

Characterization of the Interface in Polymer–Silica Composites Containing an Acrylic Silane Coupling Agent

Hyoryoon Jo and Frank D. Blum*

Department of Chemistry and Materials Research Center, University of Missouri–Rolla, Rolla, Missouri 65409-0010

Received April 30, 1999. Revised Manuscript Received July 12, 1999

Microscopic dynamics of the interfacial layer and macroscopic mechanical properties of [3-(acryloxy)propyl]trimethoxysilane (APMS) at a polymer–silica interface were studied using NMR and three-point bending tests. Wide-line deuterium NMR studies of deuterium-enriched [3-(acryloxy)propyl]trimethoxysilane-*d* (APMS-*d*), showed that when chemically bonded to silica, the acrylic group of APMS moved rapidly at the interface with air, more slowly when coated with a poly(methyl methacrylate) (PMMA) overlayer, and slowest when copolymerized with methyl methacrylate. A two-component line shape was found for the coated composite and these were assigned to relative immobile and mobile surface groups. From three-point bend tests, the PMMA/glass-fiber composite, made from glass laminates treated with APMS, had almost two times the flexural strength of a composite made from glass laminates not treated with APMS. Electron micrographs of the fracture surfaces revealed that the untreated fibers were smooth, while those from the APMS-treated glass were rougher, indicating the presence of polymer at the interface.

Introduction

The interface between a polymer matrix and an inorganic filler plays a critical role in the performance of polymer-reinforced composites.¹ To effectively transfer a load from the matrix to a reinforcing fiber, the interface between the two different materials in the composite should be highly adhesive. A silane coupling agent can enhance the adhesion between a polymer matrix and an inorganic filler. Organofunctional silanes, represented as RSiX₃, are often used as coupling agents. The methoxy or ethoxy group, represented by X, can be hydrolyzed with water and acid or a base catalyst in a protic solvent.^{2,3} The silanol groups of hydrolyzed coupling agents can be condensed with other silanol groups on a glass surface.⁴ An organofunctional group, R, such as a methacrylic or acrylic group, can be blended physically or bonded chemically to a polymer matrix to enhance the adhesion of a composite.

Acrylic or methacrylic functionalized coupling agents may be useful in various applications. Recently, a number of reports have appeared on the preparation of organic–inorganic composites by in situ polymerization of metal alkoxides in organic polymers using a methacrylic or acrylic coupling agent. Organic polymers that are end-capped with trialkoxysilane moieties facilitate cross-linking between a polymer and an inorganic oxide

network.^{5–11} These coupling agents may also be useful for applications such as UV-curable coatings.^{12–15} A methacrylic coupling agent has also been applied to a glass surface to enhance the mechanical properties of a glass-fiber reinforced composite.^{16–18}

The microscopic interfacial properties of [3-(acryloxy)propyl]trimethoxysilane (APMS) can be studied using a technique such as deuterium wide-line NMR. It is well-known that the line shape of a deuterium solid-echo spectrum is governed by molecular motions.^{20–25}

- (5) Lu, S.; Melo, M. M.; Zhao, J.; Pearce, E. M.; Kwei, T. K. *Macromolecules* **1995**, *28*, 4908.
- (6) Varma, I. K.; Tomar, A. K.; Anada, R. C. *J. Appl. Polym. Sci.* **1987**, *33*, 1377.
- (7) Ellsworth, M. W.; Novak, B. M. *Chem. Mater.* **1993**, *5*, 839.
- (8) Wei, Y.; Bakthavatchalam, R.; Whitecar, C. K. *Chem. Mater.* **1990**, *2*, 339.
- (9) Cotrain, B. K.; Landry, C. J. T.; O'Reilly, J. M.; Chamberlain, A. M.; Rakes, G. A.; Sedita, S. S.; Kelts, L. W.; Landry, M. R.; Long, V. K. *Chem. Mater.* **1993**, *5*, 1445.
- (10) Lu, S.; Melo, M. M.; Zhao, J.; Pearce, E. M.; Kwei, T. K. *Macromolecules* **1995**, *28*, 4908.
- (11) Joseph, R.; Zhang, S.; Ford, W. T. *Macromolecules* **1996**, *29*, 1305.
- (12) Chung, R. H. U.S. Patent 3,986,997, 1974.
- (13) Olson, D. R.; Webb, K. K. U.S. Patent 4,455,205, 1984.
- (14) Lewis, L. N.; Katsamberis, D. *J. Appl. Polym. Sci.* **1991**, *42*, 1551.
- (15) Sunkara, H. B.; Jethmalani, J. M.; Ford, W. T. *Chem. Mater.* **1994**, *6*, 362.
- (16) Mebarkia, S.; Vipulanandan, C. *Polym. Eng. Sci.* **1994**, *34*, 1287.
- (17) Lin, H.; Day, D. E.; Stoffer, J. O. *Polym. Eng. Sci.* **1992**, *32*, 344.
- (18) Weaver, K. D.; Stoffer, J. O.; Day, D. E. *Polym. Compos.* **1995**, *16*, 161.
- (19) Olson, J. R.; Day, D. E.; Stoffer, J. O. *J. Comput. Mater.* **1992**, *26* (8), 1181.
- (20) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193.
- (21) Fahmy, T.; Wesser, J.; Wolfgang, H.; Spiess, W. *Angew. Makromol. Chem.* **1989**, *66*, 6739.
- (22) Colletti, R. F.; Mathias, L. J. *Solid State NMR of Polymers*; Mathias, L. J., Ed.; Plenum Press: New York and London, 1991.

* To whom correspondence should be addressed at the University of Missouri–Rolla. E-mail: fblum@umr.edu. Phone: 573-341-4451.

(1) Plueddemann E. P. *Silane Coupling Agents*, 2nd ed.; Plenum Press: New York, 1991.

(2) Blum, F. D.; Meesiri, W.; Kang, H. J.; Gambogi, J. E. *J. Adhes. Sci. Technol.* **1991**, *5*, 479.

(3) Leyden, D. E.; Atwater, J. B. *J. Adhes. Sci. Technol.* **1991**, *5*, 815.

(4) Nishiyama, N.; Horie, K.; Asakura, T. *J. Colloid Interface Sci.* **1989**, *129*, 113.

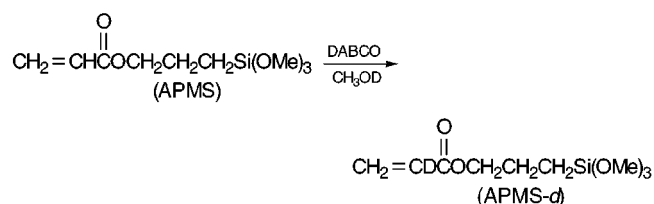
Composites were prepared, using a specifically labeled deuterium-enriched [3-(acryloxy)propyl]trimethoxysilane-*d* (APMS-*d*), to investigate the dynamics of APMS at the interface via the ^2H wide-line NMR technique. The molecular motion of APMS-*d*, immobilized on silica and copolymerized with MMA, showed differences in motion from APMS-*d* immobilized on silica and coated with poly(methyl methacrylate) (PMMA). These microscopic studies showed that the chemically bonded acrylic group of APMS moved slowly at the interface between the inorganic filler and the organic polymer matrix.

The mechanical properties of PMMA/glass fiber composites were studied to determine the effect of having APMS at the interface of a composite. One composite was prepared with MMA and glass fibers that were treated with APMS; another composite was prepared with MMA and glass fibers, without any APMS treatment. Since both composites were very brittle, the mechanical properties of these materials were evaluated using the three-point bend test.²⁶ Photographs of the fractured surfaces of the specimens, which cracked during the three-point bend test, were taken using a scanning electron microscope (SEM). These pictures showed significant differences between the APMS-treated and APMS-untreated composites.

Experimental Section

Chemicals. (3-Chloropropyl)trimethoxysilane, acrylic acid, methanol-*d* (CH_3OD), methyl methacrylate (MMA), poly(methyl methacrylate) (PMMA), and tetrahydrofuran (THF) were purchased from the Aldrich Company (Milwaukee, WI). Azobisisobutyronitrile (AIBN) and diazobicyclo[2.2]octane (DABCO) were purchased from the Eastman Kodak Company (Rochester, NY). AIBN was recrystallized from methanol. Hi-point (methyl ethyl ketone peroxide, maximum 9%) was purchased from the Witco Company (Richmond, CA). The silica, Cab-O-Sil EH-5 (specific surface area, $380 \text{ m}^2/\text{g}$), was donated by the Cabot Corporation (Tuscola, IL).

[3-(Acryloxy)propyl]trimethoxysilane (APMS) was prepared from (3-chloropropyl)trimethoxysilane and acrylic acid in triethylamine via a condensation reaction.²⁷ APMS-*d* was prepared from the reaction of CH_3OD with a catalytic amount of DABCO.²⁸ This mixture was stirred at an ambient temperature for 2 days. Dried carbon black was added to eliminate the DABCO. The reaction mixture with carbon black was then filtered, and the methanol from the filtrate was distilled under reduced pressure. The yield of APMS-*d* was about 30%. The product was deuterated in the methine position as shown below:



Cab-O-Sil-Filled PMMA Composites. APMS-*d* was adsorbed onto silica and then two different types of composites

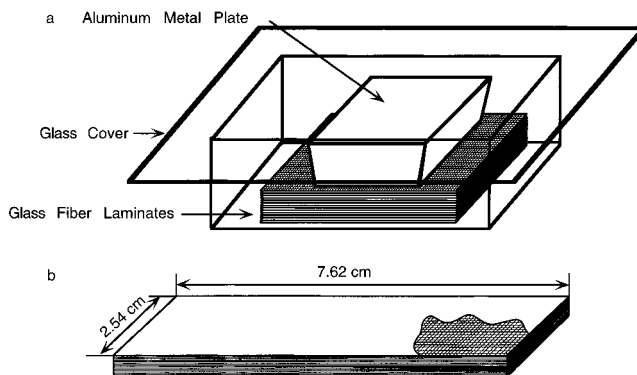


Figure 1. (a) Mold shape for PMMA/glass-fiber composite and (b) specimen shape for three-point bending test.

were prepared for the NMR dynamics study. The first one was prepared via in situ polymerization of methyl methacrylate and APMS-*d* adsorbed on the silica, and the second was prepared by coating the surface of APMS-*d* with PMMA polymer. Both were made with Cab-O-Sil EH5 as a filler. This silica was dried at 600°C for 1 day before use. A stock solution was prepared by mixing acetone, acetic acid, and water (10:2:1, respectively) and this solution was used to dissolve the coupling agent and deposit it on the silica surface. Since the dynamics study was carried out using the deuterium wide-line technique, deuterated APMS was used to make composites for the NMR study. Dried silica (1.00 g) was added to 0.54 g of APMS-*d* to make a monolayer coverage sample with 12 mL of stock solution.²⁷ Hydroquinone (0.001 g) was added as an inhibitor to prevent polymerization of the acrylic group from APMS. This mixture was left undisturbed for 3 days and then cured at 110°C for 4 days. After curing, it was washed several times with acetone to remove the hydroquinone. This sample was referred to as monolayer-APMS-*d*. MMA (0.1 g) was added to 0.2 g of monolayer-APMS-*d* with 1 mL of THF containing AIBN as an initiator. Polymerization of the acrylic group of APMS-*d* with MMA was carried out at 70°C for 2 days. This sample was referred to as PMMA-poly-APMS-*d*. PMMA (0.2 g) was dissolved in 5 mL of THF, with 0.001 g of hydroquinone as an inhibitor to protect the acrylic group of APMS-*d* from polymerization. Monolayer-APMS-*d* was added to the PMMA in a solvent, and THF was then evaporated slowly in an oven set at 70°C . This was referred to as the PMMA-coated-APMS-*d*.

Glass-Fiber-Filled PMMA Composites. Two different types of PMMA/glass-fiber composites were prepared for mechanical studies. The first composite was made from APMS immobilized on a glass surface and the other composite was prepared from plain glass laminates. The glass-fiber laminates were donated by Owens/Corning Fiberglass Inc. (Granville, OH). These were designated ECG 7268 and had 44 warps per band and 12.6 picks per centimeter. The glass laminates were heat treated at 600°C , for 2 days, to remove the sizing agents, which protected the fiber (during fabrication) from the surface. The weight of the glass-fiber laminate was 0.02 g per square centimeter. MMA was freshly distilled, and 0.3 mL of Hi-point was added to 500 g of MMA. Sixteen layers of glass-fiber laminate were impregnated with MMA. Figure 1a shows a schematic of the molding setup. Composites should be uniform when examined using the three-point bend test. To eliminate inhomogeneity caused by the waving of the glass-fiber laminates, a heavy aluminum metal plate was placed on top of the glass-fiber laminates in MMA. To reduce the number of air bubbles, the glass-fiber laminates (immersed in MMA) were degassed in a vacuum chamber for 1 h with Hi-point (methyl ethyl ketone peroxide) used as a radical initiator. The mold was then placed in a water bath at 70°C , and the polymerization was run for 60 h. This sample is referred to as the untreated composite. To make the treated composite (with APMS immobilized on a glass surface), the procedure was basically the same as for the untreated composite except that the glass fibers were treated as follows. Glass-fiber laminates

(23) Blum, F. D. *Annual Reports of NMR Spectroscopy*; Ando, I., Webb, G. A., Eds; Academic Press: London, 1994; Vol. 28.

(24) Bovey, F. A.; Jelinski, L. W. *J. Phys. Chem.* **1985**, *89*, 571.

(25) Kelusky, E. C.; Fyfe, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 1746.

(26) This test procedure was standardized with American Society for Testing and Materials D 790-90.

(27) Jo, H.; Blum, F. D. *Langmuir* **1999**, *15*, 2444.

(28) Mathias, L. J.; Colletti, R. F. *Macromolecules* **1991**, *24*, 5515.

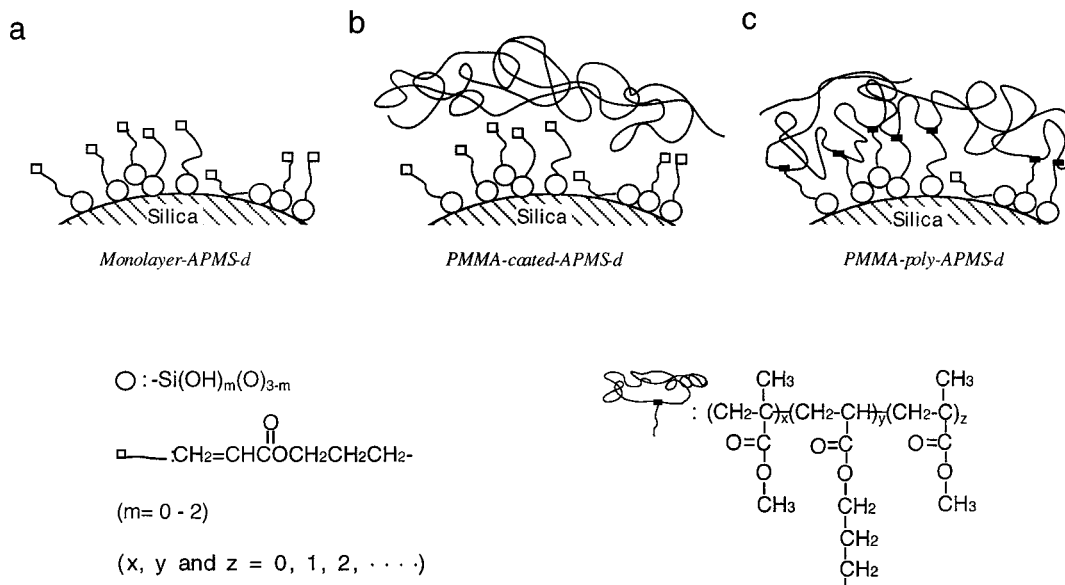


Figure 2. Schematic representation of samples used for NMR: (a) monolayer-APMS-*d*, (b) PMMA-coated-APMS-*d*, (c) PMMA-poly-APMS-*d*.

(437.70 g) were submerged in a 1.2-L stock solvent (with 95.52 g of APMS) for 3 days. The solvent (containing the glass-fiber laminates and APMS) was filtered, and the filtrate was then condensed and pyrolyzed to calculate how much APMS was adsorbed on the surface of the glass-fiber laminates using the method developed in our previous studies.²⁷ The difference between the weight of APMS in the initial solvent and the weight of APMS in the filtrate was 2.41 g. Therefore, the concentration of APMS immobilized on the glass surface was 0.55 g of APMS per 100 g of glass-fiber laminates. Glass-fiber laminates treated with APMS were dried in an oven at 60 °C for 1 day. Figure 2 is a schematic of the nature of the composite interfaces.

²H NMR, Simulation, and SEM. The deuterium wide-line experiments were performed at 61.4 MHz with a Varian-VXR 400/S NMR spectrometer at 25 °C. The quadrupole echo-pulse sequence [delay-90°_x-*t*₁-90°_y-*t*₂-echo], called "ssecho", was used with a 2.7 μs for 90° pulse to obtain the solid-state deuterium NMR spectra. A 2 kHz line broadening was applied. Data were acquired with a sweep width of 2 MHz and 4096 points. The time domain spectra were phased and then left-shifted to the top of the echo. Typically, 30 000–40 000 scans were taken at 61.4 MHz to get an adequate signal-to-noise ratio.

Deuterium wide-line shape simulations were done with a Fortran program based on the theory developed by Freed for motional electron spin resonance line shapes.^{30,31} This program was modified for deuterium wide-line simulations. The simulated spectra were compared to the experimental ones to obtain quantitative information about the molecular motion of the APMS. The simulations were based on isotropic rotational diffusion with rates of *d*_{xy} and *d*_{zz}, or a two-site jump with a rate of *k* and the angle of 54.7°. The quadrupole coupling constant used in the simulation was 165 kHz. The amounts of each component were varied to fit experimental spectra.

SEM micrographs were taken with a JEOL model JSM-35CF. Prior to taking the SEM pictures, the specimens' surfaces were coated with gold (in a sputtering chamber) to enhance conductivity.

Mechanical Properties. An untreated composite and a treated composite were prepared. The composites were cut

with a band saw; Figure 1b shows their shapes. Each composite generated five specimens. The size of each specimen was 0.32 × 2.54 × 7.62 cm. The edges and surfaces of the specimens were polished with 200 grit aluminum oxide sandpaper. The procedure used for the three-point bend tests was that specified by the American Society for Testing and Materials (ASTM).²⁶ The flexural strength, *S*, was calculated from

$$S = 3PL/(2bd^2) \quad (1)$$

where *P* is the load at break point, *L* is the span between the two supports, *b* is the width of the specimen, and *d* is the height of the specimen. The flexural modulus, *E*, can be expressed by

$$E = mL^3/(4bd^3) \quad (2)$$

where *m* is the initial slope of the load-displacement curve. The flexural strengths and flexural moduli of the treated composites and untreated composites were measured. For the three-point bend tests, an Instron model 4204 testing machine was used. The rate of cross-head motion was 0.127 cm per minute; the support span length was 5.08 cm. For each reported data point, an average of five specimens from each composite was used.

Results

Composites with APMS-*d* were used to study the dynamics at the interface. In our previous work,²⁷ we determined that monolayer coverage for APMS on a Cab-O-Sil surface corresponded to ~0.6 mmol of APMS per 100 m². The exact amount of APMS-*d* from the stock solution that was needed to form monolayer coverage was added to silica (CAB-O-Sil EH-5). The APMS-*d* was hydrolyzed and adsorbed on the silica surface through heat treatment. This sample is referred to as monolayer-APMS-*d*. A composite, prepared via in situ polymerization by adding MMA monomer to the monolayer-APMS-*d*, is referred to as PMMA-poly-APMS-*d*. To prepare PMMA-coated APMS-*d*, PMMA was adsorbed on top of the monolayer-APMS-*d* sample.

The deuterium wide-line NMR spectra and their simulations for monolayer-APMS-*d*, PMMA-coated-APMS-*d* and PMMA-poly-APMS-*d* are shown in Figure

(29) Lin, W.; Blum, F. D. *Macromolecules* **1998**, *31* (13), 4135.

(30) Freed, J. H. In *Spin Labeling: Theory and Applications*; Berliner, L., Ed.; Academic Press: New York, 1976; Vol. 1.

(31) Schneider, D. J.; Freed, J. H. In *Spin Labeling: Theory and Applications*; Berliner, L., Reuben, J., Eds.; Academic Press: New York, 1989; Vol. 8.

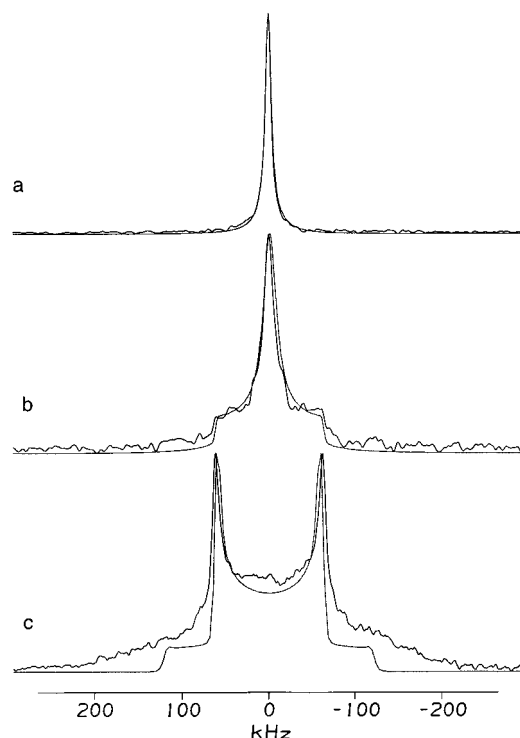


Figure 3. Deuterium wide-line spectra at room temperature of (a) monolayer-APMS-*d*, (b) PMMA-coated-APMS-*d*, and (c) PMMA-poly-APMS-*d* samples. The experimental spectra are shown along with the simulated ones (smooth curves).

3. The spectrum of the monolayer-APMS-*d* was relatively narrow with a full-width at half-height (fwhh) of 7.2 kHz. The fwhh of PMMA-coated APMS-*d* was 17 kHz with the spectra showing at least two different major components, one narrow and the other broad. The broad portion resembles a powder pattern spectrum. Due to the fairly low concentration of deuterium in the composite and the very broad nature of these resonances, a relatively noisy spectrum of PMMA-poly-APMS-*d* was observed. The line shape of PMMA-poly-APMS-*d* was similar to a Pake powder pattern with a splitting between the “horns” of about 125 kHz.

When Pake powder patterns begin to collapse, the regions between the two prominent features or “horns” become less intense as t_2 increases (τ -effect). This τ -effect is often the result of the anisotropic spin–spin relaxation in the solid sample.²⁰ This effect could be eliminated by taking many spectra and extrapolating t_2 to 0, as shown by Lin and Blum for poly(methyl acrylate) on silica.²⁹ However, since the concentration of deuterium in the PMMA-poly-APMS-*d* sample was too low to get a high signal-to-noise ratio spectrum, the τ -effect for PMMA-poly-APMS-*d* was not directly probed.

The motional rates of deuterium in composites were estimated through simulations based on the Freed model.^{30,31} Simulated spectra, optimized to match the experimental ones, are also shown in Figure 3. The simulated spectrum of PMMA-poly-APMS-*d* was generated using an isotropic-rotational-diffusion model. However, motional models based on a single component of rotational diffusion or on a single component of two-site jump motions did not produce spectra that simulated the experimental ones for monolayer-APMS-*d* and PMMA-coated-APMS-*d*. To simulate the spectrum of monolayer-APMS-*d*, two separate spectra (i.e., two

Table 1. Parameters for Simulated ^2H NMR Spectra for the APMS-*d* Samples Studied

	component 1		component 2	
	%	$d_{xy} = d_{zz}^a$ (kHz)	k^b (MHz)	$d_{xy} = d_{zz}^a$ (kHz)
monolayer-APMS- <i>d</i>	33	170	—	67
PMMA-coated APMS- <i>d</i>	56	—	1.3	44
PMMA-poly-APMS- <i>d</i>	100	2.4 or less	—	—

^a Isotropic rotational rate. ^b Two-site jump rate.

Table 2. Mechanical Properties of PMMA/Glass Fiber Composites

	treated composite	untreated composite
flexural strength (MPa)	291 (\pm 28)	158 (\pm 11)
flexural modulus (GPa)	18.7 (\pm 1.2)	19.0 (\pm 2.4)

Lorentzian components) were generated from the program with different rates. These spectra were then combined. To match the spectrum of PMMA-coated APMS-*d*, the two simulated components were generated from a two-site jump motion and an isotropic diffusion motion resonance. The two-site jump motion was used because that line shape had sharp edges²⁰ and its spectral width was close to the full width below the quarter height of the spectrum of PMMA-coated APMS-*d*. The two-site jump rate of PMMA-coated APMS-*d* was faster than the isotropic diffusion rates of any component. While the motional model for rotational diffusion was isotropic, the motional model for the two-site jump allows only restricted motion. Thus, the motional rate of the two-site jump could be faster than the motional rate of rotational diffusion. Fitting parameters are given in Table 1. The rotational diffusion rates of monolayer-APMS-*d* were much faster than those of the PMMA-coated APMS-*d*. Obviously, an overcoating slows the motion of the surface species. The polymerized sample had the slowest dynamics.

To measure the physical properties of the glass fiber-reinforced PMMA composites, two different types of in situ polymerized composites were prepared: untreated and treated composites. The flexural strengths and moduli of these composites are shown in Table 2. The flexural strength of the treated composite was almost twice that of the untreated composite. The flexural moduli of the composites were similar.

Fracture sites of the composites were visualized with SEM after bending tests (Figure 4). The composites were broken along the crack propagation line made in the three-point bending test. The surfaces of the glass fibers from the untreated composite were very clean while, in contrast, the glass surfaces of the treated composite had very rough surfaces due to the PMMA residue.

Discussion

A number of reviews of the use of deuterium NMR in polymer science have included significant discussions on spectrum line shapes and motions.^{32–34} Basically, narrower resonances were consistent with faster motions for Lorentzian components, while Pake powder patterns were an indication of slower molecular motion.

(32) Spiess, H. W. *Annu. Rev. Mater. Sci.* **1983**, *13*, 193.

(33) Jelinski, L. W. *Annu. Rev. Mater. Sci.* **1985**, *15*, 359.

(34) Spiess, H. W. *Annu. Rev. Mater. Sci.* **1991**, *21*, 131.

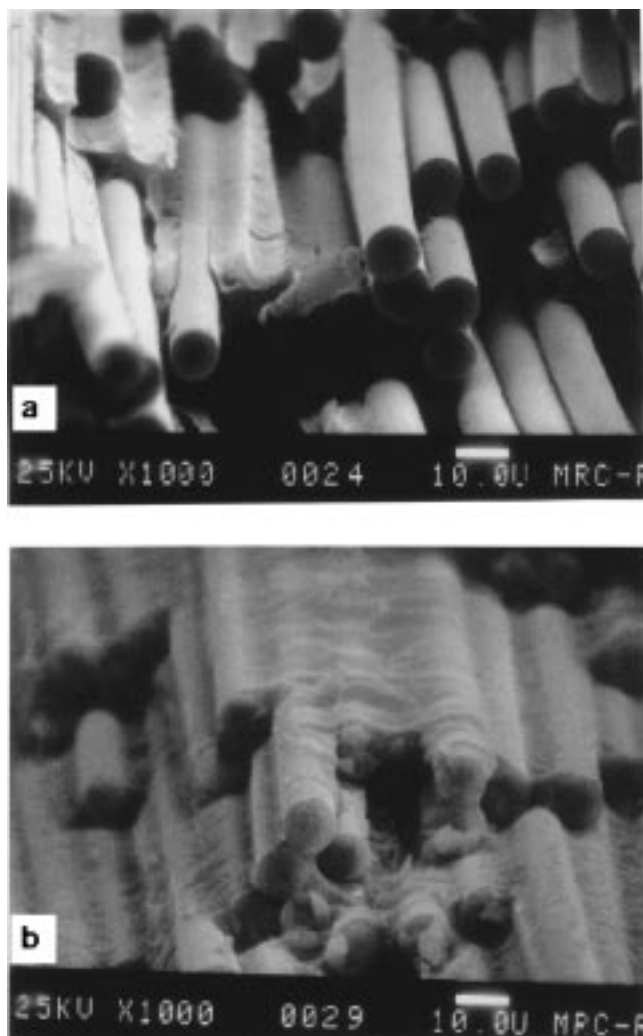


Figure 4. SEM pictures of the fracture surface of the (a) untreated composite and (b) treated composite.

The dynamics of a few coupling agents, such as (3-aminopropyl)trimethoxysilane (APS), (4-aminobutyl)triethoxysilane (ABS), etc. have been studied on silica or at the interface using deuterium wide-line NMR.^{2,35–39} Some of these studies also show how detailed information can be obtained about the mechanism and rates of motion.

The line shape for monolayer-APMS-*d* showed that the motion of the deuterium label on surface-bound APMS at the air interface was relatively fast. However, the motion was also heterogeneous and likely due to a distribution of different APMS-*d* molecules with different mobilities, even though the lines shapes could be modeled with just two. After coating a surface APMS-*d* with PMMA (PMMA-coated APMS-*d*), the alkyl group motion slowed considerably. Obviously, the PMMA overcoat restricted and slowed the mobility of the coupling agent. This is evident, not only from the spectrum itself but also from the simulations which required a change in mechanisms (to restricted jumps) for suitable fitting. It is not known if the faster

component in PMMA-coated APMS-*d* was due to little polymer interaction with the bound coupling agent in areas but the reorientation time and mechanism were similar to those of the monolayer-APMS-*d*. In contrast to PMMA-coated APMS-*d*, the line shape of PMMA-poly-APMS-*d* represented an extremely slow moving species (approximately a rigid powder spectrum). In addition, the homogeneous nature of the line shape suggested that virtually all of the surface-bound APMS-*d* species were affected by the polymerization process.

Evidence for covalent bond formation in a PMMA/silica composite at the interface between the vinyl (or acrylic) silane coupling agent and PMMA matrix has already been obtained by Niu and Fyfe.⁴¹ They studied copolymers via in situ polymerization using coupling agents such as [3-(methacryloxy)propyl]trimethoxysilane (MPS) immobilized on a silica surface. Their material had a structure similar to APMS, and they showed the formation of a covalent bond between the MMA monomer and MPS using ¹³C cross polarization and the magic-angle spinning NMR technique.⁴¹ PMMA-poly-APMS-*d* was polymerized by in situ polymerization using monolayer-APMS-*d* with AIBN and MMA to form a covalent bond. The powder pattern spectrum in Figure 3c demonstrates the reduction in motion that accompanied the polymerization.

Gambogi and Blum³⁵ studied the dynamics of aminoalkylsilane coupling agents, such as APS and ABS, on a silica surface and at the interface between silica and polymerized bis(maleimide), using the deuterium wide-line NMR technique. In the over-polymerized surface treated with bis(maleimide), the fwhh of the ABS spectrum became wider (113 kHz) than before the polymer overpolymerization was done (75 kHz). This overpolymerization resulted in the reduction of motion of the surface-bound coupling agent. This is qualitatively similar to what was found here. In our current study, the fwhh of APMS-*d* in monolayer-APMS-*d* was much narrower than those of ABS on silica or in a composite. In contrast, the slower component in PMMA-coated APMS-*d* and the only component in PMMA-poly-APMS-*d* were slower than those of APS in the composite. Different organic functional groups in organosilanes may generate varied motional rates. At the air interface, surface-bound APMS-*d*, with the label on the pendant group, was very mobile. Upon polymerization, the label became part of the polymer backbone and mobility was significantly reduced. In contrast from previous studies, the label in ABS was part of an alkyl chain able to undergo segmental motions, even in the presence of the bismaleimide polymer.

Mechanical properties were measured to determine how physical properties are influenced by the presence of a coupling agent at the interface between a polymer matrix and a glass surface. By using fracture toughness and three-point bending tests, Wang and Blum evaluated the effect of coupling agents containing amine groups, such as ABS and APS, on epoxy/glass composites.^{43,44} The flexural strength of the APS-treated com-

(35) Gambogi, J. E.; Blum, F. D. *Macromolecules* **1992**, *25*, 4526.

(36) Kang, H. Y.; Blum, F. D. *J. Phys. Chem.* **1991**, *95*, 9391.

(37) Ziegler, R. C.; Maciel, B. E. *J. Am. Chem. Soc.* **1991**, *113*, 1513.

(38) Boddenberg, B.; Grosse, R.; Breuninger, U. *Surf. Sci.* **1986**, *173*, 655.

(39) Kelusky, E. C.; Fyfe, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 1746.

(40) Lin, W.; Blum, F. D. *Macromolecules* **1997**, *30*, 5331.

(41) Fyfe, C. A.; Niu, J. *Macromolecules* **1995**, *28*, 3894.

(42) Wang, T. W. H.; Blum, F. D. *J. Mater. Sci.* **1996**, *31*, 5231.

(43) Wang, T. W. H. Ph.D. Thesis, University of Missouri at Rolla, 1995.

posite was higher than that of the ABS-treated composite.⁴⁴ On the basis of these studies, it is concluded that the dynamics of the interface plays a significant role in the determination of the physical properties of composites. Only a few studies of the mechanical properties of composites treated with MPS have been made;¹⁷⁻¹⁹ these found that MPS in a PMMA/glass composite enhanced the mechanical properties of composites. While the flexural strengths of composites containing silane coupling agents were increased over untreated composites, their flexural moduli were not changed with silane coupling agent treatment.^{44,45} When the mechanical properties of APMS were measured to evaluate the effect of APMS at the interface of a PMMA/glass composite, flexural strengths (Table 2) were almost two times higher for treated composites than for untreated composites, and the flexural moduli of treated and untreated composites were not changed. Thus, the coupling agent, APMS, enhanced adhesion between the glass fiber and PMMA in treated composites due to the chemical bond that formed at the interface.

Scanning electron microscope (SEM) pictures showed the direct effects of treatment with a coupling agent at the surface of glass fiber^{43,46} and at the interface of composites after a fracture test.^{17,45-48} Lin et al.¹⁷ showed that the fracture site of a PMMA/glass composite, treated with MPS, was clean at break temperatures below 75 °C, but became rough when temperatures were above 75 °C.¹⁷ However, the surface of a treated composite containing APMS was rough at ambient temperatures. PMMA residue was found on glass surfaces when APMS was the coupling agent at the interface, causing the polymer to stick to the glass fiber.

(44) Park, J. M.; Subramanian, R. V. *Silane and Other Coupling Agents*; Mittal, K. L., Ed.; VSP Press: Utrecht, The Netherlands, 1992.

(45) Bajaj, P.; Jha, N. K.; Kuman, R. A. *J. Appl. Polym. Sci.* **1992**, *44*, 1921.

(46) Matisons, J. G.; Jokinen, A. E.; Rosenholm, J. B. *J. Colloid Interface Sci.* **1997**, *194*, 263.

(47) Shih, G. C.; Ebert, L. J. *Composites* **1986**, *17*, 309.

(48) Gassan, J.; Bledzki, A. K. *Composites A* **1997**, *28*, 1001.

In contrast to the treated composites, the glass surfaces of the untreated composites were clean. Our SEM results are in agreement with the results of flexural strength tests. These macrophysical properties and SEM pictures showed that a composite containing a coupling agent, which formed a covalent bond at the interface, had improved performance and better interface adhesion.

Conclusions

Deuterium wide-line NMR spectra were used to study microscopic physical properties at the interface. These studies showed differences in the dynamics of monolayer APMS-*d* in composites that had been prepared via different methods. The deuterium NMR of a PMMA-coated APMS-*d* sample had slow and fast components. In contrast to PMMA-coated APMS-*d* (after in situ polymerization of the acrylic group of APMS), the motion of PMMA-poly-APMS-*d* consisted mostly of a slow-motion component due to the formation of a covalent bond at the interface. Examination of the physical properties showed that the presence of a coupling agent at the interface enhanced adhesion. The flexural strength of the treated composite was almost twice that of the untreated composite because of the APMS at the interface between the PMMA matrix and the inorganic filler. The SEM pictures showed that the glass surface of the treated composite was significantly different from that of the untreated composite. The treated composite's surface was rough because adhesion was enhanced. Microscopic results were consistent with results based on studies of physical properties.

Acknowledgment. The authors acknowledge the financial assistance of the National Science Foundation under the grant, DMR 9807696.

CM9902570