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Direct Solid-State ^{13}C NMR Evidence for Covalent Bond Formation between an Immobilized Vinylsilane Linking Agent and Polymer Matrices

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ABSTRACT: ^{13}C CP MAS NMR spectroscopy of polymer composites with immobilized ^{13}C-enriched triethoxyvinylsilane provides direct evidence for incorporation of the vinylsilane into the polymers by covalent bond formation. Approximately 12% of the vinylsilane is incorporated into polystyrene and approximately 33% into poly(methyl methacrylate) (PMMA).

Introduction

Organofunctional silanes are often used as coupling agents to improve the adhesive bond between a polymer matrix and glass reinforcements.[1] Silanes can promote both dry and wet adhesions for glass fiber reinforced polymer materials. The effect is particularly important in improving the stability of the adhesive bond against hydrolytic degradation in a wet environment.

The need for coupling agents was recognized in the 1940s when glass fibers were used as reinforcements in organic resins. Specific strength-to-weight ratios of dry glass-reinforced resin composites were very favorable, but the resins lost much of their strength during prolonged exposure to moisture. Because polymer resins containing double bonds were the most common matrix materials, various unsaturated silanes were tested as coupling agents to increase the water resistance.[2]

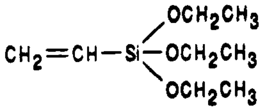
Vinylsilanes were the first silane coupling agents used in commercial glass fiber-reinforced unsaturated polyesters. It was demonstrated that vinylsilanes, $CH_2{=}CHSiX_3$ with various hydrolyzable X groups, were generally equivalent when applied to glass in the reinforced polymer composites.[3] Vinylsilanes are relatively inexpensive, as they can be produced by the one-step reaction between acetylene and the appropriate silane $HSiX_3$. The adhesive promotion with silane coupling agents was postulated to be due to the formation of chemical bonds between glass fibers and a polymer matrix through the silane bridge.[4] First, the X groups in a vinylsilane should react with silanol groups on the glass surface, as in eq 1. Then, the vinyl group in the silane should be able to copolymerize with olefinic groups to produce the polymer resin.

$$\wr\!-OH + X-\overset{|}{\underset{|}{Si}}-CH{=}CH_2 \longrightarrow \wr\!-O-\overset{|}{\underset{|}{Si}}-CH{=}CH_2 + HX \quad (1)$$

However, the actual reactions may be more complicated than the simplified picture above, and the nature and the structures of the adhesive bonds are not clear. Direct evidence of covalent linking of organofunctional silanes to silica gel has been obtained from ^{29}Si and ^{13}C solid-state CP/MAS NMR spectroscopy,[5−8] but direct detection of chemical bond formation at the interface between the immobilized vinyl groups and the resin has not been possible due to the thinness of the interface and the large interferences from the bulk polymer resin.

Thus, the purpose of the present work is to use high-resolution solid-state NMR techniques to directly investigate possible bond formation between the silane coupling agent and the polymer matrix by selective isotopic enrichment of those nuclei in the coupling agent that are thought to be directly involved in the coupling reaction to the polymer.

In order to demonstrate this, both natural-abundance and ^{13}C-enriched triethoxyvinylsilane (TEVS) (**1** and **2**)



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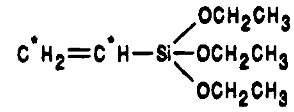

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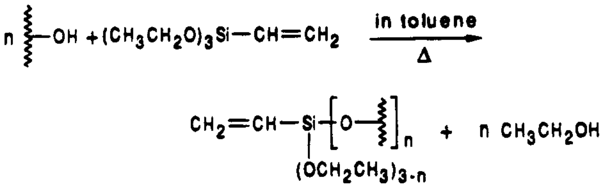
were used as coupling agents. Not only is this silane the one which is commonly used but also the ^{13}C chemical shifts for the reacted vinyl and the unreacted vinyl carbons are very different, making the detection of reacted functionalities straightforward. The unreacted vinyl carbons ($-CH{=}CH_2$) have resonances at low field, 120−140 ppm, while the corresponding reacted vinyl carbons ($>CHCH_2-$) have resonances at high field, 20−70 ppm. Silica gel was chosen as a model of the glass reinforcement substrate since it has a similar structure and surface reaction sites to glass and a much larger surface area, making higher loading of silane possible.

Experimental Section

Triethoxyvinylsilane (TEVS), 99% enriched in ^{13}C in both carbon atoms of the vinyl group, was supplied by Merck Isotopes Inc. Unlabeled TEVS was purchased from Aldrich Chemical Co., Inc., and (28−200) mesh silica gel from the Fisher Scientific Co.

Anchoring of Triethoxyvinylsilane onto Silica Gel. A total of 1.0 g of silica gel (20−200 mesh) was dried overnight at 150 °C in vacuum (1.5 mmHg) and then mixed with 20 mL of dried toluene and 0.036 mL (0.05 g) of TEVS (**1**). The mixture was heated to the toluene boiling temperature and kept refluxing for 48 h. The reaction can be represented as eq 2.



$$n\,\wr\!-OH + (CH_3CH_2O)_3Si-CH{=}CH_2 \xrightarrow[\Delta]{\text{in toluene}} CH_2{=}CH-\underset{(OCH_2CH_3)_{3-n}}{Si}\!\left[O-\wr\right]_n + n\,CH_3CH_2OH \quad (2)$$

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In order to remove any unattached TEVS, the product was then extracted by toluene for 48 h using a Soxhlet extractor. The final treated silica gel was dried at 100 °C in vacuum overnight. If desired, unreacted ethoxy groups can be hydrolyzed under acidic conditions by stirring at room temperature with aqueous HCl, then washing until the filtrate is free of Cl^- ions, and drying the gel under vacuum at 100 °C overnight.

Copolymerization of Immobilized TEVS with Styrene. TEVS-treated silica gel (0.43 g) was mixed with 1.6 mL of predistilled styrene, 4 mL of toluene, and 0.032 g of benzoyl peroxide. The mixture was refluxed at the toluene boiling temperature for 32 h under N_2 protection. It was then washed with toluene several times and extracted with toluene using a Soxhlet extractor for 48 h to remove any unbound polystyrene. It was then dried overnight in vacuum at 100 °C.

Copolymerization of Immobilized TEVS with Methyl Methacrylate. A total of 0.35 g of silica gel with TEVS anchored on it was mixed with 2.0 mL of methyl methacrylate (MMA), 5 mL of toluene, and 0.04 g of benzoyl peroxide. The mixture was kept refluxing at the toluene boiling temperature for 32 h. The resulting gel product was washed with toluene several times and then extracted with toluene for 48 h in a Soxhlet extractor to remove any unbound poly(methyl methacrylate). The final gel product was dried in vacuum at 100 °C overnight.

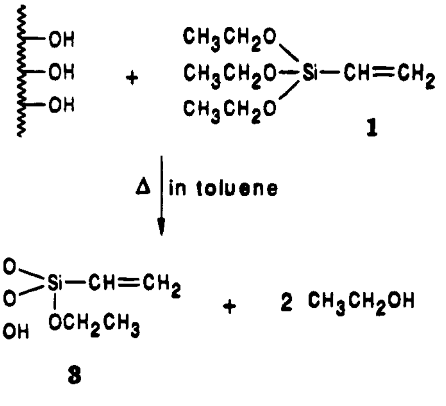
Solid-State NMR Experiments. Solid-state ^{13}C CP/MAS NMR spectra were obtained at 25 MHz using a Bruker CXP 100 spectrometer and commercial MAS probe. The magic angle was set using the ^{79}Br resonance of KBr. The 90° pulse width for ^{1}H was 3.6 μs, and the Hartman–Hahn match condition was set experimentally using adamantane. The contact time was optimized at 1.0 ms. Chemical shifts are given with respect to TMS using an external sample of solid adamantane as the secondary reference.

Results and Discussion

1. Characterization of Surface-Immobilized Vinylsilane.

Samples of natural-abundance and ^{13}C-enriched TEVS immobilized on silica gel were prepared as described in the Experimental Section. The ^{29}Si MAS NMR spectra were similar to literature data and confirmed that the bulk of the hydrolyzable ethoxy groups had been removed and that Si–O–Si bonds had been formed. Although some degree of self-condensation of the functionalized silanes may occur, it is thought that this will be very limited under the anhydrous conditions employed.

The ^{13}C solid-state NMR spectrum of the natural-abundance TEVS material is shown in Figure 1A, together with the peak assignments. The four peaks for the four different carbons in the TEVS anchored on silica gel are of approximately equal intensity, which means that two of the ethoxy groups in the TEVS have reacted with silanol groups on the silica gel surface, but, on average, one is still unreacted (eq 3).



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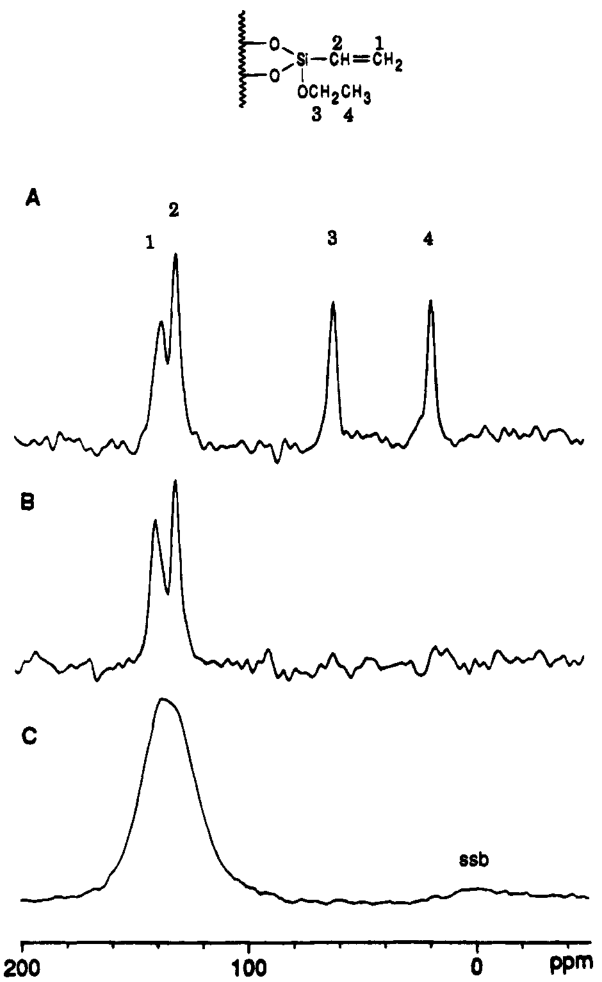


Figure 1. Solid-state ^{13}C CP/MAS NMR spectra at 25.2 MHz of (A) natural-abundance TEVS (**1**) on silica gel before hydrolysis, (B) sample A after hydrolysis with HCl, and (C) ^{13}C-enriched TEVS (**2**) on silica gel.

The remaining ethoxy group in **3** can be hydrolyzed under the acidic conditions described in the Experimental Section, as shown by the ^{13}C CP/MAS spectrum in Figure 1B, which indicates that the two peaks due to the ethoxy group have completely disappeared, whereas the vinyl resonances are still present. This means not only that the residual ethoxy groups have been completely hydrolyzed but also that the TEVS is indeed anchored on the gel and the Si–O–Si bonds formed in previous steps remain stable under these acidic conditions since the solid gel had been well washed. This is confirmed by the ^{29}Si MAS NMR spectrum.

The same procedure as above was used to anchor the ^{13}C-enriched TEVS (**2**) on the silica gel surface. Its ^{13}C solid-state NMR spectrum is shown in Figure 1C. The signal for the vinyl group in the anchored TEVS dramatically increases due to the enrichment of these two carbons. The small signals marked as "ssb" on either side of the main resonances are spinning side bands. It can be seen that the signals from the unreacted ethoxy group are essentially eliminated from the spectrum by such selective isotopic enrichment. The peak broadening and lack of resolution for the vinyl group carbons in Figure 1C are due to the ^{13}C–^{13}C scalar J and dipolar couplings in the enriched TEVS that are not present in the natural-abundance form shown in Figure 1A.

2. Copolymerization Reaction of the Immobilized TEVS with Styrene Monomer.

The sample of

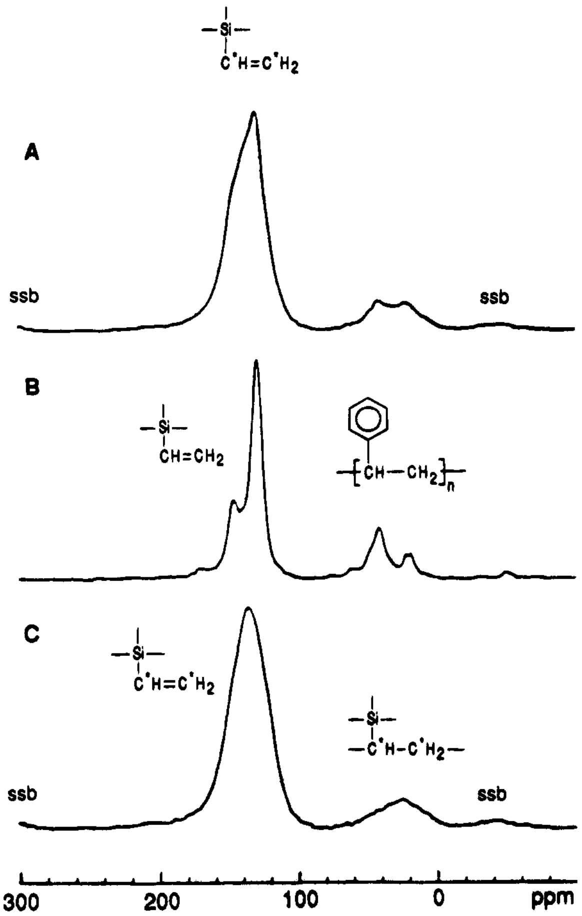


Figure 2. Solid-state ^{13}C CP/MAS NMR spectra of different samples at 25.2 MHz: (A) styrene copolymerized with ^{13}C-enriched TEVS (**2**) on silica gel; (B) styrene copolymerized with natural-abundance TEVS (**1**) on silica gel; (C) difference spectrum obtained by subtracting spectrum B from spectrum A.

^{13}C-enriched TEVS immobilized on silica gel described above was copolymerized with styrene as described in the Experimental Section. The ^{13}C CP/MAS NMR spectrum of the resulting material is shown in Figure 2A. In this spectrum, even though a major contribution will be from the enriched carbons in the unreacted and reacted TEVS on the gel, there are still some contributions from the bulk polystyrene. It cannot be determined whether the small peaks at 20–30 ppm are due to the reacted TEVS on the gel or due to the polystyrene backbone carbons. In order to quantitatively determine the percentage of the TEVS on the gel that has reacted with styrene, the influences from the bulk polymer have to be eliminated.

The exact same procedure was used to copolymerize a sample of natural-abundance TEVS immobilized on silica gel with styrene. The ^{13}C CP/MAS NMR spectrum of this final product (Figure 2B) again shows two sets of well-separated peaks. It is not possible from the spectrum to deduce whether the TEVS immobilized on the gel has reacted with styrene or not. However, if one takes spectrum A and subtracts spectrum B in Figure 2, the influences from the bulk polystyrene will be removed and the only contributions left will be from the ^{13}C-enriched TEVS on the gel. In this way, both qualitative and quantitative analyses can be made on the reaction of the enriched immobilized TEVS. Spectrum C in Figure 2 was obtained in this way. It shows that the TEVS on the silica gel indeed reacted with styrene, as a small peak due to the $-C^*HC^*H_2-$ carbons of the reacted vinyl group appears. However, the percentage of the vinyl double bonds reacting is rather low, only $\sim$12%. These spectra are considered to be quantitatively reliable, as the acquisition parameters chosen are known to give reliable spectra for amorphous organic materials; further, since both the reacted and unreacted vinyl groups contain one CH and one CH_2 function, the magnetization transfers between ^{1}H and ^{13}C in the cross-polarization experiment should be very similar in both cases.

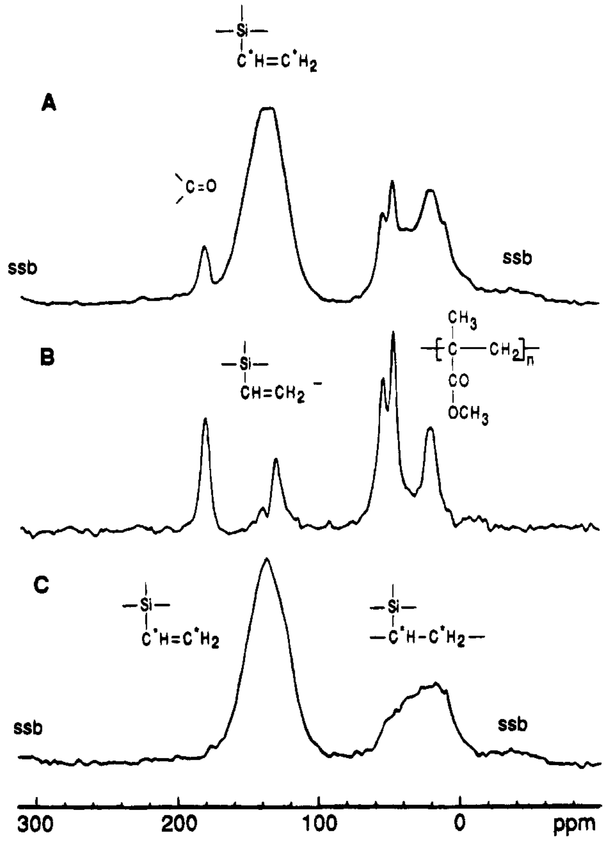
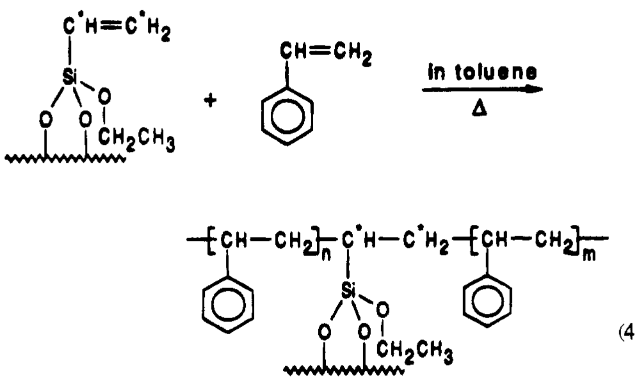


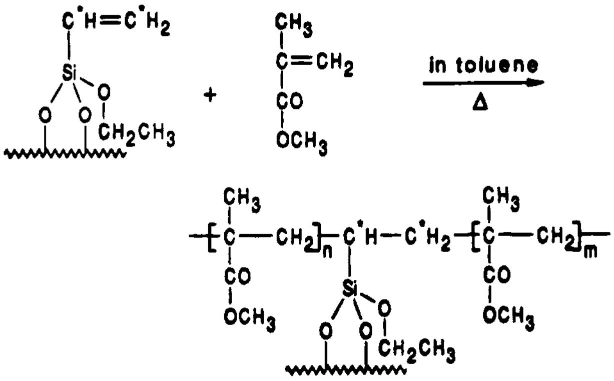
Figure 3. Solid-state ^{13}C CP/MAS NMR spectra of different samples at 25.2 MHz: (A) MMA copolymerized with ^{13}C-enriched TEVS (**2**) on silica gel; (B) MMA copolymerized with natural-abundance TEVS (**1**) on silica gel; (C) difference spectrum obtained by subtracting spectrum B from spectrum A.

The reaction can be represented as in eq 4.



(4)

3. Copolymerization of Immobilized TEVS with Methyl Methacrylate. The immobilized natural-abundance and enriched TEVS samples were copolymerized with methyl methacylate, as described in the Experimental Section. Figure 3A shows the ^{13}C CP/MAS spectrum of the ^{13}C-enriched TEVS product material and Figure 3B that of the corresponding natural-abundance sample. Figure 3C was obtained as before by subtracting spectrum B from spectrum A, giving a spectrum that only reflects the enriched TEVS immobilized on the silica gel. It shows a much larger peak at high field corresponding to the reacted TEVS than the previous styrene copolymer case (Figure 2C) and clearly demonstrates that a substantial portion of the TEVS (approximately 33%) reacted with MMA, forming direct covalent chemical bonding with the PMMA [poly(methyl methacrylate)] polymer matrix (see eq 5). From Figures 2 and 3, it can be clearly seen that copolymerization of the TEVS on the silica gel is more favorable with MMA than with styrene.



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4. Conclusions. The use of selective isotopic enrichment of the carbons of the surface-immobilized TEVS linking agent greatly enhances the contribution from the reactive functional group and reduces the contribution from the bulk polymer. By subtracting the spectrum of a similar sample when there is no isotopic enrichment, the spectrum of only the enriched functional group and its reaction products is obtained. In this way, the chemical bonding between the anchored coupling agent TEVS and polymer matrices has been observed directly by solid-state ^{13}C NMR spectroscopy.

Similar measurements could be made for other coupling agent/polymer systems and should aid in the optimization of the use of these materials.

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