Journal of Colloid and Interface Science **221,** 75–86 (2000)
Article ID jcis.1999.6577, available online at http://www.idealibrary.com on IDEAL®

Immobilizing a Fluorescent Dye Offers Potential to Investigate the Glass/Resin Interface[1]

Joseph L. Lenhart,* John H. van Zanten,§ Joy P. Dunkers,† Carl G. Zimba,† Calvin A. James,‡ Steven K. Pollack,‡ and Richard S. Parnas†,[2]

*Chemical Engineering Department, Johns Hopkins University, Baltimore, Maryland 21218; † Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899; ‡Chemistry Department and Polymer Science and Engineering Program, Howard University, Washington, DC 20059; and §Chemical Engineering Department, North Carolina State University, Raleigh, North Carolina, 27695

Received May 21, 1999; accepted October 8, 1999

Silane coupling agents are commonly applied to glass fibers to promote fiber/resin adhesion and enhance durability in composite parts. In this study, a coupling agent multilayer on glass was doped with trace levels of the dimethylaminonitrostilbene (DMANS) fluorophore. The fluorophore was immobilized on the glass surface by tethering the molecule to a triethoxy silane coupling agent, creating the DMANS/silane coupling agent molecule (DMSCA). DMSCA was then diluted with commonly used coupling agents and grafted to a glass microscope coverslip to create a model composite interface. A 53-nm blue shift in fluorescence from the immobilized DMSCA can be followed during cure of an epoxy resin overlayer, giving this technique potential to monitor the properties of the fiber/resin interface during composite processing. Contact angle measurements on these coupling agent layers were similar in the presence or absence of the DMSCA molecule, suggesting that trace levels of the fluorescent probe did not affect the structure of the layer. The immobilized DMSCA molecule behaved similarly to the DMANS precursor in solution. Both showed longer wavelength fluorescence in more polar environments.

Key Words: **fluorescence; coupling agent; interface; sensor; dye.**

INTRODUCTION

Recent advances in fiber reinforced composites have made them a valid alternative to traditional materials such as wood and metal. The major advantages of composite products include a high strength-to-weight ratio, corrosion resistance, and thermal and electrical insulating properties (1). These advantages have led to the increasing use of composites in many areas, including the transportation, aerospace, defense, construction, marine, electronics, and sporting goods industries (1).

Processing difficulties can increase cost and hinder the advancement of these materials into widespread industry use. The final properties of a fiber reinforced composite depend on the fiber properties and architecture, the extent of resin cure and resultant matrix properties, the quality of the mold filling, and the properties of the fiber/resin interface (2, 3). In general, it is poorly understood how processing conditions will influence these factors, so process optimization is largely determined by expensive and time consuming empirical techniques (4). To complicate matters, batch-to-batch variations of fiber and resin quality make reproducibility difficult. One approach to overcoming these complications is the development of sensors to monitor and optimize composite properties.

Fluorescent probe molecules have been used to monitor the properties of polymer and composite materials. For example, dimethylaminonitrostilbene (DMANS) was used to measure the glass transition of a cured epoxy resin and to study the physical aging of the resin below the glass transition (5). Fluorescence monitoring has also been used to study water sorption and diffusion in polymers (6, 7), polymer reaction kinetics (8, 9), and the onset of gelation during cure of thermosetting resins (10, 11).

Some research groups are developing practical sensor devices by combining fiber optic technology with fluorescence probe molecules. For example, after doping the resin with trace levels of a fluorescent dye molecule, both distal and evanescent mode fiber optic fluorescence methods have been used to measure the cure of epoxy (11–15) and polyurethane (11) resins. In one study, the position of the fluorescence maximum from the dye was observed to shift during the resin cure (11). In other work, the intensity changes from a fluorescing dye were monitored, via fiber optics, to follow the curing of an epoxy resin system (15).

These and other fluorescence methods for composite monitoring involve dissolving the fluorophore directly into the bulk resin. This can create problems in a manufacturing environment. First, an extra processing step may be required to mix the dye into the resin. Second, a small concentration of dye can drastically change the resin color, which could be undesirable. Finally, since the dye is dissolved in the bulk resin, the fluorescence response comes mainly from the bulk, and the behavior of the

[1] Identification of any commercial products is made only to facilitate experimental reproducibility and describe experimental procedure. It does not imply endorsement by NIST or imply that the particular product is necessarily the best for the experiment.

[2] To whom correspondence should be addressed at National Institute of Standards and Technology, Bldg. 224 Rm. B108, Rt. 270 and Quince Orchard Road, Gaithersburg, MD 20899.

0021-9797/00 $35.00

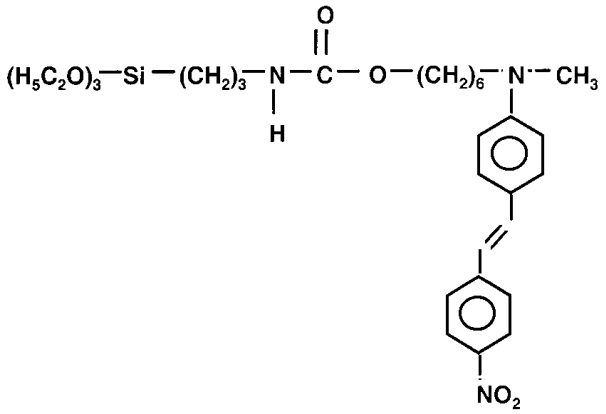

FIG. 1. The DMSCA coupling agent.

fiber/resin interface is ignored. Even if evanescent wave fiber optics are employed to focus on the interface, the evanescent wave may still propagate a micrometer or more into the resin, and much of the sensor response will be from the bulk resin (16).

The fiber/resin interphase region can make up a large fraction of the composite and thus have a dramatic effect on the final properties of the material (17–19). The size of the interphase region is approximately 100 to 500 nm and may contain composition or property gradients between those of the fiber coating and the bulk resin. The type of coupling agent used to coat the fiber, the properties of the coupling agent layer, and the interaction between the resin and coupling agent influence the interfacial region (20–22). In addition, different cure conditions may exist near the interface due to the presence of this coupling agent layer or the preferential diffusion of reactants to the surface (19). These effects can lead to a resin structure near the interface which is different from that of the bulk resin (23). Because it is difficult to relate the bulk resin structure to the interfacial properties, and since the fiber/resin interface is critical to the mechanical properties of the final composite part, it is advantageous to directly study this interfacial region.

Immobilizing a fluorescent dye onto fiber optics has been used in a variety of sensors (24) including oxygen, glucose, (25), and calcium (26) sensors. In order to make a sensor that is sensitive to the composite glass/resin interface, a fluorescently labeled silane coupling agent (DMSCA) has been chemically grafted to glass surfaces. DMSCA is a molecule that contains the dimethylaminonitrostilbene (DMANS) fluorophore tethered to a triethoxy silane coupling agent as illustrated in Fig. 1. When the fluorophore is covalently bonded at the glass surface, the fluorescence response of DMSCA can be used to directly study the glass/resin interface. In order to graft the fluorophore to the glass, the ethoxy functionalities on the silane end of DMSCA must be converted to hydroxyl groups. These hydroxyl groups can then condense with hydroxyl groups already present on the glass surface, forming covalent siloxane bonds (17).

Coupling agents are commonly used in industry to promote fiber/resin adhesion and enhance durability of the composite part by preventing water adsorption at the fiber/resin interface. The DMSCA dye is diluted in the deposition solution to trace levels (mole fraction $<0.2\%$) with another coupling agent, and this mixed coupling agent solution is grafted to the substrate. The other coupling agents used are glycidoxypropyltrimethoxysilane (GPS), isocyanatopropyltriethoxysilane (IPS), propyltriethoxysilane (PTS), and octyltriethoxysilane (OTS). The chemical structures are shown in Fig. 2. The technique is general for any coupling agent. These coupling agents were chosen to study the fluorescence behavior of DMSCA in a variety of chemical environments. Diluting the dye with another coupling agent provides a model composite interface since trace levels of DMSCA at the surface are not expected to change the structure of this region. Creating this model interface is very important, because the presence of a coupling agent layer on the glass surface can affect the structure of the interphase region. Diluting the DMSCA dye at the glass surface makes possible direct investigation of cure differences that can occur near the interface due to the presence of this coupling agent layer. These cure differences may affect the development of the fiber/resin interphase region during processing and affect the quality of adhesion and durability of the composite. Diluting DMSCA at the glass surface with another coupling agent only provides a simple model for

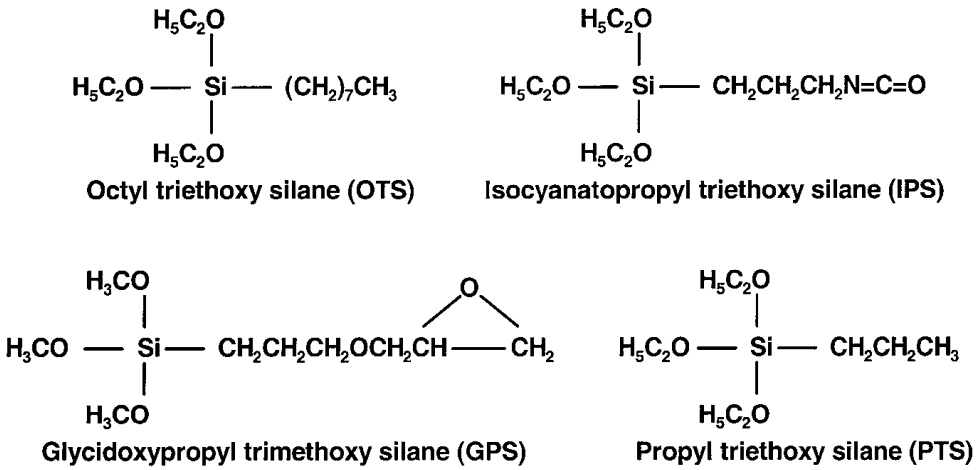

FIG. 2. Coupling agents used in the dilution of the DMSCA dye at the glass surface.

a composite interface because fibers are usually coated with a sizing package, which may also contain a lubricant, anti-static agent, and binder in addition to the coupling agent (18, 22, 27). Diluting the DMSCA fluorophore also helps avoid inner filter effects. An inner filter effect is a decrease in fluorescence intensity due to high dye concentrations. (28) If the concentration of dye becomes high enough, fluorescence from the dye can be absorbed by the solution before it is detected. This can skew the fluorescence curve and decrease its intensity.

The goal of this work is to develop a sensor technique that can monitor changes in the fiber/resin interphase region during composite processing. To do this, a silane coupling agent layer on a glass microscope coverslip was doped with small amounts of the DMSCA fluorescent probe. Fluorescence from the immobilized DMSCA was then monitored when the coated coverslip was immersed in an epoxy resin. If fluorescence changes from the DMSCA can be followed during the curing of the resin overlayer, then the technique has the potential to monitor the glass/resin interface during composite processing. In order to make an actual sensor, the fluorescence changes from DMSCA must be related to the physical changes in the interphase region during processing. The work in this paper has focused on demonstrating the potential to make a sensor using DMSCA and on understanding the fluorescence behavior of the grafted dye probe.

DMSCA SYNTHESIS

The triethoxysilyl functional fluorophore was prepared by reacting 4-[(6-hydroxyhexyl)methylamino]-4'-nitrostilbene (HMANS), first described by Robello (29), with 3-isocyanatopropyltriethoxysilane (IPS) to form a carbamate linked reactive fluorophore (DMSCA). This reaction, shown in Fig. 3, is analogous to that used by Chaput *et al.* (30, 31) in the synthesis of a triethoxylsilane functional Disperse Red 1.

Unless otherwise specified, all reagents were used as received. Isocyanatopropyltriethoxysilane (IPS) was a gift from Union Carbide. HMANS was prepared using a literature procedure (29). We also used a sample of HMANS graciously provided by Dr. Douglas Robello of Eastman Kodak. Pyridine was distilled and stored over 4-Å molecular sieves prior to use.

A 50-mL round-bottomed flask outfitted with an air condenser and maintained under a static nitrogen atmosphere was charged with 25 mL of dry pyridine, 1.03 g (2.91 mmol) of HMANS, and 0.720 g (2.91 mmol) of IPS and a magnetic stirring bar. The mixture was heated to 60°C and stirred overnight. An aliquot of the reaction was analyzed via infrared spectroscopy to ascertain whether complete reaction had occurred as monitored by the disappearance of the isocyanate peak (2230 cm^{-1}). The pyridine was removed *in vacuo* and the remaining red, resinous solid washed with toluene and dried in a vacuum oven overnight. Its spectroscopic characteristics were consistent with the desired structure. This material was used without further purification.

Carbamate linkages are subject to alkaline hydrolysis. If this hydrolysis reaction occurs in the DMSCA molecule, then the DMANS fluorophore would no longer be covalently bound in the coupling agent layer. The molecule would then be free to diffuse away from the glass surface into the curing resin. The extent of diffusion would depend on the kinetics of the resin cure. In a slow reacting system the DMANS probe could possibly diffuse into the bulk resin. In faster reacting systems, the molecule may not have enough time to diffuse away from the interphase region. To avoid hydrolysis conditions that can break this carbamate linkage, the DMSCA dye is stored in a dessicator to prevent water absorption.

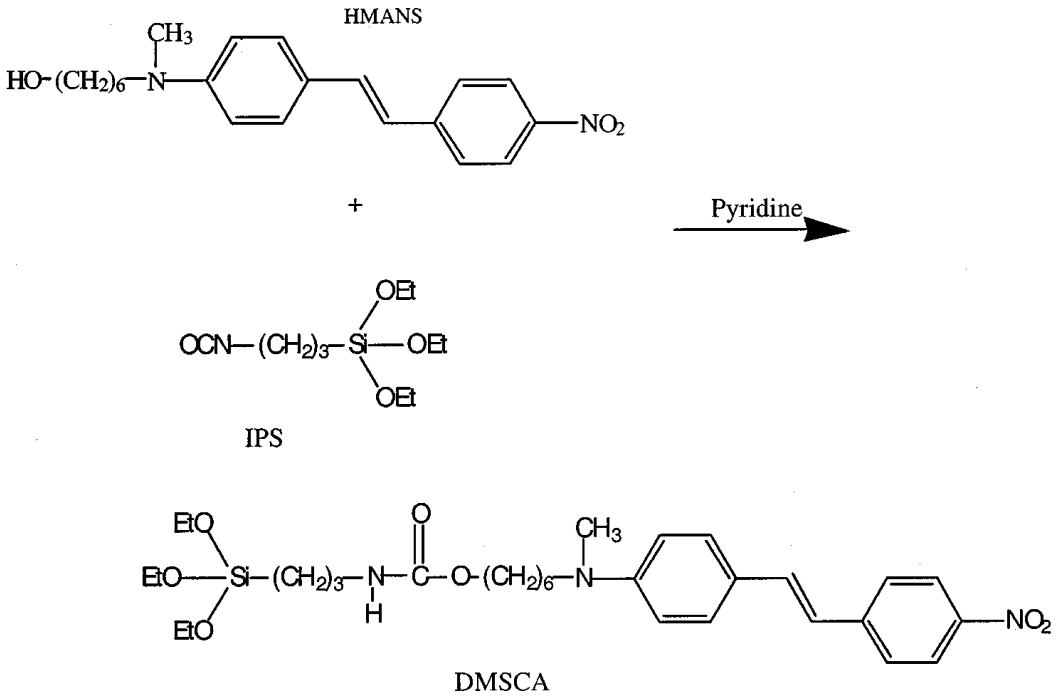

FIG. 3. A fluorescent dye is reacted with a triethoxy silane coupling agent to generate the DMSCA molecule.

MATERIALS AND METHODS

All other chemicals were used as received from Aldrich Chemical Company (Milwaukee, WI), except the coupling agents which were obtained from Gelest (Tulleytown, PA).

Two deposition procedures were used to graft the coupling agent layers to glass microscope coverslips. Water based and organic based deposition procedures were used to graft DMSCA layers when the dye was diluted with either GPS, IPS, or PTS. Because of the low solubility of OTS in the water based solution, only the organic based procedure was used to graft the layers when OTS was the diluting coupling agent.

Before any deposition procedure, all glassware was cleaned overnight in a NoChromix/sulfuric acid cleaning solution. The glassware was then thoroughly washed with water, rinsed with spectral grade acetone, and dried in an oven at 100°C until use. The glass microscope coverslips were immersed in the same cleaning solution for 1 h, washed with water, rinsed with spectral grade acetone, and dried in an oven at 100°C prior to the deposition.

For the water based deposition procedure, 0.02 mmol of DMSCA dye was weighed into a clean glass vial. Then 50 mL of an ethanol/water solution (5% water, v/v) was added to the vial. The mixture was stirred while 125 μL of 1 mol/L HCl in water was added. Then, 11 mmol of either GPS, IPS, or PTS was added to the mixture. This gave a DMSCA mole fraction of less than 0.2% relative to the diluting coupling agent. The deposition solution was stirred for 5 h at room temperature to allow for hydrolysis of the ethoxy bonds on the silane end of the coupling agents. After the hydrolysis time, clean glass microscope coverslips were added to the deposition mixture. The hydrolyzed coupling agents could then adsorb to the glass surface. After allowing 10 min for adsorption, the coated slides were removed and placed vertically in separate vials. The vials containing the coated slides were then placed in an oven to cure for 2.5 h at 100°C. This curing process dries the layer and promotes the formation of covalent siloxane bonds. These bonds attach the coupling agent to the glass surface and cross-link the coupling agents on the surface (17, 32). After curing, the coated coverslips were sealed in a vial and stored in a dark place until fluorescence and contact angle measurements were made the following day.

A two-step organic deposition procedure (33) was used to graft DMSCA when diluted with the OTS coupling agent. For this procedure 0.02 mmol of DMSCA was weighed into a clean vial and 50 mL of tetrahydrofuran was added. Then 125 μL of 1 mol/L HCl in water was added, while the deposition mixture was stirred. Next, 500 μL of water was added to the tetrahydrofuran solution. Finally, 11 mmol of OTS was added to the solution. This solution was stirred for 22 h at room temperature to allow for hydrolysis of the ethoxy bonds on the coupling agent. A longer hydrolysis time is required because the water concentration is much lower in this procedure than in the ethanol/water based deposition. After hydrolysis, 5 mL of the final tetrahydrofuran deposition solution was added to 45 mL of clean cyclohexane. This cyclohexane solution was allowed to sit for 15 min. Then, clean glass microscope coverslips were added to this solution, and 10 min was allowed for adsorption of the coupling agents to the glass surface. The coated slides were removed, placed vertically in a clean vial, and dried in an oven for 2.5 h at 100°C. Again, the coverslips were sealed in a vial and stored in a dark place until measurements were made on the samples.

The organic deposition procedure was also used to graft some coupling agent layers when DMSCA was diluted with GPS, IPS, or PTS. However, when these coupling agents were grafted using the tetrahydrofuran based technique, only 5 mmol of either GPS, IPS, or PTS were added to the 50 mL of tetrahydrofuran. In addition, the percentage of DMSCA relative to the diluting coupling agent was higher, a mole fraction of approximately 0.7%, when the organic procedure was used to deposit these coupling agents.

Control experiments were run using the same deposition procedures described above. However, for the control experiments only the diluting coupling agent and no DMSCA was added to the deposition mixture.

The chemical functionality of the coupling agents can change during the deposition procedure. For example under acidic conditions the epoxide ring on GPS can open to form a diol. Also, the isocyanate group on IPS can hydrolyze to form an amine. The chemical functionality of the coupling agent layers was not studied after the deposition procedure. The focus of this work was to immobilize a fluorescent probe on the glass surface and examine the potential use of this technique as an interface sensitive sensor. Ongoing work focuses on understanding how the chemical functionality of these grafted layers will influence adhesion and will be important for interpreting the fluorescent response of the DMSCA probe.

A schematic of the fluorescence experiments is shown in Fig. 4. The DMSCA was grafted to a glass microscope coverslip with a diluting coupling agent. Light at a wavelength of 460 nm was used to excite the immobilized DMSCA. The fluorescence response of the DMSCA was then collected in a detector at right angle geometry from the excitation light. In some experiments, the coated slide was immersed in an epoxy resin. The fluorescence response was then measured in the presence

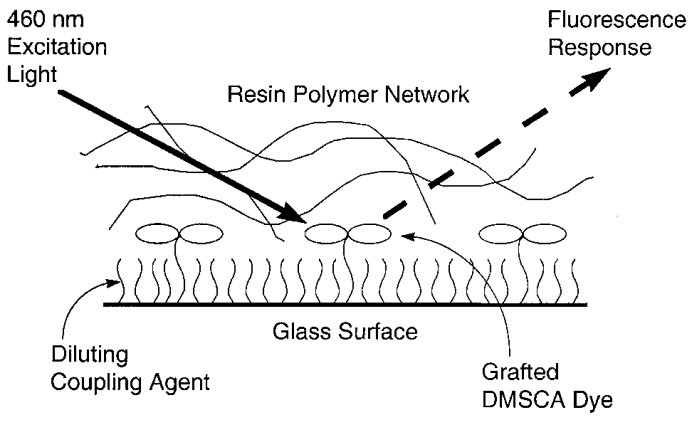

FIG. 4. A schematic of the fluorescence experiments.

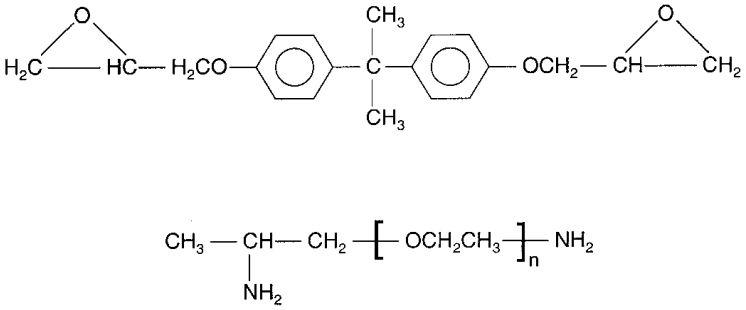

FIG. 5. The amine hardened epoxy resin system is shown above. The top structure is Tactix 123. The bottom structure is Jeffamine D400.

of the resin overlayer. The epoxy/amine resin system used in this study, shown in Fig. 5, was composed of 10 g of diglycidyl ether of bisphenol A (Tactix 123, Dow Chemical Company) mixed with 5.6 g of poly(propylene glycol) bis(2-amino propyl ether) (Jeffamine D400, Aldrich Chemical Company). The two components were mixed together using a mechanical stirrer. The resin mixture was then degassed under vacuum for 10 min before use. Figure 4 shows only a monolayer of the DMSCA and diluting coupling agent bound directly to the surface. In reality the grafted layers are multilayers ($\sim$3 μm thick) where the DMSCA dye and diluting coupling agent can potentially bond with each other in addition to the glass surface.

Contact angle measurements in water were made on the samples using a CAHN DCA 322 Dynamic Contact Angle Analyzer (Madison, WI). For each sample, four cycles were run on the contact angle. The data in this paper are from the final cycle. Each cycle involved the following steps: (i) tare the balance, (ii) detect the sample contact with water, (iii) advance the sample into the water a length of 4 mm, (iv) hold the sample in this position for 2 min, and (v) recede the sample out of the water and return the motor to the starting position. The advancing and receding speed was 80 μm/s. Samples for contact angle measurements consisted of both the grafted coupling agent layers and the same layers after a 30-min acetone wash. After contact angle measurements on the initial sample, the same sample was soaked in acetone for 30 min. During this soak, the acetone was gently stirred every 5 min. Prior to making a contact angle measurement on the washed layer, the sample was dried in an oven at 100°C for 20 min.

Fluorescence data were measured using a Spex Fluorolog Fluorimeter (Edison, NJ) in the right angle geometry collection mode. In order to minimize the amount of excitation light that was reflected into the detector, samples were placed at a 60° angle relative to the incidence light. The excitation and emission slit widths were 5 mm.

RESULTS

The results shown in Fig. 6 demonstrate the potential to use the grafted DMSCA dye as an interface sensitive cure monitoring sensor. Both a fluorescence intensity change and a blue spectral shift (to shorter wavelengths) from the grafted DMSCA can be followed when an epoxy resin cures over the mixed coupling agent layer. For Fig. 6, DMSCA was diluted with the epoxy functional coupling agent, GPS. This mixed silane layer was then grafted to the glass microscope coverslip using the ethanol/water based deposition procedure. Scanning electron microscopy (SEM) showed that the layer thickness was approximately 3 ± 1 μm. When the coated coverslip is immersed in uncured epoxy resin, the DMSCA fluoresces with maximum intensity, λ_m, at a wavelength of 632 ± 1 nm. While still immersed in the uncured resin, the same coverslip was then put in the oven for 4 h at 100°C to allow the epoxy resin to cure over the GPS/DMSCA grafted layer. The sample was removed from the oven and cooled to room temperature. When fluorescence from this layer was measured in the cured epoxy, λ_m had shifted to 579 ± 4 nm. The uncertainties given are standard deviations. This 53-nm blue shift in fluorescence, during the resin cure, gives the grafted dye technique potential to monitor a composite fiber/resin interface during processing. However, to make a practical sensor, the magnitude of this spectral shift must be related to structural or chemical changes in the interphase properties during cure. The intensity values are shown in counts per second (cps). The cps values are relative since the intensity can be scaled by adjusting the detector voltage. The same detector voltage was used for all the fluorescence measurements.

Two controls were run for Fig. 6. First, a GPS/DMSCA coated coverslip was subjected to the same 4 h, 100°C heat treatment, but was not immersed in the epoxy resin. The fluorescence from this control showed no spectral shift or intensity change after the heat treatment, demonstrating that the spectral shift was not due to the heat treatment of the coupling agent layer. The second control was a coverslip coated only with GPS that was immersed in the epoxy resin. The spectrum of the second control is shown on Fig. 6. The GPS coated coverslip showed a small fluorescence

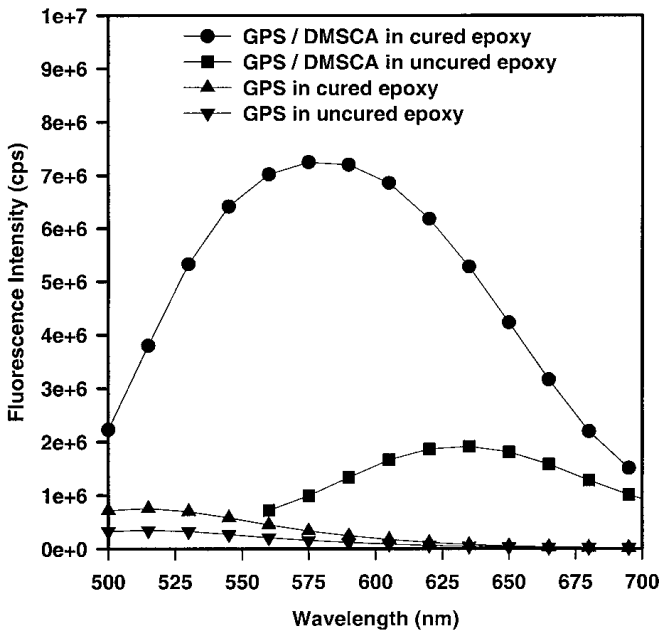

FIG. 6. A blue shift is observed from the grafted DMSCA dye during cure of an epoxy overlayer.

TABLE 1
Contact Angle Data for Samples Containing DMSCA before and after an Acetone Wash

	Before wash		After wash	
Sample	θa (degrees)	θr (degrees)	θa (degrees)	θr (degrees)
None	37.4 ± 2.9	8.2 ± 2.5	33.1 ± 2.0	8.2 ± 0.4
GPS/DMSCA	68.9 ± 2.0	40.3 ± 2.2	72.7 ± 3.1	38.9 ± 0.8
IPS/DMSCA	76.1 ± 2.0	53.3 ± 2.2	75.9 ± 1.6	54.7 ± 3.1
PTS/DMSCA	96.7 ± 4.2	68.1 ± 1.6	100.7 ± 1.4	70.6 ± 3.8
OTS/DMSCA	111.3 ± 3.0	77.9 ± 1.6	110.3 ± 3.0	76.1 ± 6.0

intensity when immersed in the epoxy. Since GPS itself does not fluoresce, the background fluorescence from this control is probably due to small amounts of fluorescent impurities in the industrial grade epoxy resin that was used in this study. Fluorescent impurities are often present in industrial grade resins (4). The fluorescence background of the GPS control, in epoxy resin, was small when compared the fluorescence of the GPS/DMSCA coated coverslip, in epoxy resin, and did not contribute to the spectral shift.

Dynamic contact angle measurements were used to characterize the mixed silane layers and assess layer stability. The contact angles were measured in water and are shown with standard deviations in Tables 1 and 2. Both the advancing (θ_a) and receding (θ_r) contact angles are shown. The contact angle measurements were made both before and after a gentle 30-min acetone wash. The contact angle data for samples before and after this wash are shown in Table 1. If the contact angle of the sample after the wash was similar to that of an uncoated slide, then the layer was unstable and completely removed by the wash. However, because the contact angles are similar before and after the acetone wash for each sample, this suggests that at least part of the layer is stable and bound to the glass surface.

Contact angle data for the control samples are shown in Table 2. The similarity between the contact angles of the controls and the contact angles of the corresponding samples containing DMSCA (Table 1) suggests that the presence of small amounts of the dye did not change the surface energetics of the layer and did not have a dramatic effect on the layer structure. Tables 1 and 2 show only contact angle data from the ethanol/water based deposition procedure when GPS, IPS, or PTS are used. Similar contact angles were obtained when the organic method was used to deposit these layers. Due to the limited solubility of OTS in the ethanol/water mixture, only the organic procedure was used to deposit the layers containing OTS. Contact angle data was taken from at least eight samples of each coupling agent layer.

TABLE 2
Contact Angle Data for Control Samples with No Wash

Sample	θa (degrees)	θr (degrees)
None	37.4 ± 2.9	8.2 ± 2.5
GPS	69.9 ± 2.2	44.3 ± 1.9
IPS	79.3 ± 0.9	58.6 ± 2.5
PTS	95.4 ± 4.5	69 ± 1.4
OTS	107.4 ± 2.9	80.6 ± 1.2

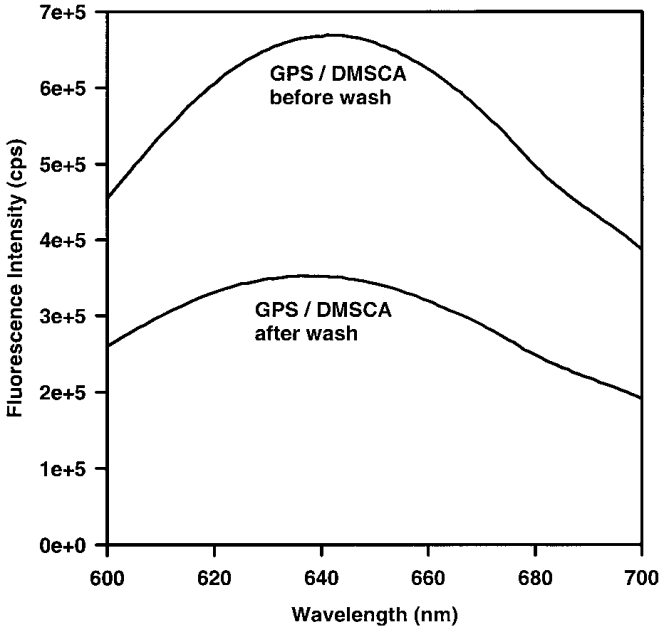

FIG. 7. A decrease in fluorescence intensity is observed from the grafted GPS/DMSCA layer after an acetone wash.

Fluorescence measurements were also made before and after the acetone wash. Figure 7 shows a typical result for the GPS/DMSCA grafted layer. The wavelength of the intensity maximum from the grafted layer before and after the wash is the same, suggesting that the layer has the same basic nature after washing. However, the relative fluorescence intensity decreases by nearly 50% after the wash. This suggests that part of the grafted layer washed off with the acetone, but some of the layer remained on the slide. The decrease in fluorescence intensity is probably due to a fraction of the GPS/DMSCA mixture that physically adsorbed to the surface and did not form covalent siloxane bonds in the interphase. Table 3 shows the average fluorescence intensity decrease from these layers after an acetone wash. The intensity data are shown with standard deviations. The intensity decrease after the acetone wash was measured as a percentage of the fluorescence intensity before the wash for each sample. Then, the average intensity decrease was calculated for the entire sample set. At least eight samples of each coupling agent layer were used to calculate the intensity decrease after washing.

To study how the chemical nature of the coupling agent layer affects the DMSCA fluorescence, the probe was diluted with OTS, PTS, IPS, or GPS. These mixed coupling agent solutions were then grafted to glass microscope coverslips. Figure 8 shows typical fluorescence emission spectra from these grafted layers before the acetone wash. The control slides showed no fluorescence and had an insignificant background intensity. The fluorescence response from the immobilized DMSCA is due only to the presence of the diluting coupling agent, because these grafted layers were not immersed in a resin overlayer. When DMSCA

TABLE 3
The Fluorescence Intensity Decrease Due to Washing the Layer in Acetone

Sample	Intensity (cps) before wash	Intensity (cps) after wash	Average intensity decrease (%)
GPS/DMSCA	(8.86 ± 2.71) E+5	(3.59 E+5) ± (9.02 E+4)	56 ± 9
IPS/DMSCA	(3.36 ± 1.47) E+6	(2.18 ± 1.07) E+6	35 ± 12
PTS/DMSCA	(2.19 ± 1.53) E+6	(2.71 ± 1.51) E+4	98 ± 2
OTS/DMSCA	(2.96 E+6) ± (7.26 E+5)	(2.41 ± 1.21) E+5	91 ± 5

Note. Intensity is given in counts per second (cps).

is diluted with PTS or OTS, the fluorescence maximum, λ_{max}, is near 560 nm. The organic functionality of both PTS and OTS is an alkane chain. Thus, it is expected that the interactions between the dye and coupling agents are similar in these layers, and the position of λ_{max} occurs near the same wavelength. However, when the organic functionality of the diluting coupling agent is changed to the more polar isocyanatopropyl group (IPS), the fluorescence emission occurs at longer wavelengths and has a λ_{max} of 593 nm. Even longer wavelength fluorescence is observed for the GPS/DMSCA mixed layer, which has a λ_{max} of 642 nm. This figure shows that the chemical functionality surrounding the DMSCA fluorophore has a significant effect on the position of the fluorescence emission from the grafted layer. The standard deviations of the position of the curves in Fig. 8 are given by the error bars for the fluorescence maximum in Fig. 9. The standard deviations of the intensities for the curves in Fig. 8 are given in Table 3.

Figure 9 shows a plot of the fluorescence wavelength maximum from DMSCA verses the advancing contact angle of the particular mixed coupling agent layer. The data in Fig. 9 were from samples produced by the organic and water based deposition procedures, both before and after the acetone wash. Error bars are displayed on the graph for each coupling agent layer and each deposition procedure to show the standard deviations of the contact angle and fluorescence maximum. The data show a clear trend. When the surface energy of the layer is high (small contact angles), the DMSCA fluoresces at long wavelengths. The GPS/DMSCA mixed layer has contact angles near 68°. These layers were the most hydrophilic of the layers used in this study and had a fluorescence maximum at long wavelengths near 638 nm. As the surface energy of the mixed layer decreases (increasing contact angles), the fluorescence intensity maximum from DMSCA occurs at shorter wavelengths. On the other extreme is an OTS/DMSCA mixed layer. The organic group on OTS is a very nonpolar eight-carbon chain. These layers have a large contact angle near 111°, representing an extremely nonpolar surface. The fluorescence maximum from DMSCA diluted in this layer occurs at wavelengths near 557 nm. Figure 9 shows that the fluorescence response from the grafted DMSCA dye is a function of the layer surface energetics and not the deposition procedure. Both the organic and the aqueous based depositions gave layers that showed the same fluorescence behavior. The structure of the coupling agent layer could be different, when different deposition techniques are used, but in this case, the

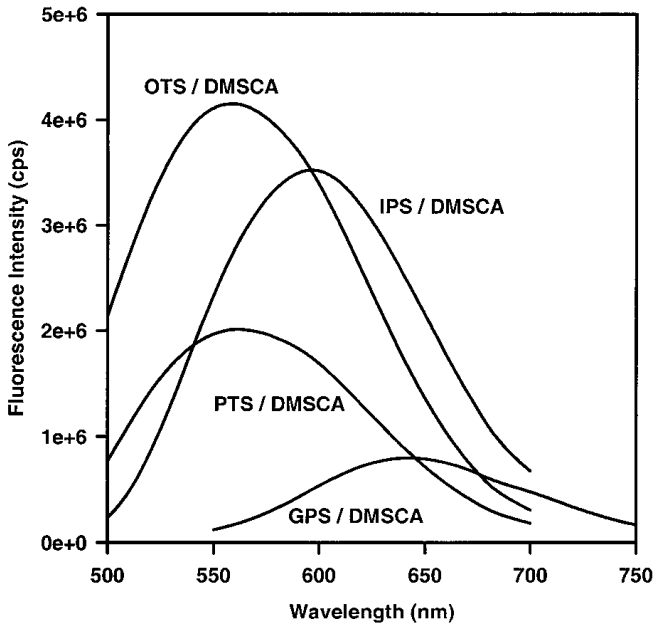

FIG. 8. Grafted DMSCA fluorescence when diluted with different coupling agents.

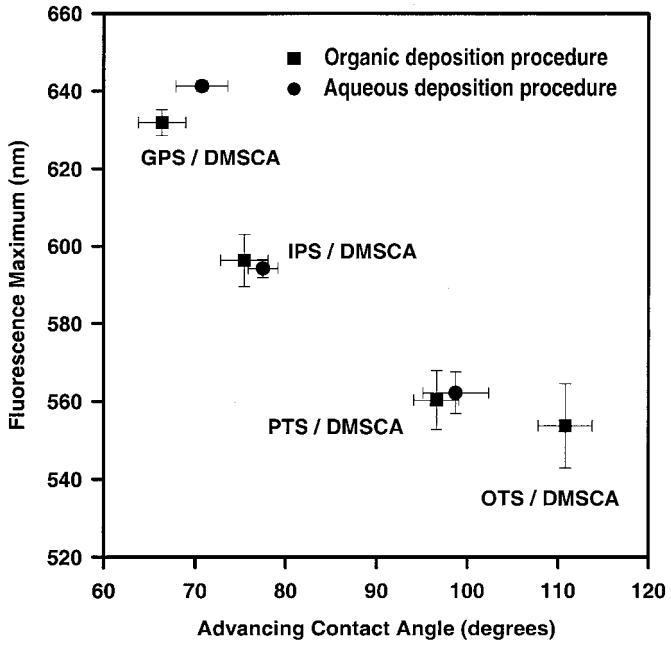

FIG. 9. Position of the fluorescence emission of the grafted DMSCA as a function of the layer surface energetics and the deposition procedure.

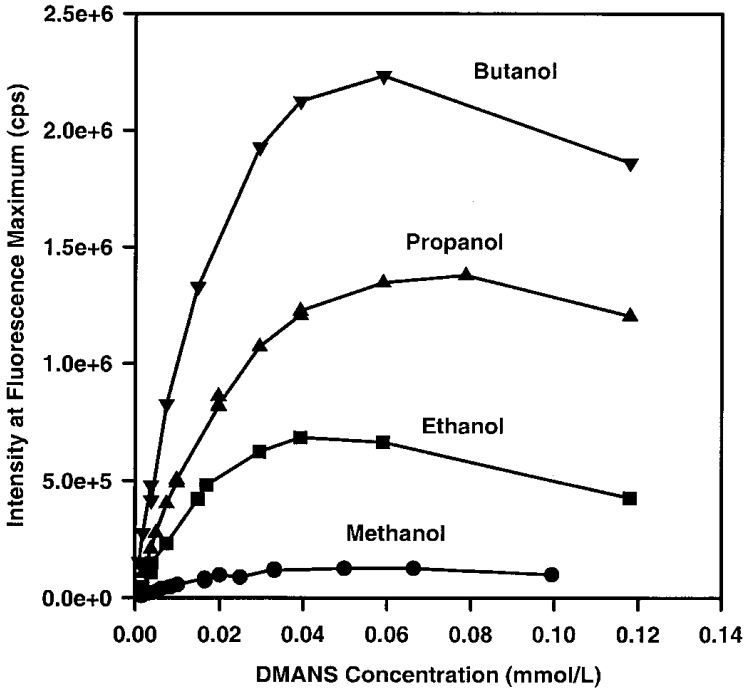

FIG. 10. Fluorescence intensity at λ_{max} for DMANS dissolved in a variety of solvents at different concentrations.

fluorescence response from DMSCA is not sensitive to these structural changes.

To verify that the DMSCA fluorophore is fluorescing as expected even when constrained to a glass surface, we chose to study fluorescence emission from the DMANS precursor to DMSCA in a variety of solvents. Figure 10 shows the DMANS fluorescence intensity, at the wavelength maximum, plotted against concentration in the various solvents. Two important trends are shown by Fig. 10. First, the fluorescence intensity from DMANS increases as the solvent dielectric constant decreases. In methanol, the solvent with the highest dielectric constant, DMANS shows low intensity fluorescence. However, in butanol, which has a lower dielectric constant, the fluorescence intensity is much higher. Figure 10 also shows that the DMANS fluorescence intensity is extremely dependent on the fluorophore concentration. At high concentrations, the fluorescence intensity can actually decrease. The curves in Fig. 10 could be reproduced within 6% of the intensity for a given concentration.

Figure 11 plots the DMANS fluorescence maximum in various solvents versus the dielectric constant of that solvent. A larger dielectric constant represents a more polar solvent environment. The position of the fluorescence maximum had a standard deviation of ± 1 nm and did not change with concentration over the range shown in Fig. 10.

DISCUSSION

As the epoxy resin cures, a fluorescence intensity increaseand blue shift in λ_{max} was observed from DMANS, when the dye was bound in the layer by the DMSCA coupling agent. These changes in fluorescence emission are due to both an increase in the resin viscosity and a decrease in the resin dielectric constant during cure.

When a fluorescent molecule absorbs a photon, the dipole moment of the molecule increases and the molecule is sent to a higher energy level. A solvent relaxation process occurs, where the solvent molecules reorient their dipole moments around the new dipole moment of the excited molecule. This reorientation of the solvent cage can dissipate the excited state energy of the dye molecule and offer a nonradiative pathway to the ground state. When the epoxy resin reacts, the dielectric constant of the resin decreases due to a decrease in the dipole moments of the resin molecules. As the dipole moments decrease, the solvent relaxation process is not as effective at this energy dissipation. More of the excited state molecules are forced to release the energy through fluorescent pathways. This causes an increase in the quantum yield and an increase in fluorescence intensity.

It has been observed that the fluorescence quantum yield from DMANS increases as the polarity of the solvent decreases, up to an intermediate polarity. After this intermediate polarity, the quantum yield will decrease again as the solvent polarity is further decreased (34, 35). The change in quantum yield with solvent polarity is due to two nonradiative processes. One process is the *trans* to *cis* isomerization around the stilbene double bond. The *trans* isomer is more polar than the *cis* isomer. In extremely low polarity solvents, the *cis* isomer is favored because of its nonpolar nature. Since the *cis* isomer does not fluoresce, the quantum yield of DMANS is small in very low polarity solvents. As the solvent polarity increases, the *trans* isomer is stabilized and the quantum yield increases because the *trans* isomer is fluorescent. When the solvent polarity further increases, DMANS molecules can form twisted internal charge transfer

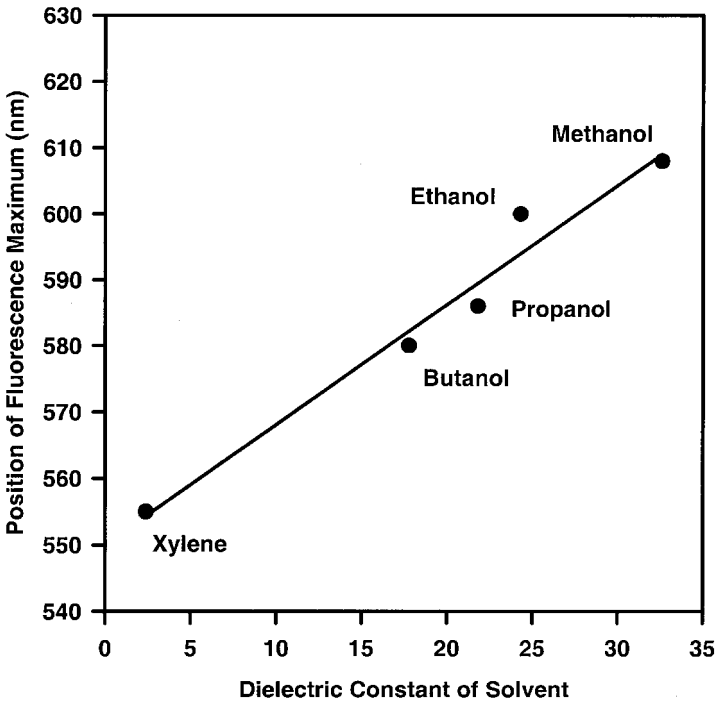

FIG. 11. Position of the fluorescence maximum from DMANS when dissolved in solvents of different polarity.

states (TICT). These TICT states result from rotations around the single bonds of DMANS. The TICT states are usually nonfluorescent and stabilized in polar solvents. So, as the solvent polarity further increases the quantum yield will decrease again. In alcohol solvents the *trans* to *cis* isomerization is negligible due to the low polarity of the *cis* isomer (35). Since the glass surface and the coupling agent layer may contain many hydroxyl groups, we expect to be in the higher polarity regime, where the DMANS fluorescence intensity will decrease with increasingly polar environments.

The viscosity increase in the epoxy resin during cure also contributes to the increase in fluorescence intensity. Both the *trans* to *cis* isomerization and TICT formation are nonradiative pathways that require a certain amount of free space for rotations to occur around the bonds of DMANS. The free space is provided by the free volume of the resin (36). As the resin reacts, the free volume decreases. As the free volume decreases, the efficiency of these reactions is reduced. More of the DMANS molecules are forced to release the excited state energy through the fluorescence pathway. This increases the fluorescence intensity.

In addition to intensity, the position of the fluorescent emission will also be affected by the decrease in the dielectric constant and increase in viscosity during cure. The Lippert equation (Eq. [1]) predicts how a decrease in the solvent dielectric constant will cause a blue shift in λ_{max} (28),

$$\nu_a - \nu_f \cong \frac{2}{hc}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)\frac{(\Delta\mu)^2}{a^3} + \text{const}, \qquad [1]$$

where ε is the solvent dielectric constant, n is the refractive index of the solvent, c is the speed of light, h is Plank's constant, a^3 is the volume occupied by the fluorophore, $\Delta\mu$ is the dipole moment change of the fluorophore between the ground and excited state, and ν_a and ν_f are the wave numbers (cm^{-1}) of the absorption and emission intensity maximum, respectively. The Stoke's shift is defined as the difference between the absorption and emission intensity maximum of the fluorophore. It is a measure of the energy dissipated from the excited state molecule before releasing a fluorescence emission. The refractive index contribution accounts for the ability of the solvent electrons to reorient themselves in order to stabilize the dipole moment of the fluorophore in the excited state. The dielectric constant term accounts for the solvent relaxation process, which will decrease the energy difference between the ground and excited states. The constant term in Eq. [1] accounts for additional mechanisms of energy dissipation, such as vibration to lower energy excited states.

As the epoxy resin reacts, the dipole moments of the resin are weakened, which causes a decrease in the dielectric constant (37). Equation [1] predicts that this will generate a blue shift in fluorescence. In addition, the refractive index of the epoxy resin increases during cure. Again, Eq. [1] predicts that this change in refractive index will cause a blue shift. Typically, the refractive index changes from 1.5 to 1.6 during cure of epoxy resins (38). The dielectric constant can decrease by nearly 10 times the change in the refractive index (37). By assuming some typical numbers for the dielectric constant and refractive index of epoxy resins, the blue shift can be estimated from Eq. [1]. The parameters for the DMSCA dye must also be estimated. The absorption maximum for DMANS in epoxy occurs near 445 nm. For DMANS the dipole moment change between the ground and the excited state has been estimated between 6.7×10^{-29} and 1.5×10^{-28} C·m (34, 39). The value of a for DMANS has been estimated to be 8 Å (34). After including a 1000 cm^{-1} shift due to vibrational dissipation of energy, and using a value of 1.2×10^{-28} C·m for the dipole moment change from DMSCA, a dielectric constant of 15, and a refractive index of 1.5 for the uncured epoxy resin, Eq. [1] predicts a fluorescence maximum of 624 nm in uncured epoxy. Using a dielectric constant of 10 and a refractive index of 1.6 for the cured epoxy, Eq. [1] predicts a fluorescence maximum of 580 nm in the cured epoxy. The blue shift, predicted by Eq. [1] using typical dielectric and refractive index values for epoxy resin systems, qualitatively agrees with the experimental data observed in Fig. 6. These calculations are only an estimate, because the dielectric and refractive index values were not measured for this resin system. In addition, the presence of the diluting coupling agent could affect these numbers. Finally, Eq. [1] accounts only for general solvent effects, not for specific interactions between the resin and dye. Equation [1] also ignores the effects of viscosity on fluorescence emission.

Increasing viscosity at the glass/resin interface during cure may also contribute to the blue shift in fluorescence observed from the grafted DMSCA. Two effects contribute to the viscosity change at the interface. First, an increase in the epoxy molecular weight and cross-link density occur during polymerization. Second, the amine functionality on the Jeffamine D400 curing agent can cross-link with the epoxy group on the GPS coupling agent. Viscosity induced shifts have been observed for dye molecules in vitrified solvents (28, 35). Huge viscosity changes are necessary to induce these shifts. At gelation of thermosetting resins the viscosity diverges to infinity, so the viscosity contribution to this blue shift could be significant near or after gelation.

The viscosity induced blue shift occurs as the relaxation time of the polymer, τ_p, approaches the fluorescence lifetime of the excited state dye molecule, τ_d. When the resin viscosity increases so that τ_p is approximately τ_d, then the solvent relaxation process occurs on the same time scale as the fluorescence emission. When τ_p is much larger than τ_d, then no solvent relaxation occurs to dissipate the excited state energy of the dye. The dye is forced to release fluorescence from a higher, unrelaxed energy level. This results in a blue shift in the fluorescence emission. The fluorescence lifetime for DMANS in low viscosity solvents is approximately 1–3 ns depending on the solvent (40). The kinetics of excited state reactions (i.e., for stilbene dyes *trans–cis* isomerization or TICT formation) can decrease during cure of epoxy resins (36). This is because the free volume of the resin decreases during cure, which hinders these excited state reactions.

Since these reactions often provide nonradiative pathways to the ground state, a decrease in the kinetics of these reactions would increase the fluorescence lifetime of the dye molecule. Because of this, it is likely that τ_d increases significantly for DMANS as the epoxy resin cures. However, for epoxy thermosets, a typical relaxation time (τ_p) can be on the order of seconds, or even hours for the long term relaxation processes (41, 42). Since it is likely that τ_p for a cured epoxy thermoset will be much larger than τ_d for DMANS in the resin, the viscosity increase during cure probably contributes to the blue shift in fluorescence.

The goal of this work is to make a practical fiber optic sensor device to monitor the properties of the composite resin, and interphase region during processing. Although the fluorescence intensity increase from grafted DMSCA is large during the epoxy resin cure, monitoring the blue shift in λ_{max} is more practical. To measure the fluorescence peak position, the only requirements are (i) to have a good signal-to-noise ratio and (ii) to account for the instrumentation function. In order to accurately measure intensity changes, the thickness of the coupling agent layer, and the concentration of DMSCA in the layer must also be known. In addition, fluctuations in the excitation power supply and the effects of photo-induced degradation must be corrected. Finally, the effects of quenching on the fluorescence intensity need to be estimated. Oxygen is a common fluorescence quencher. In order to estimate its quenching effect on DMANS, the solubility of oxygen in epoxy must be known, at different temperatures and extents of cure. So, it is potentially difficult to make an intensity based sensor, where the fluorescence intensity accurately reflects the resin structure.

The Beer Lambert Law, Eq. [2], can be used to show how the DMSCA surface concentration and layer thickness influence the fluorescence intensity,

$$\text{absorption} = \ln\frac{I_0}{I} = \sigma C t, \qquad [2]$$

where I_0 is the intensity of the incoming light and I is the intensity of light after it has traveled through the sample, C is the dye concentration, σ is the extinction coefficient of the dye, and t is the thickness of the coupling agent layer. In a nonscattering system, the amount of photons absorbed by the DMSCA dye is proportional to the difference between the incoming and outgoing intensity of light. In the Beer Lambert regime, the fluorescence intensity is also proportional to the amount of photons absorbed by the DMSCA dye. This proportionality constant is called the quantum yield of the fluorophore. The fluorescence intensity, F, becomes

$$F = \phi(I_0 - I) = \phi I_0\left(1 - e^{-\sigma C t}\right), \qquad [3]$$

where ϕ is the quantum yield of the fluorophore in that layer. Equation [3] shows how thickness or concentration variations between the samples influence fluorescence intensity.

Table 3 shows the fluorescence intensity measured before and after the acetone wash. The decrease in fluorescence intensity after the acetone wash can be attributed to weakly bound coupling agent material that was washed from the surface. The IPS/DMSCA and GPS/DMSCA layers were more stable than layers containing PTS or OTS. The relative stability of these layers can be explained by the ability of the organic end of the coupling agent to interact with hydroxyl groups on the glass surface and on neighboring coupling agents. Both the isocyanate group on IPS and the epoxy group on GPS can interact strongly with a hydroxyl group. However, the hydrocarbon ends on PTS and OTS cannot. The extra reactive site on IPS and GPS may lead to a more cross-linked and stable grafted layer. Experimental evidence from the organic based deposition procedure supported this conclusion. With solutions of IPS in tetrahydrofuran, the coupling agent would precipitate from solution, where as the solutions containing GPS, PTS, or OTS showed no precipitation. Because the tetrahydrofuran solvent tends to prevent condensation of coupling agents (33), this precipitation could be due to a reaction between the organic group on the coupling agent and the hydroxyl group on neighboring coupling agents generating small oligomers. Eventually the oligomers formed would be large enough to precipitate from solution.

In addition to the reactivity of the organic end of these coupling agents, the orientation of the coupling agent molecules on the glass surface may have a significant effect on layer stability. The PTS and OTS layers were extremely unstable and lost over 90% of their fluorescence intensity during the wash. This could be due to preferential alignment of the nonpolar organic end of these coupling agents away from the glass surface and into the organic solvent. The hydroxyl groups on the coupling agents would then be next to the glass surface, and the remaining coupling agents would have very few hydroxyl sites on which to adsorb. The result would be a thin layer of covalently bound material close to the glass surface, with the rest of the layer physically adsorbed. This physically adsorbed material is weakly attached to the surface and would be easily removed during the wash. Experimental evidence supported this speculation when PTS or OTS was grafted using a modified version of the organic deposition procedure described in the experimental section. For the modified procedure, after adsorption the coated glass coverslip was washed in clean cyclohexane to remove excess and physically adsorbed coupling agents. X-ray reflectivity measurements on these samples did not detect a coupling agent layer, but contact angle measurements on the samples gave advancing contact angles of greater than 90°. The large contact angle suggest that the alkane chains of the PTS or OTS were aligned away from the glass surface. X-ray reflectivity can detect layers as thin as 25 Å. Since the X-ray reflectivity measurements did not detect a layer, this suggests that only a monolayer was present with the alkane chains facing away from the surface.

In order to measure the fluorescence of these layers using a standard fluorimeter and to demonstrate the principle of this fluorescence cure monitoring technique, the grafted layers in this paper have been made much thicker than typical coupling agent layers used in the composites industry. Because the layers

are very thick, a larger portion of the coupling agents may be physisorbed to the surface. The stability of the grafted layer is important. In order to make a practical sensor device, these layers must be grafted to a glass fiber optic which can be inserted into the composite mold. The layer must be able to withstand the resin injection process, in order for the sensor to work. We are currently developing a fiber optic evanescent wave fluorimeter that will measure the fluorescence from very thin, grafted DMSCA layers. For future experiments we will graft layers approximately 100 nm thick, which is a reasonable thickness for coupling agent sizing packages applied onto the fiber preforms used in industrial composite materials. (18, 22, 43)

Figures 8 and 9 show that the fluorescence response of the grafted DMSCA depends on the chemical functionality of the diluting coupling agent. As the polarity of the diluting coupling agent increases the fluorescence response from that layer occurs at longer wavelengths. This trend is predicted by Eq. [1] and was discussed previously. The intensity variations for the different layers in Fig. 8 could be due to the chemical functionality of the diluting coupling agent, which would affect the quantum yield of the DMSCA, or to thickness and DMSCA surface concentration variations between the layers. Thickness and concentration differences between the layers could occur due to adsorption differences between the coupling agents. Current work is focused on developing infrared spectroscopy techniques to measure trace levels of DMSCA in the coupling agent layer. The adsorption behavior and its effect on layer thickness is also being studied further.

A similar trend was observed when the DMANS fluorophore was not grafted to the surface, but free in a bulk solvent. Figures 10 and 11 again show that as the solvent polarity increases, the fluorescence response occurs at longer wavelengths. A direct comparison between the grafted and free DMANS fluorescence behavior was not made in this study. However, Fig. 9 and 11 show that the dependence of λ_{max} on solvent polarity is qualitatively similar whether DMANS is in a bulk solvent or grafted to the glass surface. The specific effect that covalently grafting DMSCA in the coupling agent layer has on its fluorescence response is currently being studied. Figure 10 shows that the fluorescence intensity is extremely dependent on the DMANS concentration. Since we expect the grafted DMSCA to behave in a similar manner, the surface concentration of the dye must be known in order to make an intensity based sensor.

The fluorescence changes from grafted DMSCA during resin cure give the technique potential to monitor the fiber/resin interface during composite processing. In order to make a practical sensor device, the magnitude of this spectral change must be related to the physical properties of the interfacial region, such as the extent of cure, cross-link density, glass transition temperature, modulus, or interfacial shear strength. Because the dye is immobilized on the glass surface, the fluorescence response is sensitive to the properties of the interphase. These interphase properties are critical to the quality of the fiber/resin adhesion. Contact angle data can be used to determine when a resin should wet the fiber. When measured in water, a large contact angle represents a low energy surface, and a smaller contact angle represents a higher energy surface. Minimization of fiber/resin surface energy is the thermodynamic driving force that promotes fiber wetting and quality adhesion at the fiber/resin interface. Although other factors, such as the presence of a reactive coupling agent or the extent of interphase formation, may also contribute the interfacial strength, if the resin does not wet the fiber, then the interface will be weak. Figure 9 shows that the fluorescence response from the immobilized DMSCA is sensitive to the surface energetics of the coupling agent layer. This result suggest that the DMSCA fluorescence response can be related to the ability of the resin to wet the fiber and the quality of the fiber/resin adhesion.

SUMMARY

The DMSCA fluorescent dye probe can be grafted to the glass surface with a diluting coupling agent. A blue shift and fluorescence intensity increase from the grafted DMSCA can be followed during the cure of an epoxy overlayer, giving this technique potential to monitor the fiber/resin interface during composite processing. These fluorescence changes are due to the combined effect of a decrease in the dielectric constant of the resin and an increase in the interfacial viscosity during cure. However, monitoring the spectral shift from the grafted dye would be more practical than monitoring intensity changes in fluorescence. Contact angle data showed that the presence of DMSCA in the coupling agent layer had a negligible effect on the surface energy of the layer. The fluorescence response of the DMANS fluorophore is qualitatively similar when the molecule is dissolved in a solvent or immobilized in a coupling agent layer. In an increasingly polar environment, the fluorescence from both DMANS and the grafted DMSCA occurs toward longer wavelengths.

In order to make a practical sensor device using this technique, three requirements must be met. First, a fluorescence change from DMSCA must be measurable during resin cure. This work has demonstrated that requirement. Second, the coupling agent layers should be made thinner and be grafted to a glass fiber optic. The fiber optic could then be inserted into a composite mold and used as an *in situ* cure monitoring sensor. Since the DMSCA dye is grafted to the glass surface, the technique would be sensitive to the critical interfacial region in a composite material. Finally, in order to interpret the sensor response, the magnitude of these spectral changes must be related to physical changes in the interphase region. The results of Fig. 9 suggest that the fluorescence response of the grafted dye can be related to the resin adhesion to the surface.

Many variables can influence the fluorescence response from the grafted DMSCA molecule. For example, the chemical functionality and reactivity of the diluting coupling agent, the layer stability, surface roughness, density, and thickness can all affect the ability of the resin to penetrate and interact with the coupling

agent layers and thus affect the dye response. The relationship between the structure of the coupling agent layer and the quality of the fiber/resin adhesion is the focus of ongoing research. The goal of this work is to relate the fluorescence response from the immobilized DMSCA to the structural changes that occur in the interphase region during processing and to use this fluorescence response to predict the quality of the adhesion.

ACKNOWLEDGMENTS

Special thanks to Mr. Kwame Griffith, Dr. Ashebir Fiseha, and Dr. Ryan Cameron for aid in the synthesis of the DMSCA dye, to Dr. Douglas Robello for useful discussions about the synthesis and supplying the HMANS molecule, and to Dr. William Birch for suggestions about the organic based deposition procedure.

REFERENCES

1. Hazen, J. R., and editorial staff, *Compos. Technol.* **4**(3), 6–25 (1998).
2. Parnas, R. S., Salem, A. J., Kendall, K. N., and Bruschke, M. V., "*U.S. Department of Commerce, National Institute of Standards and Technology*," No. 5373. NISTIR, Gaithersburg, MD, 1993.
3. Advani, S. G., "Flow and Rheology in Polymer Composites Manufacturing." Elsevier, New York, NY, 1994.
4. Hunston, D., McDonough, W., Fanconi, B., Mopsik, F., Wang, F., Phelan, F., and Chiang, M., "*U.S. Department of Commerce, National Institute of Standards Technology*," No. 4514. NISTIR, Gaithersburg, MD, 1991.
5. Schwab, S. D., and Levy, R. L., *in* "Polymer Characterization: Advances in Chemistry Series 227," p. 397. ACS, Washington, DC, 1990.
6. Sung, C. S. P., and Sung, N. H., *Mater. Sci. Eng.* A **162,** 241 (1993).
7. Miller, D. E., Krueger, R. H., and Torkelson, J. M., *J. Polym. Sci.* B **33,** 2343 (1995).
8. Sung, C. S. P., and Sun, H. L., *Macromolecules* **19,** 2922 (1986).
9. Sung, C.S.P., and Song, J. C., *Macromolecules* **26,** 4818 (1993).
10. Lin, K. F., and Wang, F. W., *Polymer* **35,** 687 (1994).
11. Neff, R. A., Woerdeman, D. L., and Parnas, R. S., *Polym. Compos.* **18**(4), 518 (1997).
12. Woerdeman, D. L., Spoerre, J. K., Flynn, K. M., and Parnas, R. S., *Polym. Compos.* **18,** 133 (1997).
13. Paik, H.-J., and Sung, N. H., *Polym. Eng. Sci.* **35**(12), 1025 (1994).
14. Dang, W., and Sung, N. H., *Polym. Eng. Sci.* **34**(9), 709 (1994).
15. Fuchs, A., and Sung, N. H., *in* "Polymer Surfaces and Interphases: Characterization, Modification and Application," pp. 345–360, SPE Symposium ANTEC, 1995, VSP, Boston, 1997.
16. Parnas, R. S., and Woerdeman, D. L., "Proceedings, ASME International Mechanical Engineering Congress and Exposition, Dallas, TX." 1997.
17. Plueddemann, E. P., "Silane Coupling Agents." Plenum, New York, 1982.
18. Plueddemann, E. P., "Composite Materials: Interfaces in Polymer Matrix Composites," Vol. 6. Academic Press, New York, 1974.
19. Palmese, G. R., and McCullough, R. L., *J. Adhes.* **44,** 29 (1994).
20. Nishiyama, N., Komatsu, K., Fukai, K., Nemoto, K., and Kumagai, M., *Composites* **26**(4), 309 (1995).
21. Hamada, H., Ikuta, N., Nishida, N., and Maekawa, Z., *Composites* **25**(7), 512 (1994).
22. Larson, B. K., and Drzal, L. T., *Composites* **25**(7), 711 (1994).
23. Moussawi, H. A., Drown, E. K., and Drzal, L. T., *Polym. Compos.* **14**(3), 195 (1993).
24. Ingersoll, C. M., and Bright, F. V., *Chem. Technol*. Jan., 26 (1997).
25. Rosenzweig, Z., and Kopelman, R., *Sen. Actuators B.* **35–36,** 475 (1996).
26. Shortreed, M., Kopelman, R., Kuhn, M., and Hoyland, B., *Anal. Chem.* **68**(9), 1414 (1996).
27. Thomason, J. L., *Composites* **26**(7), 487 (1995).
28. Lakowicz, J. R., "Principles of Fluorescence Spectroscopy." Plenum, New York, 1983.
29. Robello, D. R., *J. Polym. Sci.* A **28**, 1 (1990).
30. Chaput, F., Riehl, D., Lévy, Y., and Boilot, J.-P., *Chem. Mater.* **5,** 589 (1993).
31. Chaput, F., Riehl, D., Boilot, J.-P., Cargnelli, K., Canva, Lévy, Y., and Brun, A., *Chem. Mater.* **8,** 312 (1996).
32. Ishida, H., and Koenig, J. L., *J. Colloid Interface Sci.* **64**(3), 555 (1978).
33. Peanasky, J., Schneider, H. M., Granick, S., and Kessel, C. R., *Langmuir* **11,** 953 (1995).
34. Lapouyade, R., Kuhn, A., Letard, J.-F., and Rettig, W., *Chem. Phys. Lett.* **208**(1,2), 48 (1993).
35. Gruen, H., and Gorner, H., *J. Phys. Chem.* **93,** 7144 (1989).
36. Strehmel, B., Strehmel, V., and Younes, M., *J. Polym. Sci.* B **37,** 1367 (1999).
37. Nass, K. A., and Seferis, J. C., *Polym. Eng. Sci.* **29**(5), 315 (1989).
38. Wang, F. W., and Fanconi, B. M., "*U.S. Department of Commerce, National Bureau of Standards*," 87-3581. NBSIR, Gaithersburg, MD, 1987.
39. Warman, J. M., De Hass, M. P., Hummel, A., Varma, C. A. G. O., and Van Zeyl, P. H. M., *Chem. Phys. Lett.* **87**(1), 83 (1982).
40. Shorygin, P. P., and Ivanova, T. M., *J. Soviet Phys. Doklady* **3,** 764 (1958).
41. Montserrat, S., *J. Polym. Sci.* B **32,** 509 (1994).
42. Montserrat, S., Gomes Ribelles, J. L., and Meseguer, J. M., *Polymer* **39**(16), 3801 (1998).
43. Palmese, G. R., and McCullough, R. L., *J. Adhes.* **52,** 101 (1995).