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Characterization of Silane-Treated Glass Fibers by Diffuse Reflectance Fourier Transform Spectrometry

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Silane coupling agents are organosilicon compounds used to improve the interfacial bonding between the reinforcement and the matrix resin in polymer composites. For a polyester/glass fiber composite, γ -methacryloxypropyltrimethoxysilane (γ -MPS) is an appropriate coupling agent. After hydrolysis this silane will react with a glass fiber surface by condensation of SiOH groups and can also bond with a polyester resin by free radical reaction of C=C groups. These reactions, as well as the structure of γ -MPS, were studied on glass fiber surfaces by diffuse reflectance infrared Fourier transform spectrometry (DRIFT) as a function of time and temperature. Diffuse reflectance offered the advantage of following the reactions *in situ* as they occurred on the fiber surface. Quantitative information on the rates of silanol condensation and double bond reaction was derived from the reaction studies.

Silane coupling agents are an integral part of modern reinforced plastics and composites. Surface treatment of glass fibers with coupling agents to improve the mechanical performance of the composite is almost universal. While coupling agents have been extensively studied, there is still considerable controversy about the mechanism by which they improve composite performance. Many theories have been proposed to explain this mechanism. Each theory approaches the problem from a different perspective drawing on ideas from surface chemistry, adhesion, polymer science, glass science, and mechanics. Two of these theories can be summarized in the following manner:

1. Coupling agents chemically bond to both the glass fiber surface and the matrix resin. Thus, primary chemical bonds connect the matrix to the reinforcement and provide for effective transfer of stress across the interface.

2. Coupling agents modify the resin layer in the vicinity of the glass surface. This produces a more flexible resin interphase capable of relieving residual stresses and stress concentrations by undergoing plastic deformation.

For proper chemical bonding to the glass some of the silanol groups of the adsorbed silane must condense with surface silanols to form silane-glass siloxane bonds. The formation of siloxane bonds between adjacent silane molecules is also important to give the adsorbed silane layers some mechanical integrity. The ability of the siloxane layers to modify the resin depends upon their mobility in the resin and, hence, how well they have been cured on the glass fiber surface. Several excellent review articles (1-4) discuss the different coupling agent theories in detail.

There are many different methods of characterizing the molecular structure of silane coupling agents. These methods are normally used to study the structure of silane on the glass fiber surface in the absence of matrix. Therefore, an implicit assumption of these studies is that silane structure on the glass surface is similar to the structure in the composite. Studies of a silane coupling agent in a cured composite are extremely difficult and few have been attempted. These molecular

methods often have difficulty detecting the presence of a small amount of silane such as a monolayer or less. Yet, a monolayer of coupling agent can make a significant difference in the mechanical response of the composite.

Fourier transform infrared spectrometry (FTIR) is a particularly useful technique to study silane coupling agents adsorbed onto glass surfaces. The advantages of infrared spectrometry in determining chemical and structural information are well known. The very small amount of coupling agent normally applied to the glass surface often gives a poor signal to noise ratio in IR, making the detection of small bands difficult. Furthermore, strong bands from the glass substrate obscure coupling agent peaks, again because of the very low silane content. Sample preparation for a standard transmission experiment involves grinding the sample to a fine powder and pressing it into a potassium bromide pellet. The limitations of sample preparation and low S/N ratio can be substantially overcome by using FTIR diffuse reflectance spectrometry (DRIFT). This technique is more surface sensitive than standard transmission and does not require any destructive sample preparation. Furthermore, DRIFT can be applied directly to silane-treated glass fiber samples.

One of the goals of our research is to study the molecular structure of silane with respect to the effect on the mechanical properties of the composite. For γ -methacryloxypropyltrimethoxysilane (γ -MPS) coupling agent to bond with the resin, the carbon-carbon (C=C) double bond of the silane must be available at the time of resin cure. However, for the same coupling agent to bond properly with the glass surface, coupling agent silanol groups should react with glass surface silanols well before resin cure. Thus, if chemical bonding is important, then premature reaction of the C=C of γ -MPS is undesirable, yet proper condensation of silanol groups to siloxane bonds is necessary. Heat normally provides the basis for siloxane cure, but heat can easily cause premature polymerization and/or oxidation of the silane unsaturation. Therefore, it is important to have some understanding of the effect of heat on the rate of Si-O-Si condensation and the rate of premature C=C reaction.

The following brief outline summarizes the work reported in this paper:

1. The curing reactions of a simple model system of silane oligomer were studied. This system was chosen to simulate the structure of γ -MPS on glass fiber surfaces.

2. The curing reactions of γ -MPS adsorbed on E-glass fibers were studied by DRIFT as a function of time and temperature. Diffuse reflectance offered the advantage of following the curing reactions *in situ* as they occurred on the fiber surface.

3. Quantitative information on the rates of silanol condensation and double bond reaction was derived from the reaction studies.

EXPERIMENTAL SECTION

The E-glass mats used in this study were kindly supplied by F. J. Crane, Jr., of Crane and Co. The fibers in these mats have a nominal diameter of 4 μm . Prior to use, the mats were heat cleaned at 500 °C for 20 h to remove a binder and any other

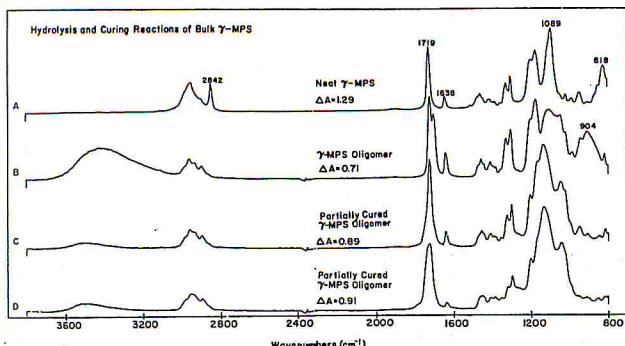


Figure 1. Transmission spectra, plotted in absorbance [$-\log_{10}(I/I_0)$], of neat γ -MPS (A), γ -MPS oligomer, and partially cured oligomer. Curing was done by heating the oligomer (B) at 140 °C for 15 min (C) and 45 min (D).

surface treatment. The coupling agent, γ -methacryloxypropyl-trimethoxysilane (γ -MPS), was purchased from Petrarch Systems, Inc., and was used as received.

The E-glass mats after heat cleaning were treated with γ -MPS by the following procedure. The γ -MPS was hydrolyzed in deionized, distilled water which had been adjusted to pH 3.5 with acetic acid. The hydrolysis time varied between 1 and 3 h according to the solution concentration. The E-glass mats were immersed into the hydrolyzed silane solution for 5 min before being removed and suction filtered to remove excess solution which clings to the glass mats. Within 15 min after suction filtration, samples of E-glass were placed inside the spectrometer for analysis. These samples were then alternately removed for heating in a convection oven and reanalyzed in the spectrometer. These curing studies were performed at 80, 100, and 120 °C with variable heating cycles. A control sample which was not heated was reanalyzed at the same time intervals as the heated samples to correct for any curing which might occur at room temperature.

Bulk siloxane oligomer was obtained by the following procedure: (1) neat γ -MPS, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$; (2) hydrolyzed γ -MPS, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OH})_3$; (3) oligomerized γ -MPS, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OSi}-)_2\text{OH}$. A 10% by weight concentration of γ -MPS was hydrolyzed in pH 3.5 deionized, distilled water. The solution was set aside for several days. The hydrolyzed silane condensed to a siloxane oligomer which phase separated from the solution. This siloxane oligomer was stored in a vacuum desiccator.

The infrared analysis was done by using a Fourier transform infrared spectrometer (Digilab FTS-20E) with a dry nitrogen purge and a mercury cadmium telluride (MCT) detector. A Digilab diffuse reflectance cell (Model DRA-100) was placed inside the spectrometer to collect the diffuse spectra. Typically between 100 and 200 scans were coadded at a resolution of 2 cm^{-1} throughout the range of 3800–700 cm^{-1} . All transmission spectra are shown in absorbance mode. All diffuse reflectance spectra are shown in Kubelka-Munk format [$1 - R$] $^{2/2R}$ (where R is the reflectivity ratio). No sample preparation was done on the E-glass mats for the diffuse studies. The mats were used neat and ratioed against a KBr powder background. Samples of siloxane oligomer were deposited from a THF solution onto a KBr plate. Digital subtractions of spectra were done on the basis of least-squares curve fitting analysis.

RESULTS

Figure 1 summarizes the model study of γ -MPS under various conditions. Figure 1A is a transmission spectrum of the neat γ -MPS as received. The peaks at 2840–3000 cm^{-1} result from carbon–hydrogen stretching vibrations. The strong peak at 1719 cm^{-1} is the carbonyl $\text{C}=\text{O}$ stretching mode, while the band at 1638 cm^{-1} is the vinyl $\text{C}=\text{C}$ stretching mode. The bands at 1300 cm^{-1} and 1325 cm^{-1} are associated with the ester functionality (5). The peaks at 1167 cm^{-1} and 1192 cm^{-1} are also due to ester vibrations (6–9), while the bands at 1089 cm^{-1} and 818 cm^{-1} result from $\text{Si}-\text{O}-\text{CH}_3$ asymmetric and symmetric stretching vibrations, respectively (10, 11). The peak at 941 cm^{-1} originates from the vinyl wagging vibration.

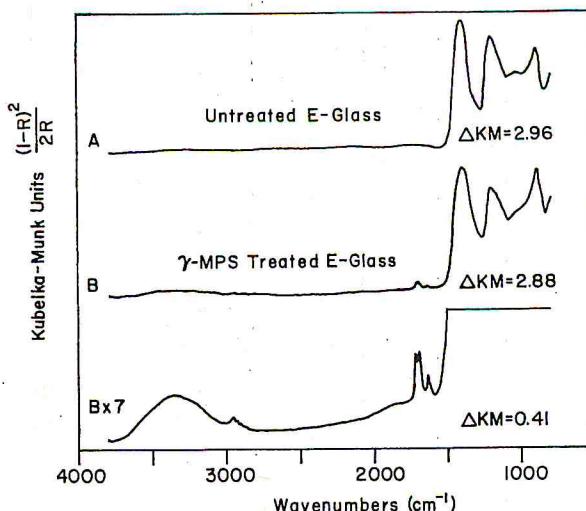


Figure 2. Diffuse reflectance spectra of pristine and γ -MPS treated E-glass fibers. Spectra are from neat fiber samples (i.e., the fibers were not ground to a powder or otherwise altered).

Figure 1B is a transmission spectrum of the bulk siloxane oligomer obtained by allowing a concentrated solution of hydrolyzed γ -MPS to condense and phase separate. The band at 1042 cm^{-1} is assigned to the $\text{Si}-\text{O}-\text{Si}$ antisymmetric stretching mode. The appearance of this band is consistent with the formation of a siloxane oligomer. The new broad band at 3430 cm^{-1} can be assigned to the hydrogen bonded $\text{O}-\text{H}$ stretching vibrations of SiOH and water. The 904- cm^{-1} band can be assigned to the stretching mode of the $\text{Si}-\text{OH}$ group. The new shoulder at 1697 cm^{-1} appears because the carbonyl hydrogen bonds with the hydroxyl groups of SiOH and water (12). The drastic reduction in absorbance of the 818- cm^{-1} symmetric $\text{Si}-\text{O}-\text{CH}_3$ stretch, and the 2842- cm^{-1} symmetric $\text{C}-\text{H}$ stretch of the SiOCH_3 group confirms that nearly complete hydrolysis has occurred.

Figure 1C,D shows transmission spectra representing samples prepared by heating the siloxane oligomer at 140 °C in air for different periods of time (15 and 45 min, respectively). Heating in air promotes further reaction of SiOH to SiOSi , as evidenced in Figure 1C by the large intensity decrease in the 904- cm^{-1} and 3430- cm^{-1} peaks and the shoulder at 1697 cm^{-1} which is due to the hydrogen bonded carbonyl. Heating in air also promotes polymerization and/or oxidation of the $\text{C}=\text{C}$ double bond. A variety of products are formed by the oxidation process including ketones, aldehydes, and low molecular weight oxygen copolymers (13–17). Oxygen-induced polymerization of the vinyl group of γ -MPS was found to occur over time at temperature above 110 °C by Ishida et al. (18). Significant changes take place in the four bands associated with the ester group vibrations (1325, 1300, 1192, and 1167 cm^{-1}). These band changes are complex. The carbonyl stretching frequency region is less complicated. Since the carbonyl is resonance stabilized by the adjacent $\text{C}=\text{C}$ double bond, reaction of this double bond shifts the carbonyl stretching mode to a higher frequency. The $\text{C}=\text{C}$ peak area will decrease with increasing polymerization. These effects are observed in spectra of Figure 1C,D. The weak shoulder at 1734 cm^{-1} observed in Figure 1C becomes much larger in Figure 1D. The relative area of $\text{C}=\text{C}$ as compared with the carbonyl mode is obviously less in Figure 1D than in Figure 1C.

Figure 2 shows Fourier transform diffuse reflectance spectra of neat E-glass mat (Figure 2A) and E-glass mat treated with γ -MPS (Figure 2B). A 2.0 wt % aqueous solution of γ -MPS was used to treat the E-glass mat of Figure 2B, while an aqueous solution without silane was used to treat the control sample in Figure 2A. The most obvious difference between

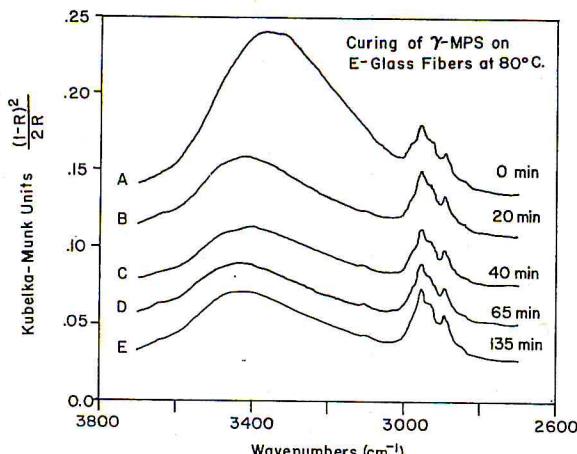


Figure 3. Diffuse reflectance spectra of γ -MPS treated E-glass fibers as a function of cure time at $80\text{ }^{\circ}\text{C}$. These spectra monitor the curing process on the glass fiber surface, *in situ*, and as it occurs.

the bulk silane transmission spectra of Figure 1 and the adsorbed silane reflectance spectra of Figure 2 is the effect of the glass fiber substrate. The strong bands of the E-glass substrate are strongly absorbing and, hence, difficult to subtract in a linear fashion. However, it is not necessary to subtract the E-glass substrate to observe the coupling agent bands above 1500 cm^{-1} at this silane concentration. These bands are well within the Kubelka-Munk linear region.

Normally in diffuse reflectance spectrometry the sample, if not already in powder form, is ground to a fine powder of controlled particle size and mixed with powdered KBr also of controlled particle size. The single beam spectrum of this sample is then ratioed against a background spectrum of pure powdered KBr. To maximize the γ -MPS peaks relative to the glass absorbances, the mats are used neat rather than ground to a powder. Grinding exposes newly fractured surfaces that are not covered by the silane. Since, DRIFT is surface sensitive, new glass surfaces give a stronger glass signal. Obviously, this is an undesirable situation for obtaining a quality spectrum of the surface-treated species. The fibers of the E-glass mat are of sufficiently small diameter to give good reflectance across the entire spectral range studied. The theory and application of diffuse reflectance spectrometry have been discussed in detail elsewhere (19–23).

An important aspect of using DRIFT to study the curing of γ -MPS adsorbed on E-glass is that the amount of water picked up by the silane-coated fibers can also be monitored. This capability allowed us to distinguish between any water picked up by the fibers alone and water which was hydrogen bonded to the adsorbed γ -MPS silanol groups. These observations would not be possible with standard KBr pellet transmission techniques. Furthermore, because of the *in situ* capability and high signal-to-noise ratio of DRIFT, the infrared spectrum could be observed at a much earlier stage of drying than with other infrared techniques. The water picked up by the control fibers was insignificant compared with that of the silane-treated fibers. It was difficult to distinguish between spectra of the control fibers run immediately after treatment and spectra run after 20 h of drying time. This was of course not the case for the silane-treated samples.

Figures 3 and 4 show representative DRIFT spectra from the *in situ* curing studies. Figure 3 concentrates on the hydrogen bonded O-H stretching region, and Figure 4 centers on the carbonyl stretching region. All of the spectra in Figure 3 have been normalized by use of the small glass overtone which occurs in this region. One immediately notices the rapid decrease in the large broad hydrogen-bonded O-H band, and the corresponding frequency shift between Figure 3A and Figure 3B due to increased contribution of the SiOH groups

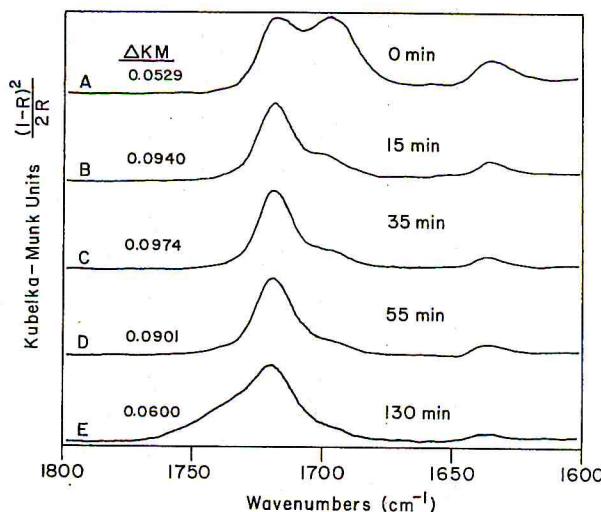


Figure 4. Diffuse reflectance spectra of γ -MPS treated E-glass mats as a function of cure time at $120\text{ }^{\circ}\text{C}$. These spectra monitor the curing process on the glass fiber surface, *in situ*, and as it occurs.

that exist in the silane layers. These data will be discussed as a whole later in this paper.

The band shifts in Figure 4 are well understood and can be interpreted in terms of structural variations. As mentioned before the band at 1718 cm^{-1} is the carbonyl stretching vibration and the shoulder at 1696 cm^{-1} is the hydrogen bonded carbonyl stretch. The spectrum in Figure 4A shows that a significant portion of the carbonyl groups are hydrogen bonded to SiOH and HOH. This spectrum was run within 15 min after the E-glass mat had been treated with the coupling agent. However, mats that were not heat cured but instead air-dried at room temperature showed little reduction in the amount of hydrogen-bonded carbonyl even after 2 h. To achieve the same reduction in the 1696-cm^{-1} band as obtained by only a few minutes of heating, the unheated samples had to be air-dried for at least 20 h. Sometime between 1 and 2 h of curing at $120\text{ }^{\circ}\text{C}$ a shoulder at 1734 cm^{-1} appears in Figure 4. This shoulder arises due to polymerization and/or oxidation of the C=C bond. If that bond reacts, the carbonyl stretching mode will shift to higher frequencies (18).

Another interesting aspect of the spectra of Figure 4 is the band around 1640 cm^{-1} . Both the aforementioned C=C stretching vibration (1638 cm^{-1}) and the water bending mode (1635 cm^{-1}) should absorb in this area. In fact, the broad band at 1635 cm^{-1} in Figure 4A shifts slightly to a higher frequency in Figure 4B-E upon thermal drying. Since it is known from the hydrogen-bonded carbonyl band that a large amount of -OH is lost between Figure 4A and Figure 4B, and since very little C=C polymerization has taken place in Figure 4B (as evidenced by the lack of a 1734-cm^{-1} shoulder), it seems logical that this small shift is representative of the relative concentration changes between the C=C and HOH bands.

All of the band shifts occurring in Figure 4 can be thought of as relative concentration changes among several different components. Thus, one can use these relative concentration differences to spectrally separate these "mixtures" into pure components. The linearity of the Kubelka-Munk function makes this possible. Essentially, each mixture spectrum represents a system of linear equations (i.e., each frequency data point is a separate equation). Each component is an unknown variable in that set of equations. It is intuitively apparent that if there are more (or the same number) mixture spectra than components, one can "solve" the equations to obtain the unknown components. Normally, factor analysis, a powerful technique for extracting pure components from mixture spectra, could be applied to our coupling agent system.

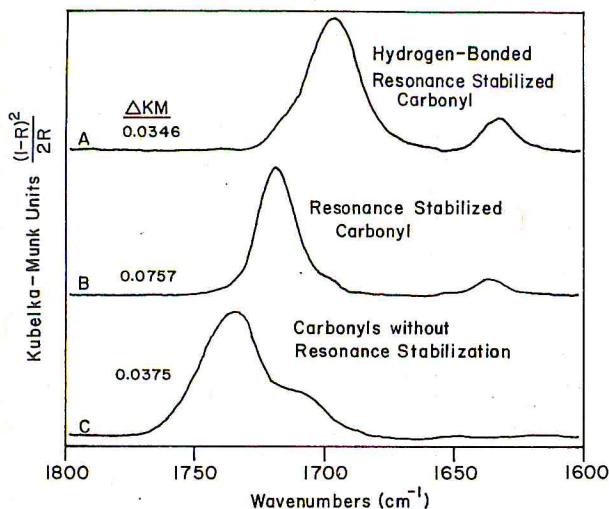


Figure 5. Comparison of the different carbonyl components of γ -MPS deposited on E-glass fibers. These components were separated by spectral subtraction.

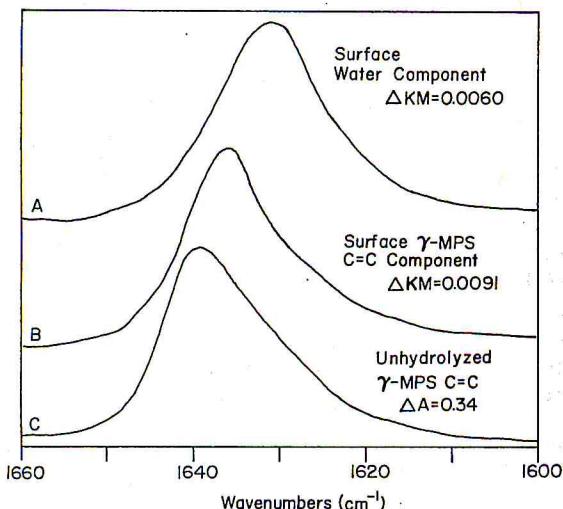


Figure 6. Spectral comparison of (A) surface water component, (B) $C=C$ vinyl component of γ -MPS deposited on E-glass fibers, and (C) $C=C$ vinyl band from unhydrolyzed, neat γ -MPS. These components were separated by spectral subtraction.

However, factor analysis requires that each component have an isolated (i.e., not overlapped) band (24, 25). The bands in our system are heavily overlapped such that the preferred method of factor analysis cannot be used. Instead, we have used digital subtractions to sequentially "strip" out the component spectra from the mixture spectra. The scaling parameters for these digital subtractions were determined by least-squares curve fitting (26–28) and by inspection. This sequential subtraction stripping procedure was performed on the mixture spectra in Figure 4. The resulting extracted component spectra are shown in Figures 5 and 6.

The regions stripped were the $1780\text{--}1660\text{-cm}^{-1}$ carbonyl stretching region, and the $1660\text{--}1600\text{-cm}^{-1}$ $C=C$ stretching and H–O–H bending region. Three components were assumed for the carbonyl region: the hydrogen-bonded, resonance-stabilized carbonyl which absorbs at 1696 cm^{-1} , the non-hydrogen-bonded, resonance-stabilized carbonyl which absorbs at 1718 cm^{-1} , and the non-hydrogen-bonded, nonresonance-stabilized carbonyl which absorbs at 1734 cm^{-1} . The 1696-cm^{-1} component shown in Figure 5A was obtained by subtracting a spectrum similar to Figure 4B from one similar to Figure 4A. A similar procedure was used to extract the 1718-cm^{-1} component (Figure 5B). The 1734-cm^{-1} component (Figure

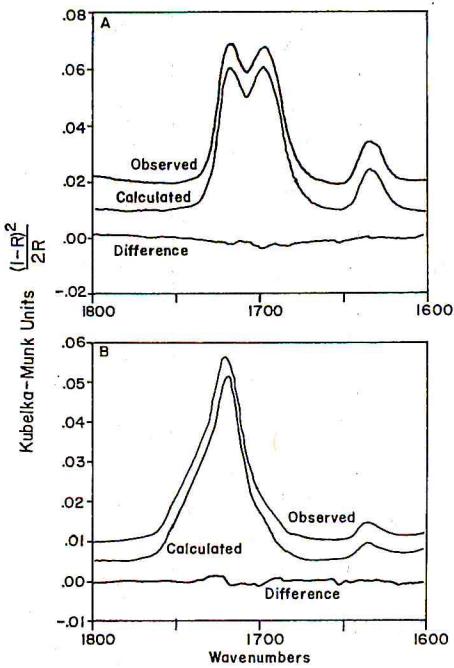


Figure 7. Least-squares fit of extracted components to the observed spectrum for (A) γ -MPS deposited on E-glass before heating and (B) γ -MPS on E-glass after heating at $100\text{ }^{\circ}\text{C}$ for 130 min. The spectra have been shifted vertically for the purpose of comparison.

5C) was generated by subtracting the spectra in Figure 5A and Figure 5B from a spectrum similar to Figure 4E. This subtraction was based on least-squares analysis of the carbon–carbon double bond $1660\text{--}1610\text{-cm}^{-1}$ region. The resulting subtraction spectrum had no $C=C$ peak or presumably any $C=C$ resonance stabilized carbonyl.

At present we have three spectroscopically stripped components in Figure 5. One of these spectra may contain one or two additional components. Examination of Figure 5C reveals that one of the three stripped components is not completely pure. The shoulder at 1710 cm^{-1} in Figure 5C is believed to be the hydrogen-bonded, nonresonance-stabilized carbonyl. In fact, for a completely rigorous treatment, this band should be included as a fourth component in the stripping procedure. The difference between the 1710 cm^{-1} and the 1734 cm^{-1} components was too small to separate by spectral stripping. The original three components (1734 , 1718 , 1696 cm^{-1}) are now curve fit by least-squares methods to the sample spectra from Figure 4 and data at other cure temperatures.

The second region stripped ($1660\text{--}1600\text{ cm}^{-1}$) proved more difficult than the first. The two components, $C=C$ and HOH, were heavily overlapped and separated by only a few wavenumbers. To separate the $C=C$ component required use of spectral information from throughout the entire spectral region. Without the large change in relative concentration of water observed previously, this spectral stripping operation would have been even more difficult. A spectrum similar to Figure 5A was subtracted from one similar to Figure 5B until the water band at 1632 cm^{-1} had been removed. This produced the pure $C=C$ band shown in Figure 6B. The water bending mode was then itself produced by a similar procedure using the newly obtained $C=C$ band. The $C=C$ band of unhydrolyzed γ -MPS (as received) run in transmission is also shown in Figure 6 for comparison purposes. From this band one can see that the spectral stripping procedure gives reasonable results for this system.

In two separate sets (one for each frequency region) of least-squares curve fitting operations, the separated components were fit to the three sets of cure rate spectra. These

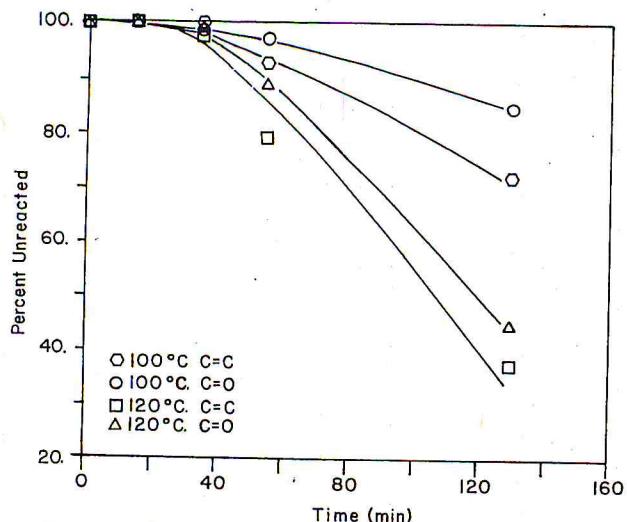


Figure 8. Curing of γ -MPS on E-glass fibers. The two different bands (carbonyl and vinyl) used to measure the degree of cure are plotted here for comparison.

fits gave scaling factors for the amount of each component in the mixture spectra. Two sample curve fits are shown in Figure 7. These fits are typical of those for all of the cure studies and represent the two extremes in the concentrations of the three carbonyl components.

Quantitative data showing the rate of $C=C$ reaction is plotted in Figure 8. Two sets of data points are shown for each curing temperature. The two data sets at each temperature were derived from the two sets of least-squares scaling parameters. The first set of parameters gave the relative contributions of each of the three carbonyl components. The peak areas of the three respective bands were normalized by the area of the carbon-hydrogen stretching peaks. As already mentioned, the 1734-cm^{-1} band is characteristic of nonresonance stabilized carbonyl and, hence, reflects the concentration of the carbon-carbon double bond groups which have undergone polymerization or oxidation. The second set of parameters gave the relative contributions of the $C=C$ and water bands. Again the parameters were normalized by the carbon-hydrogen stretching bands. The area of the $C=C$ stretching band of course is a direct measure of the amount of unsaturation present.

These two different methods of measuring $C=C$ reaction give comparable results as seen in Figure 8. There does seem to be some systematic difference between the two methods. While the method of directly measuring the $C=C$ band area might seem preferable, there are several reasons for using the information from the carbonyl stretching region. First, the carbonyl bands are much more intense than the $C=C$ band. As the amount of coupling agent on the glass fibers is decreased, it becomes preferable to measure the $C=C$ concentration by the carbonyl band area. Second, the double bond and water bands are much closer together (6 cm^{-1}) than the carbonyl bands and, hence, their separation by spectral stripping becomes less reliable. Third, just as the carbonyl is resonance stabilized by the presence of the $C=C$ group, the opposite is also true. Thus, when the carbonyl band is shifted to lower frequency because of hydrogen bonding, the $C=C$ stretching mode will also shift slightly to lower frequency. It would be very difficult to distinguish such a shift from the water bending mode. Therefore, it is not surprising that there is some systematic difference between the two methods of Figure 8.

Figure 9 shows the rate at which $-OH$ groups are removed from the system, whether by condensation of $SiOH$ to $SiOSi$ or evaporation of hydrogen-bonded water molecules. The

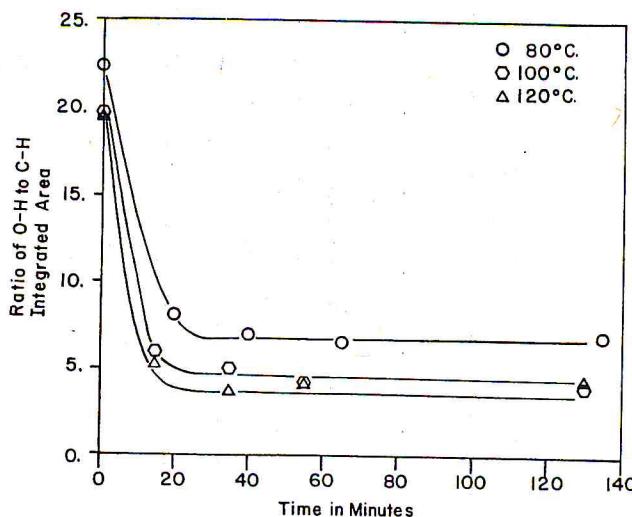


Figure 9. Curing of γ -MPS on E-glass fibers. Total area of the hydrogen bonded $O-H$ stretching band is normalized by the $C-H$ stretching band.

integrated area of the 3430-cm^{-1} band was divided by the integrated area of the $C-H$ band to obtain these plots for the three different curing temperatures. Initially, there is a steep drop in the amount of $-OH$ present; the curve then levels off to a constant value. This behavior was observed for all three curing temperatures studied as can be seen in Figure 9. It is well known that the specific absorptivity of the OH stretching mode changes drastically as the strength of hydrogen bonding changes. Hence, the OH bands with different frequencies should not be used for a quantitative purpose. In spite of a relatively minor frequency shift observed in Figure 3, the intensity variation shown in Figure 9 should be considered in a semiquantitative fashion.

DISCUSSION

Comparison of Figure 1 with Figures 2-4 shows that the bulk model system studied by transmission exhibits similar curing reactions to the real system studied *in situ* by diffuse reflectance. The model system behaves in the same manner as the real system, with carbonyl bands and hydrogen bonded $-OH$ bands changing in position and intensity as curing proceeds. We can of course study the γ -MPS peaks below 1500 cm^{-1} in our model system. This region is important because of the $Si-O-Si$ (1100 and 1040 cm^{-1}) and $Si-OH$ (904 cm^{-1}) stretching modes. Thus, model studies of siloxane oligomer could be useful to study curing kinetics of the backbone $Si-O-Si$ group. It is also evident that the γ -MPS is completely hydrolyzed when applied to the glass fiber surface. The symmetric $C-H$ stretch of the $Si-O-CH_3$ group (2842 cm^{-1}) present in Figure 1A is absent in Figure 3.

The components extracted by sequential subtraction or "spectral stripping" shown in Figure 5 are not really separate components in the chemical sense. They are all part of a silane oligomer. However, they are separable components in the spectroscopic sense. To a good first approximation the intensity at a given frequency in a spectrum is just the sum of intensities at that frequency from all the different bands in the spectrum. Thus, bands in a spectrum which arise from different functional groups can be thought of as different components. If the concentration of these different bands varies as a function of temperature etc., then they can be separated and their relative concentrations determined explicitly. Thus, we can use the carbonyl bands as a structural probe of the silane on the glass fiber surface. The components shown in Figure 6 are truly separate in the chemical sense. The reasons for using the carbonyl bands to measure the rate of $C=C$ reaction in addition to the $C=C$ stretching band itself

have already been mentioned. There is one other motivation for using the carbonyl region. If KBr pellet transmission methods were used instead of diffuse reflectance methods, the rate of C=C reaction could still be followed. Since KBr is very hygroscopic, water adsorbed by the KBr during grinding usually overwhelms the C=C stretching mode but has little effect on the carbonyl bands. The reasonable agreement between the two methods shown in Figure 8 indicates that transmission methods would give relatively reliable C=C curing results.

The cure rate data plotted in Figures 8 and 9 indicate that heating beyond 40 min at the two higher temperatures studied may be more harmful than beneficial. If long heating times are desired, then it would seem desirable to use temperatures of 80 °C or lower.

Registry No. γ -MPS, 2530-85-0.

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