight oligomers in the GPC analysis. This is characteristic of all the substrate surfaces exhibiting a near-neutral aqueous slurry pH as seen in Table II and Figure 9. The chemisorbed layers on neutral substrates are highly condensed poly([(methacryloxy)propyl]silsesquioxanes) exhibiting extensive Si–O–Si networks, which makes their removal and dissolution extremely difficult. On both acidic and basic mineral particulates the chemisorbed layers should be similar to that observed in the pH-adjusted bulk samples, yet their retention on the surface when submitted to a mild THF wash is probably more influenced by the substrate surface functionality, surface area, and surface morphology.

A high degree of silanol condensation does not by itself indicate high molecular weight poly([(methacryloxy)propyl]silsesquioxane) since it is believed that silanes can form either closed or open structures. Closed or cyclic



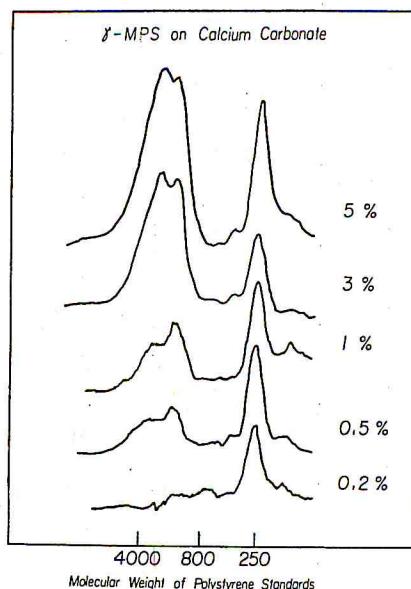
**Figure 13.** GPC chromatograms of the THF extracts from the surfaces of  $\gamma$ -MPS-modified clay (pH 4.1) dry-blended with increasing amounts of  $\gamma$ -MPS.

structures such as a cubical octamer require a high degree of condensation but do not necessarily result in high molecular weight polymers. As a result, the pH effect of the substrate surface may determine the molecular weight of the oligomeric species in part by controlling the amount of open and closed structure in the polysiloxane network.

The physical role of the substrate surface is also extremely important in controlling the structure of the adsorbed silane. When hydrolyzed silanes are applied to fiber and particulate surfaces it is always in very small quantities and therefore, the substrate surface determines the effective concentration and mobility of the silane molecules. Low surface coverages tend to reduce the extent of the condensation reaction between the hydrolyzed silanes and limits the molecular weight of the polysiloxane oligomers just as reaction rates are dependent on the concentrations of the reacting species. Therefore, when silane molecules are present as a well-distributed monolayer the condensation reaction would be more difficult, and little if any oligomeric species is expected to be removed from the surface.

The formation of high molecular weight polysiloxanes at low percent surface treatments is also limited by the shrinkage of the monomer packing upon condensation. The bond distance in the condensed Si—O—Si linkage is less than the distance between hydrogen-bonded silanols, and this both increases the distance between neighboring hydrolyzed silane molecules and reduces the likelihood of extensive polycondensation. As the amount of deposited coupling agent is increased, the mobility of the molecules is increased because more molecules are no longer restricted by the surface. Therefore, increasing amounts and increasing molecular weight of the oligomeric species would be expected with increasing degrees of surface treatment.

This trend is observed on the surfaces of both clay (pH 4.1) and calcium carbonate (pH 9.4) in Figures 13 and 14. At a 0.2% silane treatment on clay, which is the equivalent of about one-fifth of a monolayer, no oligomeric species is extracted from the surface. The amount and molecular weight of the physisorbed oligomers increases up to a silane modification of 3%, at which the poly[(methacryloxy)propyl]silsesquioxane structure is observed in the pH 4.1 system. It is interesting to note that at and above 3% treatment



**Figure 14.** GPC chromatograms of the THF extracts from the surfaces of  $\gamma$ -MPS-modified calcium carbonate (pH 9.4) dry-blended with increasing amounts of  $\gamma$ -MPS.

as mobile and have the same effective concentration as in the bulk. The calcium carbonate sample has a lower surface area and thus oligomeric formation is expected to be observed at a lower percent treatment since fewer molecules would be restricted by the surface. Slight oligomeric formation in the physisorbed layers on calcium carbonate is observed at 0.2% in Figure 14. The increase in molecular weight of the oligomers continues up to 3% treatment, after which the structure remains constant and resembles that observed in the pH-adjusted bulk oligomers (Figure 12). The concentration effect on the polycondensation reaction is caused simply by the physical surface area and thus the amount of surface coverage and is not due to acid/base characteristics. This is apparent since similar trends are observed on both clay and calcium carbonate which have very different acid/base characteristics and surface chemical functionalities. It should be noted that above 3% treatment on clay and above 2% treatment on calcium carbonate approximately the same intensity of the oligomeric species is observed due to the evaporation of the coupling agent as previously demonstrated by infrared measurements.

The consequences of the observed particulate mineral surface effects on composite performance should be substantial. Tightly bound high molecular weight silane structures obtained at neutral pH should provide more protection to chemical and water attack at the interface but will reduce both the migration of silane oligomers and the interpenetration of the resin into the silane layers. We can hypothesize that hydrothermal stability will be the highest when the particulate imparts a neutral environment to the adsorbing methacryl silane molecules. If migration of silane molecules is important to processability, then acidic or basic surfaces may be more desirable to modify the methacryl silane structures.

### Conclusion

The substrate has a controlling influence on the molecular structure of [ $\gamma$ -(methacryloxy)propyl]trimethoxysilane ( $\gamma$ -MPS) deposited on the surfaces of particulate mineral substrates. The deposited silane molecule

amount of deposited silane, and (iii) the pH environment imposed by the acid/base properties of the substrate. The degree of chemisorption is the highest on neutral substrates and more dependent on surface chemical functionality for acidic and basic substrates.

The physisorbed layer is capable of diffusing into a matrix resin and consists of unhydrolyzed or partially hydrolyzed monomer and polysiloxane oligomer with a molecular weight up to several thousand. The molecular weight of this physically adsorbed methacryl silane is also a function of the acid/base characteristics of the substrate and decreases in the order neutral > basic  $\geq$  acidic. The acid/base effect can be modeled by adjusting the pH of the treating solution and depositing oligomers in bulk form.

The substrate characteristics which affect the molecular structures of the deposited hydrolyzed trifunctional silanes do so by influencing the rate, extent, and mechanism of condensation. Control of the surface reactions, polymerization, and the resulting molecular structures may be possible with an increased understanding of the surface effects.

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**Registry No.** Hydrite R, 1318-74-7; calcium carbonate, 471-34-1; [ $\gamma$ -(methacryloxy)propyl]trimethoxysilane, 2530-85-0; iron(III) oxide, 1309-37-1; titanium oxide, 13463-67-7; zirconium oxide, 1314-23-4; aluminum oxide, 1344-28-1; tin(IV) oxide, 18282-10-5; tungsten oxide, 1314-35-8; copper(II) oxide, 1317-38-0; aluminum silicate, 1335-30-4; silica, 7631-86-9; nickel oxide, 11099-02-8; calcium oxide, 1305-78-8; calcium hydroxide, 1305-62-0; magnesium oxide, 1309-48-4; barium hydroxide, 17194-00-2; lead oxide, 1335-25-7; wollastonite, 13983-17-0; calcium metasilicate, 10101-39-0; zinc oxide, 1314-13-2.

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