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DYNAMICS OF ACRYLIC COUPLING AGENTS AT INTERFACES OF COMPOSITES

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Introduction

Most applications of polymers involve composites, wherein a polymer is used in conjunction with another material, typically a solid fiber or filler.<sup>1</sup> A coupling agent can enhance the adhesion between a polymer matrix and an inorganic filler. Organofunctional silanes, RSiX<sub>3</sub>, are often used as coupling agents. The methoxy or ethoxy group, X, can typically be hydrolyzed with water and an acid or a base catalyst in a protic solvent. The silanol groups of a hydrolyzed coupling agent can condense with other silanol groups from a glass surface, while the alkyl group, R, blends physically or bonds chemically to the polymer matrix, thereby enhancing adhesion.<sup>1</sup>

In addition to their use as coupling agents in mineral-filled organic composites, organofunctional silanes that contain acrylic or methacrylic groups have been applied to the surfaces of organic-inorganic hybrid materials (OIC).<sup>2,3</sup> Acrylic silanes may also be useful for ultraviolet (UV) coatings because their structures contain acrylic functional groups.<sup>4</sup>

Magnetic resonance (ESR and NMR) studies have been especially useful in determining both the structures and the dynamics of interfacial and surface specimens. Since solid state NMR studies are not adversely affected by the presence of solid fillers or the optical clarity of a sample, they are well suited for studies of filled systems. Both NMR and ESR have been used to investigate the dynamics of samples at interfaces and on the surface. The line shapes of deuterium solid-echo spectra are governed by molecular dynamics.<sup>5,6</sup> Blum et al. have studied the mobility of coupling agents such as aminopropyltrimethoxysilane and aminobutyltrimethoxysilane at the air-solid interface using the deuterium line-shape method.<sup>7</sup>

In this study, the interfacial properties of deuterated 3-acryloxypropyltrimethoxysilane (APMS-*d*) were investigated using the deuterium wide-line NMR line-shape method. The motion of the deuteron placed on an acrylic polymer backbone was investigated. A sample having monolayer coverage of APMS-*d* on a silica surface was polymerized with methyl acrylate (MA), and an organic-inorganic hybrid material was prepared with MA, APMS-*d*, and tetramethoxysilane. Spectra of these polymerized samples showed relatively slower motion on the polymer backbone.

Experimental

**Chemicals.** 3-chloropropyltrimethoxysilane, acrylic acid, methanol-*d* (CH<sub>3</sub>OD), methyl acrylate (MA), tetramethoxysilane (TMOS), and tetrahydrofuran (THF) were purchased from the Aldrich Company (Milwaukee, WI). Azobisisobutyronitrile (AIBN) and triethylene diamine (DABCO) were purchased from the Eastman Kodak Company (Rochester, NY). AIBN was recrystallized from methanol. The silica, Cab-O-Sil EH-5 (specific surface area: 380 m<sup>2</sup>/g), was donated by the Cabot Corporation (Tuscola, IL). 3-acryloxypropyltrimethoxysilane (APMS) was prepared from 3-chloropropyltrimethoxysilane and acrylic acid in triethylamine via a condensation reaction. APMS-*d* was prepared from APMS and methanol-*d*.

**Materials.** Fumed silica, Cab-O-Sil grade EH-5, (surface area of 180 m<sup>2</sup>) was dried in an oven for 1 day at 600 °C, prior to use. A stock solution was prepared by mixing acetone, acetic acid and water (10:2:1, respectively) and hydroquinone (a catalytic amount). APMS-*d* was added to the fumed silica from a stock solution. We estimated that monolayer coverage was 0.6 mmole of APMS per 100 m<sup>2</sup> of fumed silica.<sup>8</sup> The sample, which was covered by a monolayer of APMS-*d*, 0.31 g (1.3 mmole) of APMS-*d*, was added to a tube containing 0.5 g of silica. A 12-ml aliquot of the stock solution was then added using a syringe. This sample tube was agitated in a sonicator for several hours, left at rest at room temperature for 3 days and then dried at 110 °C for 3 days. It is referred to as the monolayer sample. To prepare the polymer composite with an inorganic filler, 3 g of MA were added to 1 g of the monolayer sample with a small amount of AIBN as a free radical initiator. Polymerization was carried out at 70 °C for 2 days. This sample is referred to as PMA-APMS-silica. APMS-*d* was also polymerized with MA in dry THF.

1 g of APMS-*d* was copolymerized with 1.1 g of MA at 70 °C, for 1 day, by adding 0.001 g of AIBN, to 20 ml of THF. Half of the product, from which the THF was evaporated, was collected; this polymer is referred to as PMA-APMS(OMe)<sub>3</sub>. 3 ml of an acetic acid and water mixture (2:1 volume ratio, respectively) were added to the other half of the product, which still contained THF, to hydrolyze the methoxy group from APMS. 1 ml of TMOS was then added to be copolymerized with the silane of APMS. This sample is called PMA-APMS-TMOS.

**Measurement.** Deuterium wide-line NMR spectra were taken on a modified Varian VXR-400/S spectrometer operating at 61.395 MHz. The quadrupole-echo pulse sequence [delay-90°x-t<sub>1</sub>-90°y-t<sub>2</sub>-echo], called "ssecho", was used with a 2.7 μs 90 ° pulse to overcome receiver dead time. A 30 μs echo delay time (t<sub>1</sub>); 4,096 or 2,048 points, 1.024 ms acquisition time, 2 MHz sweep width, 2.5 s recycle time and 3000 to 20000 scans (depending on the deuterium amount) were used with appropriate phase cycling. The quadrupole-echo spectra were taken with delays, t<sub>2</sub>, and adjusted, so that the exact point of echo maximum could be reached, and the echo was then Fourier transformed.

Results

To investigate the molecular motion of deuterated 3-acryloxypropyltrimethoxysilane (APMS-*d*) at the interface between a silica surface (or silica network) and an organic polymer filler using deuterium NMR, PMA-APMS-silica and PMA-APMS-TMOS were prepared. The quadrupole-echo NMR spectra for PMA-APMS-silica were taken as a function of temperature and are shown in Figure 1. At lower temperatures, a powder pattern was evident. The splitting in this powder pattern was 125 KHz between the tallest vertical features, i.e. the "horns". The powder pattern showed a gradual broadening of the horns and an increase in intensity in a central component. At 100 °C, a powder pattern was still evident.

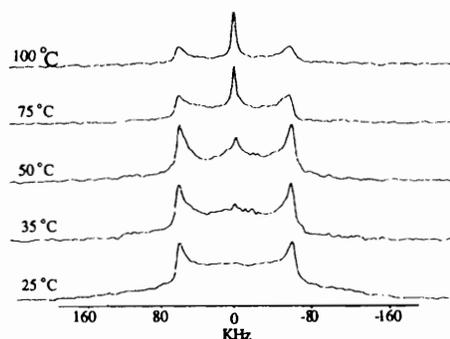


Figure 1. Deuterium spectra of PMA-APMS-Silica from 25 to 100 °C

The quadrupole-echo spectra of PMA-APMS, prepared from the polymerization of methyl acrylate (MA) and APMS-*d*, are shown in Figure 2. The powder pattern started to collapse at as low as 18 °C and a central resonance was evident. This narrow component grew at 45 °C and almost all of the Pake pattern was gone. The temperature at which the Pake powder pattern grew into a narrow central component was noticeably lower and the temperature range over which this occurred was smaller than those for the other samples (PMA-APMS-TMOS and PMA-APMS-silica).

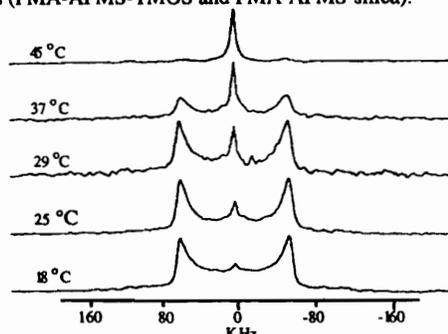


Figure 2. Deuterium spectra of PMA-APMS from 18 to 45 °C

The spectra of the PMA-APMS-TMOS, prepared from PMA-APMS and added to TMOS as a function of temperature, are shown in Figure 3. The narrow component started to emerge at around 50 °C, and almost all of the powder pattern's intensity was gone at 100 °C.

The samples, which were prepared via polymerization of the APMS with the MA acrylic group (or APMS immobilized on silica), have common features in the collapse of their powder patterns. These samples (PMA-APMS-Silica, PMA-APMS and PMA APMS-TMOS) have deuterium on the backbone of the organic polymer. When their powder patterns started to collapse, the regions between their two horns became less intense as  $t_2$  increased ( $\tau$ -effect).<sup>5</sup> The  $\tau$ -effect is the result of anisotropic spin-spin relaxation in the solid sample. Lin and Blum removed  $\tau$ -effect of deuterium in poly(methyl acrylate) by extrapolating spectra to  $\tau = 0$ .<sup>9</sup> Spectra of PMA-APMS showed that the  $\tau$ -effect was significant and distortions of spectra of PMA-APMS-silica and PMA-APMS-TMOS were also similar to those of PMA-APMS, as shown in Figures 1 and 3. However, a lengthy acquisition time was required to eliminate the  $\tau$ -effect for these spectra because concentrations of deuterium in these samples were low. Extrapolated spectra for other cases were not practical. As the temperature increased, mobile components appeared as narrow central peaks, while static components appeared as distorted powder patterns. The ranges of the collapsing of the powder patterns of these samples were different. The initial temperature at which the powder pattern of PMA-APMS collapsed was lower, and the temperature range over which the powder pattern of PMA-APMS collapsed was shorter than that of the other polymerized sample.

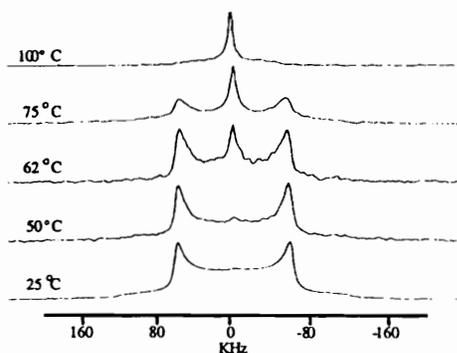


Figure 3. Deuterium spectra of PMA-APMS-TMOS from 25 to 100 °C

## Discussion

The line shapes of samples with an organic polymer shared a common feature. After polymerization of the acrylic group of APMS-*d* and MA, the deuterium was placed on the polymer backbone (in the case of PMA-APMS-silica) and the line shapes of these samples formed a powder pattern at room temperature. The splitting of the aliphatic deuterium in the static pattern was approximately 125 kHz due to a quadruple coupling constant of about 165 KHz. Therefore, motions of the organic polymer backbone were slow on the NMR time scale due to polymerization.

The motion was changed after in-situ polymerization and formation of a covalent bond with deuterium in the backbone. Niu and Fyfe<sup>10</sup> showed that covalent bond formation occurred between the vinyl group from triethoxyvinylsilane (TEVS), immobilized on the silica surface, and the monomer, methyl methacrylate (MMA), using <sup>13</sup>C cross-polarization and magic angle spinning NMR. Gambogi and Blum<sup>11</sup> studied the dynamics of 4-aminobutyltriethoxysilane (ABS) on a silica surface and at the interface between the silica and polymerized bismaleimide using deuterium wide-line NMR. In the treated over-polymerized surface with bismaleimide, the motion of ABS became slower than before polymerization. The APMS in PMA-APMS-silica showed similar results with over-polymerization of bismaleimide on the ABS. The motion of deuterium in the monolayer was changed by over-polymerization of the acrylic group of APMS with MA. The singlet line shape of the monolayer was converted to the powder pattern from PMA-APMS-silica at 25 °C. The motion of the deuterium became slower after co-polymerization.

In the polyacrylate family, the initial temperatures for the collapse of a Pake powder pattern were low. Colletti and Mathias<sup>12</sup> showed that these temperatures for poly(butyl acrylate), poly(ethyl acrylate) and poly(methyl

acrylate) (PMA) are -13 °C, -8 °C and 32 °C, respectively. Lin and Blum<sup>13</sup> showed that the collapse temperatures of PMA, which had low molecular ( $M_w$ :  $7 \times 10^4$  g/mole) and high molecular weight ( $M_w$ :  $1.1 \times 10^6$  g/mole), were about 37 to 44, respectively. Since the larger ester group apparently creates more free volume, the initial temperatures for the Pake powder pattern collapse for polyacrylates are lower for the polymers with the larger ester groups. However, even though PMA-APMS has a large ester group, the initial temperature when the Pake powder pattern collapsed, starting at 20 °C and the temperature range of the collapsing of the PMA-APMS Pake powder pattern was from 20 to 35 °C. This may have been caused by the use of MMA (with a higher  $T_g$  than the other polyacrylates). After adding the TMOS to an acidic aqueous solution, the silanol group of hydrolyzed PMA-APMS condensed with the silanols from hydrolyzed TMOS or other hydrolyzed PMA-APMS. The motion shifted to slower motions after an inorganic polymer formed a network in the composite.

The spectra of samples having an organic polymer and an inorganic network had slower motions than PMA-APMS. Because of the presence of the rigid inorganic polymer in the composite, the deuterium in the polymer backbone moved slower than in the sample without an inorganic matrix. Also, the inorganic matrix samples had a greater temperature range for collapse of the Pake powder pattern than the samples without an inorganic matrix. There was not a great difference between PMA-APMS-TMOS and PMA-APMS-silica in terms of the powder pattern collapse and the temperature range for the collapse.

## Conclusion

Using deuterium wide-line NMR, the motion of APMS-*d* at the interface of a composite was investigated. When the acrylic group of APMS was polymerized with methyl acrylate (MA), with or without an inorganic polymer, the motion of the segments having deuterons on the polymer backbone resulted in a powder pattern at around room temperature. The powder pattern of PMA-APMS became distorted at temperatures as low as 18 °C. However, after adding TMOS to PMA-APMS with an acidic aqueous solvent, the initial temperature of collapse for the powder pattern of PMA-APMS-TMOS shifted to a higher temperature and the temperature range broadened. A similar phenomenon occurred when a composite, prepared from polymerization of MA and APMS, was immobilized on silica (PMA-APMS-silica). The presence of a rigid inorganic polymer slowed the motion of the organic polymers and broadened the temperature range at which the Pake powder pattern collapsed.

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## References

- (1) Plueddemann E. P. *Silane Coupling Agent*; Plenum Press: 2nd Ed, New York, 1991
- (2) 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
- (3) Wei, Y.; Bakthavatchalam, R.; Whitecar, C. K. *Chem. Mater.* **1990**, *2*, 339
- (4) Chung, R. H. U.S. Pat. 1974, 3,986,997
- (5) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193
- (6) Fahmy, T.; Wesser, J.; Wolfgang, H.; Spiess, W. *Ang. Makro. Chemie.* **1989**, *66*, 6739
- (7) Blum, F. D.; Meesiri, W.; Kang, H. J.; Gambogi, J. E. *J. Adhesion. Sci. Technol.* **1991**, *5*, 479
- (8) Jo, H.; Blum, F.D. *Langmuir* in press
- (9) Lin, W.; Blum, F. D. *Macromolecules* **1997**, *30*, 5331
- (10) Fyfe, C. A.; Niu, J. *Macromolecules* **1995**, *28*, 3894
- (11) Gambogi, J. E.; Blum, F. D. *Macromolecules* **1992**, *25*, 4526.
- (12) Colletti, R. F.; Mathias, L. J. *Solid State NMR of Polymers*; Matias, L. J., Eds.; Plenum Press, New York and London, 1991
- (13) Lin, W.; Blum, F. D. *Macromolecules* **1998**, *31*, 4135