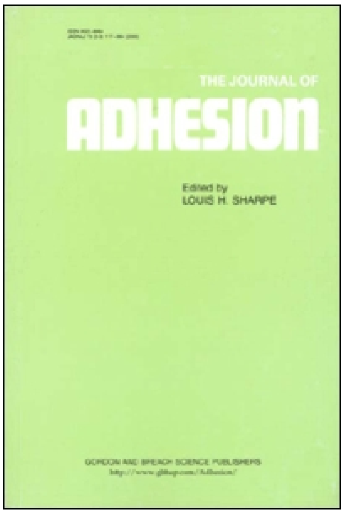

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Effect of Processing Variables on the Solution Characteristics of γ-Glycidoxypropyltrimethoxysilane (γ-GPS)

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The effects of the hydrolysis and condensation processes on the molecular structure of γ-glycidoxypropyltrimethoxysilane (γ-GPS) in aqueous solutions were investigated using Fourier-transform nuclear magnetic resonance (FT-NMR) spectroscopy and FT-Raman spectroscopy. Hydrolysis was characterized by monitoring the production of methanol and the decrease in concentration of $SiOCH_3$ groups in 1% solutions of deuterium oxide using proton NMR. The production of methanol and loss of methoxy groups in 25% solutions of γ-GPS in water was characterized using Raman spectroscopy. Hydrolysis was found to be a very rapid process, whose rate could be increased or decreased by altering the pH of the solution. NMR spectroscopy showed that hydrolysis was complete in a 1% γ-GPS solution in deuterium oxide after 34 minutes. Raman spectroscopy also showed hydrolysis to be rapid and complete in a 25% solution of γ-GPS in water after 1 hour. Condensation, on the other hand, took a relatively long time to occur. In the NMR spectra, condensation was observed by the broadening of peaks due to the protons on the carbon atom adjacent to the silicon atom. In the Raman spectra, condensation was characterized by the disappearance of the SiOH band near 725 cm^{-1} and the development of an SiOSi band near 600 cm^{-1}. In addition to the proton NMR, Si-29 NMR was used to characterize the silane in 10% solutions of γ-GPS in water. The Si-29 NMR showed oligomer growth with respect to time. The oligomer growth was correlated with mechanical test results.

Keywords: γ-glycidoxypropyltrimethoxysilane (γ-GPS); hydrolysis; condensation; silane; NMR spectroscopy; Raman spectroscopy

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I. INTRODUCTION

Silane coupling agents have been used for some time to enhance adhesion of polymers to inorganic substrates such as metals and glasses. Silanes provide a relatively simple but highly effective method to improve adhesion. Coupling agents can improve adhesion, give increased mechanical strength, and impart moisture resistance to bonds between organic polymers and inorganic substrates.

Most silane coupling agents have the form

$$R{-}(CH_2)_3{-}Si{-}X_3$$

where R represents an organofunctional group that is usually selected for compatibility with the polymer and X is a hydrolyzable group such as an alkoxy. Silanes with several different organofunctional groups R are available for use with different polymers.

In order for a silane coupling agent to be effective, two processes, hydrolysis and condensation, have to occur. In the presence of water, hydrolysis of an alkoxysilane will occur. This stepwise reaction converts the alkoxy groups into silanol groups and results in the formation of an alcohol as a byproduct. After hydrolysis has occurred, condensation of the silanol groups to form polysiloxanes will occur. These reactions can be shown schematically as

$$R'Si(OR)_3 + \text{excess } H_2O \rightleftharpoons R'Si(OH)_3 + 3ROH$$
$$R'Si(OH)_3 + R'Si(OH)_3 \rightleftharpoons R'Si(OH)_2Si(OH)_2R' + H_2O$$

Hydrolysis and condensation reactions of silanes have been thoroughly investigated [1–2] using several techniques including Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), and Raman spectroscopy. The rate of hydrolysis has traditionally been investigated by monitoring the amount of alcohol produced from the hydrolysis reactions. Pohl and Osterholz showed that the hydrolysis of silanes at very low concentrations in buffered solutions follows first order kinetics [1], but only when the concentrations are low enough that water consumption by the silane can be neglected. At higher concentrations, when water uptake must be considered, the overall rate of reaction is second order, but first order in respect to the silane. Leyden and Atwater investigated several trialkoxysilanes in water/acetone mixtures. Their studies showed that when multiple silane groups are involved in the hydrolysis, as in a trimethoxysilane, the molecule undergoes three pseudo-first order reactions [2].

The hydrolysis and condensation processes of a silane are only two of several variables that affect the performance of the silane as an adhesion promoter. Several studies have been reported in which the effects of processing variables, including hydrolysis time, solution pH, and solution concentration, on the performance of silane coupling agents as adhesion promoters have been investigated [3–6]. Mazza and Kuhbander [3] showed that crack growth in aluminum/epoxy wedge test specimens depended strongly on processing variables involved in the adherend pretreatment. They prepared wedge test specimens from adherends that were grit-blasted and coated with thin films of γ-GPS cast from aqueous solutions. The effectiveness of the adherend pretreatment was related to processing variables such as concentration, hydrolysis time, and pH of the γ-GPS solution and drying time and drying temperature of the film deposited on the aluminum adherends.

Mazza and Kuhbander [3] also showed that γ-GPS primers were most effective when the hydrolysis time of 1% solutions was about 1 hour. Wedge tests showed that specimens prepared from adherends treated with solutions hydrolyzed for shorter and longer times had greater crack growth rates. These results indicated that γ-GPS solutions had an effectiveness "window". If the hydrolysis time was too long, condensation of the silane in solution occurred, decreasing the effectiveness of primer films cast from the solution. If the hydrolysis time was too short, the extent of hydrolysis of the silane was decreased and the effectiveness of primer films cast from the solution also decreased.

Despite the large amount of research that has been done on silanes, there are still significant questions regarding the mechanisms by which they function. In order to understand these mechanisms, it is important to determine the properties of silanes at each step in the application process. This includes characterization of the coupling agents in aqueous solutions as well as in thin films applied to inorganic substrates. Much of the research on hydrolysis and condensation reactions of silanes has been conducted on buffered solutions or in water/solvent mixtures. The purpose of this research was to determine the rates of reaction and structural changes that occurred during hydrolysis and condensation reactions of γ-GPS in unbuffered solutions since these solutions are used in the field repair procedures described by Mazza and Kuhbander [3]. These structural changes were then correlated with the mechanical test results obtained by Mazza and Kuhbander [3].

II. EXPERIMENTAL

Hydrolysis and condensation of γ-GPS in 1% solutions in deuterium oxide (D_2O) were monitored by proton nuclear magnetic resonance spectroscopy (NMR) using a Bruker Model AC-250 broadband variable temperature spectrometer. Proton NMR spectra were recorded at 250.13 MHz. With respect to the acquisitions, the spectral width was 5 kHz and the Fourier Transform size was 8.1 K points. Each spectrum was obtained by averaging 10 scans. Proton pulse widths were approximately 6 μs. The solutions were prepared under nitrogen in a glove box to help assure the absence of moisture and were continuously stirred throughout the hydrolysis reaction. Aliquots were taken from the solution at times ranging from 5 minutes to 94 hours and analyzed by NMR. In the hydrolysis experiments, the solution was analyzed every 5 minutes after initial mixing. In the condensation experiments, the solution was analyzed on an hourly basis. 3-(Trimethyl-silyl) propionic acid, sodium salt (DSS), was the reference for the NMR investigations and assigned to 0 ppm.

The rates of hydrolysis and condensation of γ-GPS in aqueous solutions were also determined by FT/Raman spectroscopy using a spectrometer consisting of a Bio-Rad FTS 60A optical bench, a ND:YAG laser, a liquid-nitrogen-cooled Ge detector, and an SPC 3200 data station. The laser power used for these experiments was approximately 200 mW. A capillary tube was used as the sample holder. Due to the relatively low signal-to-noise ratio, 25% solutions of γ-GPS were used. In the hydrolysis experiments, spectra were obtained by averaging 64 scans at a resolution of $16\,cm^{-1}$. Aliquots of the solution were analyzed at 5-minute intervals. In the condensation experiments, spectra were obtained by averaging 64 scans, but at a resolution of 8 cm^{-1}. The solution was analyzed on an hourly basis. Experiments were also performed where small amounts of diluted hydrochloric acid (0.01 M) or benzyldimethylamine (BDMA) were added to the silane solution to determine the effect of pH on the rates of hydrolysis and oligomerization. In the acid-catalyzed experiments, the pH of the solution was adjusted to approximately pH 4. The spectra were obtained at times of 1, 4, 6, 8, 10, 15, 30, and 60 minutes using a resolution of 16 cm^{-1} and averaging 64 scans. In the base-catalyzed reaction, two drops of BDMA were added to the solution.

Oligomerization of 10% γ-GPS solutions in water was monitored by Si-29 nuclear magnetic resonance spectroscopy (Si-29 NMR) using a Bruker 400 broadband wide-bore spectrometer. Si-29 NMR spectra were recorded at 79.5 MHz. For the acquisitions, spectral widths were 25 kHz and Fourier Transform (FT) sizes were 16 K points. Si-29 pulse widths were approximately 12 μs. Aliquots of the solution were analyzed using NMR at hydrolysis times ranging from 2 to 20 hours. The solutions were stirred for 1 hour before the analysis began. Spectra were obtained by averaging 976 scans. DSS was used as a standard.

III. RESULTS AND DISCUSSION

The proton NMR spectrum of a 1% solution of γ-GPS in deuterium oxide after 5 minutes of hydrolysis is shown in Figure 1. NMR peak assignments of the γ-GPS protons are summarized the Table I. The spectrum consisted of various multiplets at chemical shifts of approximately 0.7, 1.7, 2.8, 3.0, and 4.0 ppm that were not directly involved with the hydrolysis reaction. Multiplets at 0.7 and 1.7 ppm were assigned to the "A" and "B" protons, respectively. Multiplets at 2.8 and 3.0 ppm were due to the "E", "F", and "G" protons on the carbons of the epoxide ring. There were two multiplets that were directly involved with hydrolysis. These were at 3.3 ppm and 3.6 ppm and were assigned to protons in methyl groups of methanol and to the protons in methoxy groups of the silane ("H" protons), respectively. A multiplet was observed at 4.0 ppm, which was related to protons on the carbon atoms of the ether group ("C" and "D" protons). A singlet was also observed at 4.6 ppm due to the protons from a small amount of HDO in the deuterium oxide.

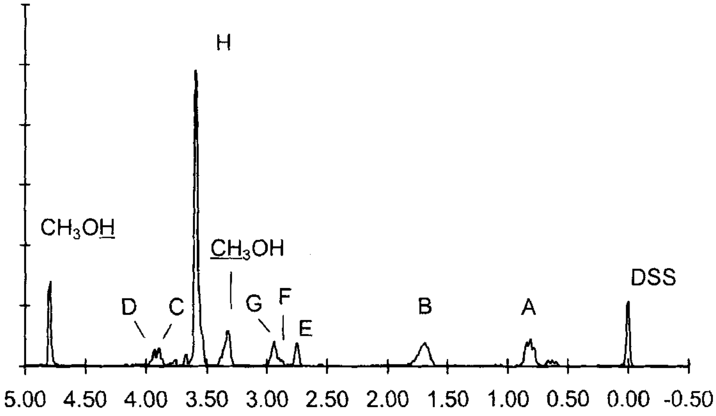


FIGURE 1 The proton NMR spectrum of 1% γ-GPS in deuterium oxide w/DSS after 5 minutes of continuous stirring.

TABLE I Peak assignments for the proton NMR spectrum of 1% γ-GPS in deuterium oxide

Peak position (ppm)	*Peak type*	*Proton type*
0.6–0.9	Multiplet	H_A-Attached to the carbon adjacent to the silicon group
1.6–1.9	Multiplet	H_B-Attached to the second carbon from the silicon group
2.7	Triplet	H_F-Attached to the first carbon of the epoxide group
2.9	Triplet	H_G-Attached to the first carbon of the epoxide group
3.3–3.4	Multiplet	H_E-Methyl protons of methanol
3.6	Singlet	H_H-Methoxy protons
3.8	Multiplet	H_C-Attached to the distal carbon of the ether group*
3.9	Multiplet	H_D-Attached to the proximal carbon of the ether group*
4.8	Singlet	Protons due to hydrogen contamination in the deuterium oxide

* Relative to the epoxide group.

The conversion of methoxy groups to methanol during hydrolysis was observed by NMR spectroscopy. Figure 2 shows the NMR spectra of a 1% γ-GPS solution at various hydrolysis times. The peaks at 3.3 ppm and 3.6 ppm changed in intensity as a function of time. At the beginning of hydrolysis, the peak at 3.6 ppm was much greater in intensity than the peak at 3.3 ppm. After 14 minutes hydrolysis time (Fig. 2B), both peaks were equal in intensity. After 34 minutes (Fig. 2C), the hydrolysis appeared to be nearly complete, with the peak at 3.3 ppm much greater in intensity than the peak at 3.6 ppm. Spectra taken at times up to 3 hours did not show any additional significant

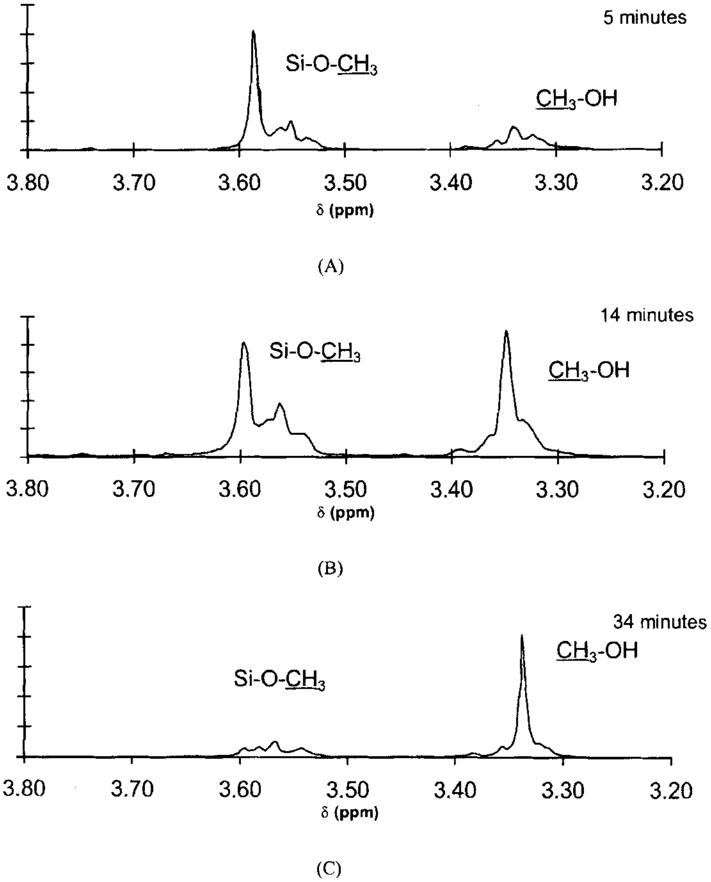


FIGURE 2 Proton NMR spectra of a 1% γ-GPS solution in deuterium oxide showing the peaks due to the methoxy protons of the silane and the methyl protons of methanol after hydrolysis times of (A)-5 minutes, (B)-14 minutes and (C)-34 minutes.

changes in the intensities of these two peaks. Thus, hydrolysis of γ-GPS in deuterium oxide was essentially complete after approximately 34 minutes. By using the heavier hydrogen isotope (deuterium), the rapid ester-to-alcohol hydrolysis was easier to follow because the deuteron transfer was slower than the proton transfer, possibly by as much as a factor of 2[4]. Therefore, the hydrolysis reaction of γ-GPS in a 1% H_2O solution would occur at a much higher rate and would probably be complete in less time than 34 minutes.

In addition to the changes in the peaks at 3.3 and 3.6 ppm due to hydrolysis and methanol production, a change was also seen in the multiplet at 0.7 ppm due to the "A" protons with respect to time (see Fig. 3). At the beginning of hydrolysis, the multiplet consisted of three large peaks near 0.78, 0.81, and 0.85 ppm and some peaks of very low intensity between 0.59 and 0.72 ppm. As hydrolysis continued, peaks near 0.60, 0.74, 0.67, and 0.71 ppm increased in intensity and peaks

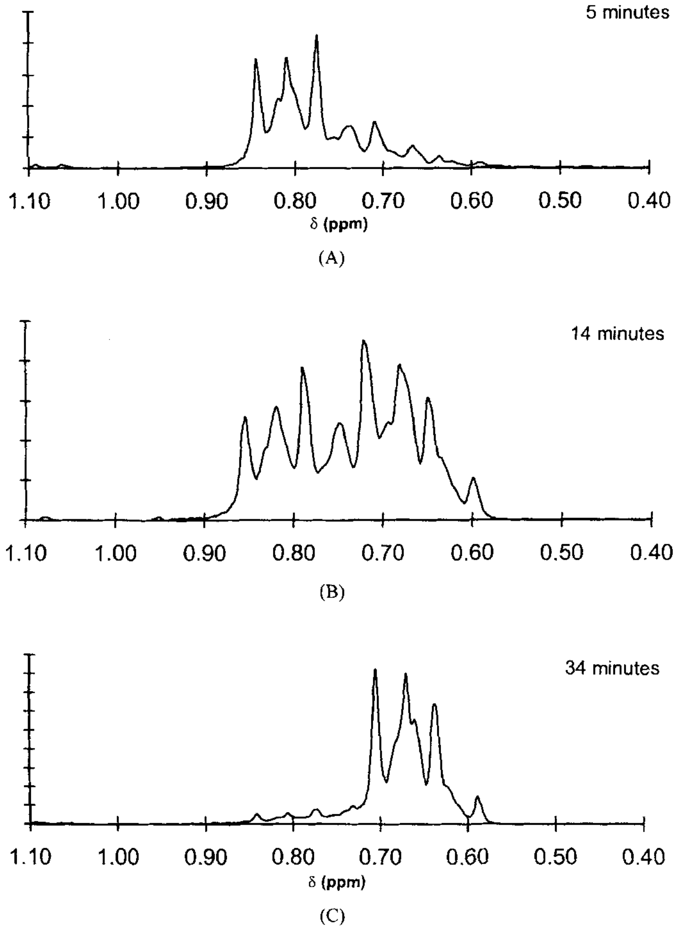


FIGURE 3 Proton NMR spectra of a 1% γ-GPS solution in deuterium oxide showing the peaks due to the "A" protons after hydrolysis times of (A)-5 minutes, (B)-14 minutes and (C)-34 minutes.

near 0.78, 0.81, and 0.85 ppm decreased. This change in peak intensities was probably due to the different environments that the protons on the carbon adjacent to the silicon experienced during the conversion of methoxy groups to silanol groups. This change in peak intensitites was also completed within 34 minutes.

Hydrolysis of γ-GPS in H_2O was also investigated using FT-Raman spectroscopy. The FT-Raman spectrum of neat γ-GPS is shown in Figure 4. Bands characteristic of the epoxide ring were observed near 3070 cm^{-1} due to CH_2 stretching and near 1246, 890, and 850 cm^{-1} due to ring breathing. A band due to an SiOC stretching mode appeared at 636 cm^{-1}. Other bands were observed near 2930, 2842, and 1454 cm^{-1} and assigned to CH_2 asymmetric and symmetric stretching and CH_2 deformation, respectively.

Without a catalyst, the hydrolysis reactions for a 25% solution of γ-GPS with a pH of 6.5 took between 45 minutes and one hour to reach equilibrium (see Fig. 5). After a hydrolysis time of 5 minutes (spectrum A), there was a large band near 643 cm^{-1} due to $SiOCH_3$, but no band near 1013 cm^{-1} due to methanol. There was a shift in the SiOC band from 636 cm^{-1} in the neat sample to 643 cm^{-1} in the aqueous solutions due to the interaction of the SiO groups with the OH groups of the solvent. By 30 minutes of hydrolysis (spectrum B), the band at 643 cm^{-1} had started to decrease in intensity and a band near 1013 cm^{-1} due to methanol production had formed. At 60 minutes of hydrolysis time (spectrum C), the band near 643 cm^{-1} had disappeared and the methanol band near 1013 cm^{-1} had reached its maximum intensity. The bands at 643 and 1013 cm^{-1} changed in intensity at the

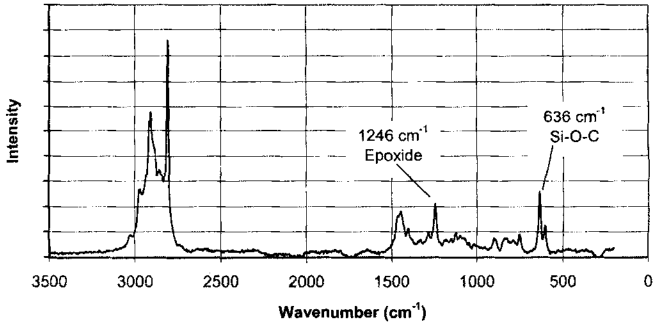


FIGURE 4 Raman spectrum of neat γ-GPS.

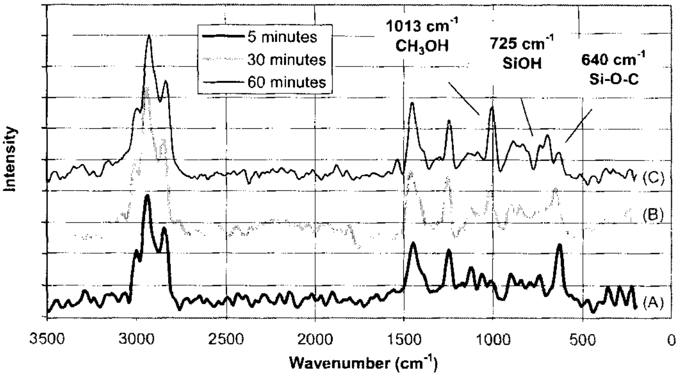
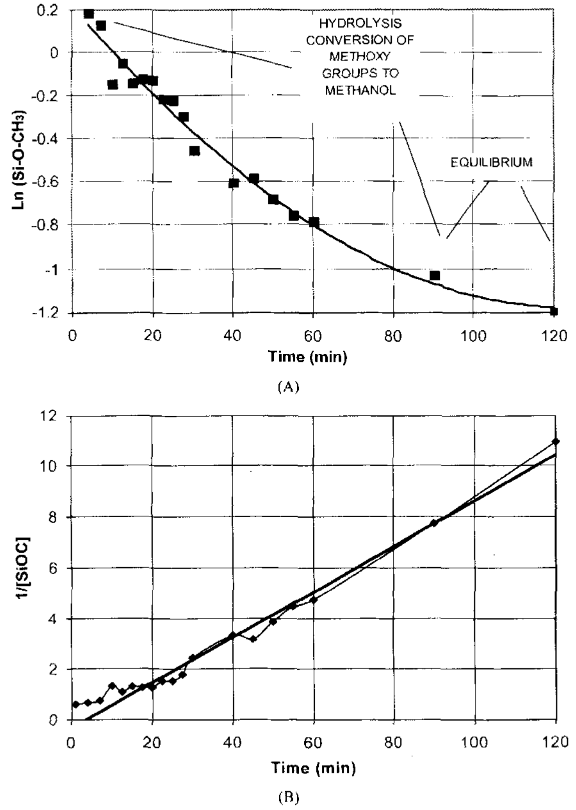


FIGURE 5 Raman spectrum of a 25% γ-GPS solution in water at various hydrolysis times.

same rate, since the methoxy groups were converted into methanol molecules due to the hydrolysis reaction. A band near 707 cm^{-1} due to silanol groups had also developed by 60 minutes. Hydrolysis of γ-GPS in the 25% solution had reached equilibrium after 60 minutes, implying that 1% solutions, which were used by Mazza and Kuhbander, would hydrolyze much faster since there was a much higher water-to-silane ratio in the 1% solution than there was in the 25% solution.

A plot of the natural log of the intensity of the SiOC band (near 640 cm^{-1}) in the Raman spectra of the 25% solution of γ-GPS in water *versus* time is shown in Figure 6A. This plot showed the loss of methoxy groups, as determined by the decrease in intensity of the SiOC band, due to the hydrolysis reactions as a function of time. The plot was not linear, suggesting that, in this system, hydrolysis did not follow first-order kinetics. The plot showing hydrolysis of the silane as second order is shown in Figure 6B. The data are more linear when plotted as a second-order function than when plotted as first-order. Hydrolysis could be second-order since there were two materials contributing to the rate of reaction, the silane and the water. In a 25% solution of γ-GPS in water, the molar ratio of silane-to-water was ~1:12, which was not great enough to make the effects of the consumption of water negligible. Our results agreed with those obtained by Leyden and Atwater [2], who showed that water



(A)

(B)

FIGURE 6 Hydrolysis of the Si-O-C groups plotted *versus* time shown as (A) a first-order function and (B) a second-order function.

consumption was a contributor to the kinetics even when there was a 1:15 molar ratio of silane-to-water. Although our system followed second-order kinetics, the hydrolysis of silanes in water has been shown to follow first-order kinetics in work by Pohl [1], but only in very dilute solutions (0.001 M to 0.03 M).

Hydrolysis of γ-GPS in 25% solutions in H_2O occurred at a faster rate when catalyzed with acetic acid. Raman spectra of the acid-catalyzed silane solution (pH 4.0) at various hydrolysis times are shown in Figure 7. After 1 minute of hydrolysis, the spectrum (A) was similar to the spectrum of an uncatalyzed solution. There was a band

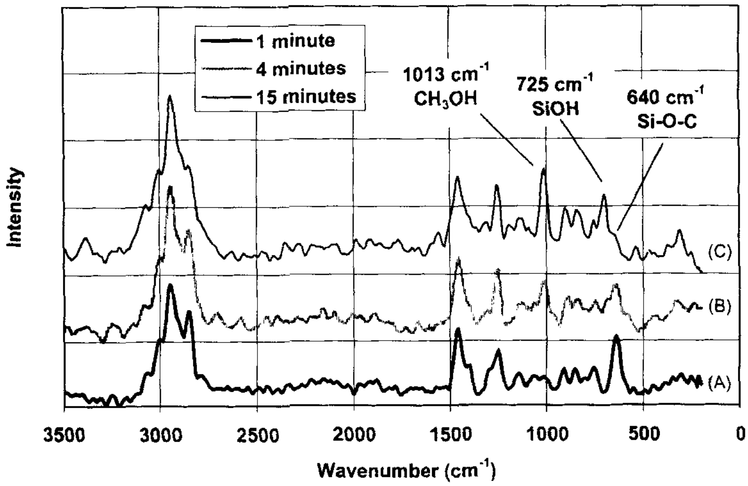
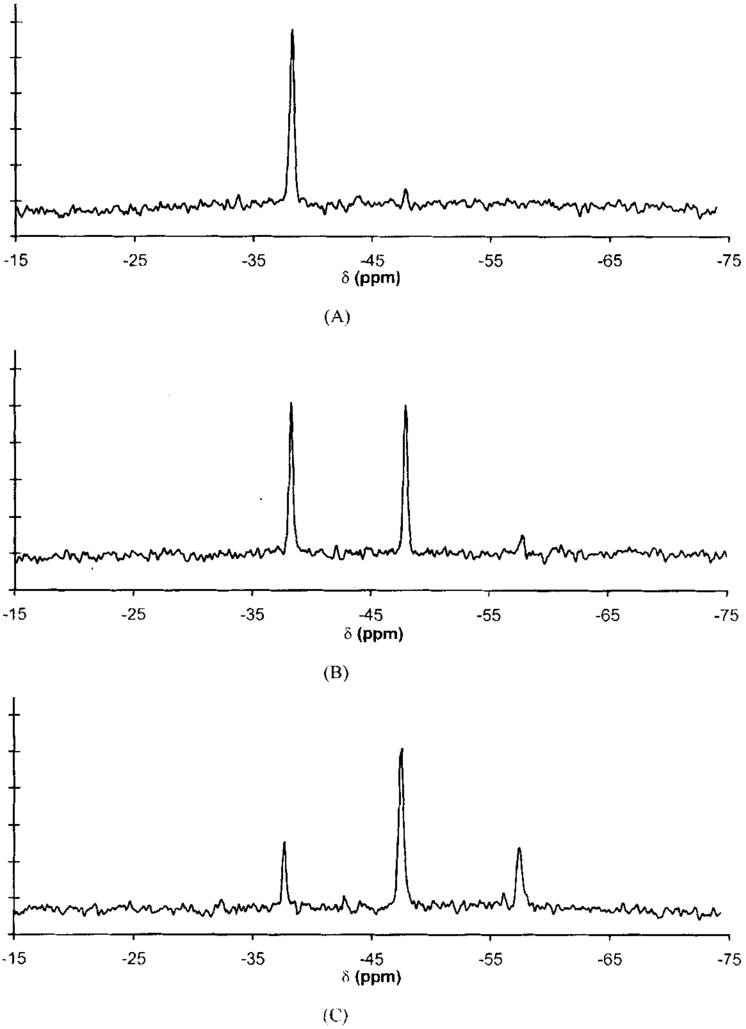


FIGURE 7 Raman spectra of a 25% solution of γ-GPS in water catalyzed by acetic acid.

near 643 cm^{-1} due to $SiOCH_3$ but no band near 1013 cm^{-1} due to methanol. After 4 minutes hydrolysis (spectrum B), the band near 643 cm^{-1} decreased greatly in intensity and a band near 1013 cm^{-1} had appeared. The spectrum of γ-GPS in solution after 8 minutes of hydrolysis (spectrum C) showed that all of the methoxy groups had been consumed in the hydrolysis reaction to form methanol. In addition, a band due to silanol groups had formed near 707 cm^{-1}. Formation of silanol was complete between 15 and 30 minutes of hydrolysis time.

Short-term oligomerization ($<$ 24 hours) was investigated using Si-29 NMR spectroscopy. When a 10% solution of γ-GPS in **water** was analyzed after an hour of stirring, there was only one peak at -38 ppm corresponding to SiOH groups. This peak shifted downfield from -43 ppm to -38 ppm due to the formation of SiOH bonds through the hydrolysis process [5]. In Figure 8, the NMR spectra of a 10% solution of γ-GPS in **water** at various hydrolysis times are shown. At approximately 2 hours hydrolysis (see Fig. 8A), there were two peaks, one due to SiOH and the other due to a dimeric species. A third peak, possibly due to a network species, did not develop until the ninth hour of hydrolysis (see Fig. 8B). After 9 hours of hydrolysis, the total oligomer concentration of the solution was 65%, which consisted of 60% dimeric



(A)

(B)

(C)

FIGURE 8 Si-29 NMR spectra of a 10% γ-GPS solution in water at hydrolysis times of (A)-2 hours, (B)-9 hours and (C)-20 hours.

species and 5% network species. As time increased, the peak due to SiOH decreased in intensity and peaks due to the dimeric and network species increased. After 20 hours, the spectrum of the 10% γ-GPS solution in water (see Fig. 8C) still contained three peaks, with approximately 62% of the silicon in the dimeric state and 21% in the network state. Peaks due to successive oligomers (dimers, trimers, tetramers, *etc.*) occur ~10 ppm apart in Si-29 NMR spectra of alkoxysilanes [5]. Results from the NMR experiments on the 10% solutions should correlate with the 1% solutions of γ-GPS used as the primer in the experiments performed by Mazza and Kuhbander [3]. Other researchers have shown that the rates at which the different oligomeric species of γ-GPS occur in 1% and 10% aqueous solutions are similar [6]. Although the concentration was higher, the solvent (water) that was used in these experiments was the same solvent used by Mazza and Kuhbander.

In Figure 9, plots of the relationship between silanol concentration, oligomer concentration, network concentration and hydrolysis time are shown for a 10% solution of γ-GPS in water. The silanol and oligomer concentrations were found by integrating the area under the peaks in the Si-29 NMR spectra. As time increased, the concentration of silanol decreased due to the condensation of silanol species to form oligomers. As hydrolysis time increased, the dimeric and network silane species increased in concentration. The network silane species was considered to be three or more silane molecules bonded together by Si-O-Si bonds. The majority of the oligomerized species were dimeric silane species. After 20 hours of hydrolysis, 17% of the silicon was in the form of silanol, 62% of the silicon was in the form of a

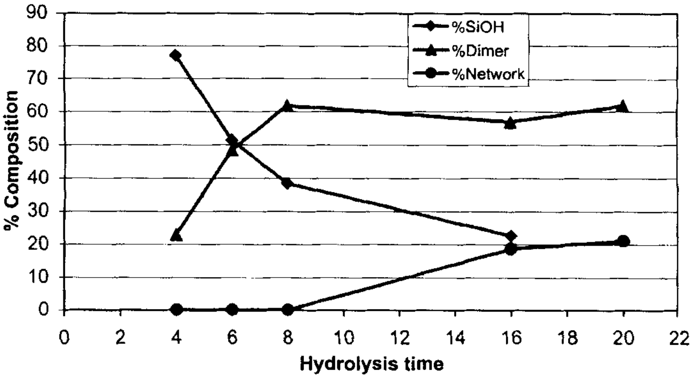


FIGURE 9 A plot showing the relationship between composition and hydrolysis time for a 10% solution of γ-GPS in water.

dimeric species, and 21% of the silicon in the solution was in the form of a network oligomer.

The relationship between oligomer concentration in a 10% γ-GPS solution and total crack length of wedge-test specimens prepared by Mazza and Kuhbander [3] from adherends treated with a 1% γ-GPS solution is shown in Figure 10. As the concentration of dimers and network species increased in the solution, the crack length increased as well. **This suggested that the amount of dimers and network oligomers in the solution had an effect on the performance of the deposited silane film as an adhesion promoter on wedge-test specimens.** Therefore, a direct relationship could be seen between oligomerization of the silanol in solution and durability of the wedge test specimens prepared using substrates pretreated with the solutions. To the best of our knowledge, this is the first time that a correlation has been observed between the structure of a silane in solution and the performance of the silane as a primer.

Oligomerization at longer times was investigated using proton NMR spectroscopy. Several peaks in the NMR spectra of a 1% γ-GPS solution in deuterium oxide changed over extended periods of time, apparently due to oligomerization. The majority of the changes were observed in the two sets of peaks that were due to the protons of the carbon adjacent to the silicon atom and the protons of the second carbon from the silicon

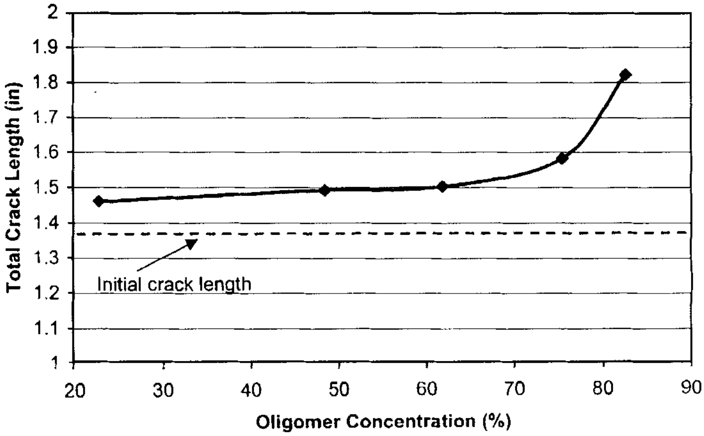


FIGURE 10 A plot showing the relationship between the composition in a 10% solution and total crack length of wedge-test specimens prepared from adherends treated with a 1% γ-GPS solution.

atom, referred to as the "A" and "B" protons, respectively (see Fig. 11). After 28 hours of continuous stirring, the peaks due to the "A" protons were at the same position as the peaks due to the "A" protons after the silane had been hydrolyzed for 34 minutes (compare Figs. 3C and 11A). After 122 hours of stirring, the peaks shown in Figure 11A had broadened and the small peaks that were due to the "A" protons in the vicinity of a silicon atom bonded to a methoxy group had disappeared. This broadening continued as shown in the spectrum of a 1% γ-GPS solution that had been stirred for 194 hours (Fig. 11C). The peaks shown

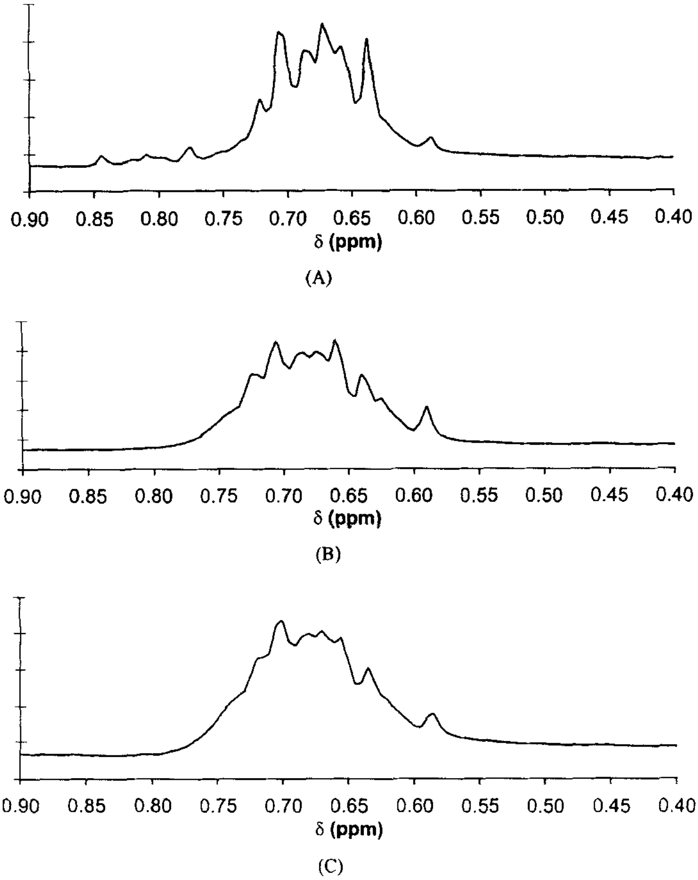


FIGURE 11 Proton NMR spectra of a 1% γ-GPS solution in deuterium oxide showing the peaks from the "A" protons of the molecule after stirring for (A)-28 hours, (B)-122 hours and (C)-194 hours.

in Figures 11A and B were very similar, in that all the peaks in the one spectrum corresponded to peaks in the other spectrum. The peaks in the spectrum of the 122-hour solution were not as intense as the peaks in the spectrum of the 28-hour solution. By 194 hours, several of these small peaks could not be distinguished.

The spectra of the "B" protons (Fig. 12) also broadened as a function of time. At 28 hours, there were five distinguishable peaks due

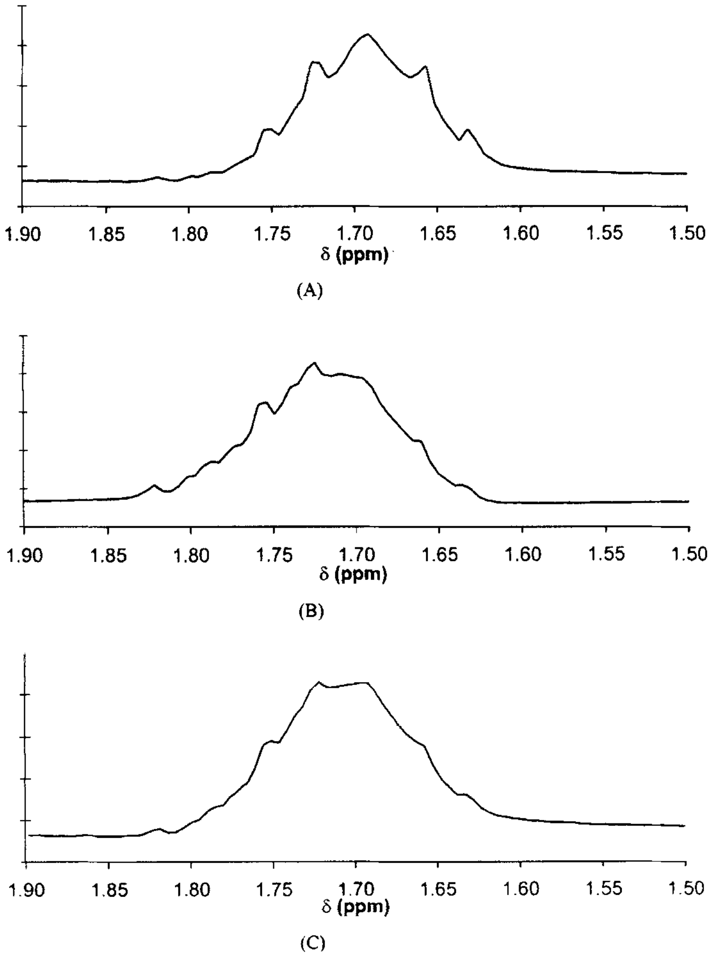


FIGURE 12 Proton NMR spectra of a 1% γ-GPS solution in deuterium oxide showing the peaks from the "B" protons of the molecule after stirring for (A)-28 hours, (B)-122 hours and (C)-194 hours.

to the “B” protons, which theoretically was the correct number of peaks if the protons were only being split by their neighboring protons. By 122 hours of stirring, the spectrum of the “B” protons showed approximately 10 small peaks due to the broadening of the peaks. After 194 hours, the spectrum consisted of a single broad peak instead of the smaller peaks, which comprised it at earlier hours.

The condensation process was also investigated using Raman spectroscopy. Results similar to those obtained in the NMR experiments were observed. Oligomerization took place over a longer period of time than did hydrolysis. Since Raman experiments were performed on 25% γ-GPS solutions in deionized water, condensation occurred much faster than in the 1% solutions analyzed using NMR. Nonetheless, condensation was still much slower than hydrolysis. Figure 13 shows FT/Raman spectra of a 25% γ-GPS solution after being stirred (hydrolyzed) for 5, 8, and 27 hours. After stirring the solution for 5 hours, the intensity of the silanol band at 707 cm^{-1} was similar to the maximum intensity of the band seen after 60 minutes of hydrolysis, but by 8 hours the silanol band started to decrease in intensity. After 27 hours, the band had decreased in intensity even more. With the silanol band decreasing, there must have been formation of either siloxane bonds (SiOSi) from condensation or SiOCH$_3$ groups from the reversal of hydrolysis. Since the equilibrium

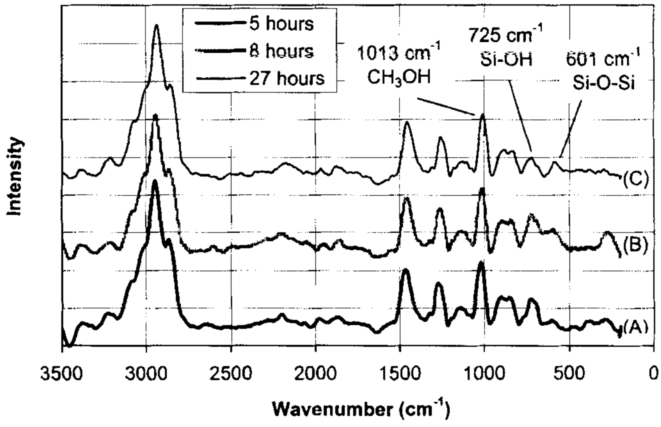


FIGURE 13 Raman spectra of a 25% γ-GPS solution in water at various hydrolysis times.

was not disturbed in this experiment, the latter will not be considered. So, if the silanol groups were being consumed, there should have been the formation of a band due to SiOSi. Unfortunately, the SiO band does not appear as strongly in Raman spectra as it does in infrared spectra. Therefore, it was possible for SiOSi bonds to have formed in this experiment. They were just not detectable using Raman spectroscopy. Nonetheless, since the γ-GPS in solution did not condense at short hydrolysis time (< 8 hours), films can be deposited after the solution has been hydrolyzed without the risk of depositing high molecular weight oligomers that could have adverse effects on adhesion.

IV. CONCLUSIONS

Hydrolysis of γ-GPS in water was determined to be a step-wise reaction that occurred very rapidly. Proton NMR results showed that hydrolysis of the γ-GPS in 1% solutions in deuterium oxide was complete after 30 minutes of stirring. 25% solutions of γ-GPS in water that were analyzed by Raman spectroscopy showed hydrolysis to be complete after 1 hour of stirring. It was also determined that the rate of hydrolysis of the 25% γ-GPS solution in water followed second-order kinetics. This rate could be increased by altering the pH of the solution. Raman spectroscopy showed that as the pH was lowered from ~ 5.5 to 4, the rate of reaction increased by at least a factor of 2.

Si-29 NMR spectroscopy was used to characterize the condensation reactions by determining the silane structures with respect to time. Results showed that 10% solutions of γ-GPS in water contained only monomer, dimer, and the trimer/network species after a 20 hour period. By comparing the Si-29 NMR results with the results from wedge tests, a direct correlation was shown between the concentrations of dimers and trimer/network species in the 10% γ-GPS solution and total crack length of the wedge tests. As the oligomer concentration in the 10% silane solution became larger, the crack lengths of the wedge test specimens became larger. Therefore, the presence of the oligomers was related to the decrease in performance of the silane pretreatment in the wedge tests. Mazza and Kuhbander found that their silane films did not yield good moisture durability results when deposited from solutions after 8 hours of hydrolysis. The NMR spectra in both water and deuterium oxide showed a peak due to a trimeric/network silane species that developed at approximately 8 hours of hydrolysis. Therefore, the decreasing performance in the wedge tests could be related to the development of this trimeric/network species in the silane solution.

NMR spectroscopy and Raman spectroscopy were also used to characterize the condensation reactions that occurred in solution. These two techniques were not as sensitive as Si-29 NMR for determining structure differences. Condensation took a relatively long time to occur. The Si-29 NMR spectra of a 1% γ-GPS solution in deuterium oxide over time showed that oligomerization took greater than 28 hours to occur. Raman experiments performed on 25% solutions of γ-GPS in water showed appreciable oligomerization occurring between 5 and 8 hours. Even when a 25% solution of γ-GPS was used, oligomerization was not detected at short hydrolysis times. Therefore, the presence of highly oligomerized species in the 1% solutions hydrolyzed for short periods of time was highly unlikely. The rate of oligomerization was found to increase when the pH of the solution was increased to ~8.3 (at 22°C) by adding BDMA.

The results obtained on the hydrolysis and condensation reactions show that hydrolysis was a rapid reaction, whereas condensation took a relatively long time. This explained why Mazza and Kuhbander [3] found good adhesion in their wedge tests when hydrolyzing for 1 hour. After 1 hour, the hydrolysis reactions had reached equilibrium, but little, if any, oligomerization had taken place. Since very little oligomerization has occurred, the silane solution can be deposited without high molecular weight oligomers being present. The oligomerization that is also needed for good adhesion with the silane films can then be obtained through drying the film at elevated temperatures.

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