Interfacial Response of a Fluorescent Dye Grafted to Glass

Joseph L. Lenhart,† John H. van Zanten,‡ Joy P. Dunkers,§ and Richard S. Parnas*,§

Chemical Engineering Department, Johns Hopkins University, Baltimore, Maryland 21218, Chemical Engineering Department, North Carolina State University, Raleigh, North Carolina 27695, and Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received April 12, 2000

The properties of an epoxy/glass interfacial region are studied by covalently grafting a fluorescent probe to the glass surface. A dimethylaminonitrostilbene fluorophore is tethered to a triethoxysilane-coupling agent, generating a fluorescently labeled silane coupling agent (FLSCA). The glass surface is coated with a silane layer that was doped with small amounts of FLSCA. When the FLSCA-doped, silane-coated glass is immersed in epoxy resin, a 42-nm blue shift in fluorescence occurs during resin cure over the grafted FLSCA layer. When the dye is dissolved in bulk epoxy a 64-nm blue shift occurs during resin cure. The difference in blue shift is attributed to higher polarity and enhanced mobility in the buried interface.

Introduction

The surface properties of polymers are known to be different from those of the bulk polymers and many techniques have been used to probe these surface properties. The mobility and glass transition behavior of a polymer at surfaces and interfaces may be different from the bulk polymer behavior. Preferential segregation of low-molecular-weight polymer fractions, or chain ends to the interface,[1] and lower entanglement density near the interface[2] could reduce the glass transition in this region. For linear polymers, the perturbed polymer structure will typically extend on the order of a radius of gyration away from the surface. Mobility in the interfacial region is dominated by the interaction between the substrate and the polymer. Keddie et al. used ellipsometry to observe that the glass transition of thin polystyrene films on silicon oxide surfaces was lower than the bulk glass-transition temperature (T_g).[3] Reiter observed, using X-ray reflectometry, that thin polystyrene films could dewet a silicon wafer even below the glass transition of the bulk polymer, suggesting a lower effective T_g in the thinner films.[4] The interaction between the silicon oxide surface and polystyrene is weak. When poly(methyl methacrylate) (PMMA) films are cast on a silicon wafer, the interfacial mobility can decrease because of the strong interaction between the oxide surface and PMMA. For example, the glass transition of PMMA films on a silicon wafer can increase by ∼30 °C.[5] Also, the thermal expansivity of thin PMMA films on a silicon wafer were lower than the bulk PMMA, both above and below the T_g.[6]

For thermosetting resins near a solid surface, the problem is even more complicated than with linear polymers. In addition to the effects of the solid surface, a thermoset is reacting in the presence of the substrate. Thermosetting resins can contain impurities, and often a mixture of many monomers, which can vary both in composition and molecular weight.[7,8] Preferential diffusion of different monomers or low-molecular-weight plastizers to the surface can change the interfacial cure behavior. In addition, the substrate surface is often coated with a sizing layer (often a silane coupling agent) to promote adhesion and durability at the interface.[9−11] The sizing layer can vary in thickness from tens of angstroms to hundreds of nanometers depending on the application. In fiber-reinforced composites, the sizing layer may also include processing aids such as a film former, anti-static agent, and lubricant, in addition to the coupling agent. The presence of the sizing layer, interpenetration between the sizing layer and the curing thermoset, and potential reactivity between the sizing and resin can further alter the interfacial structure. Because of these factors, the interfacial region for a thermosetting resin can extend 100−500 nm away from the substrate and may extend several microns in certain cases (much farther than a radius of gyration of a typical linear polymer). The cure difference near the interface causes a composition gradient that extends from the substrate into the resin. This compositional and resultant morphological difference may cause the interfacial region to have different properties from the bulk resin. These differences are manifested by changes in the T_g, coefficient of thermal expansion, and the viscoelastic properties of the interfacial region when compared with the bulk resin.[12] These differences will

* To whom correspondence should be sent.
† Johns Hopkins University.
‡ North Carolina State University.
§ National Institute of Standards and Technology. 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.

(1) Mayes, A. M. *Macromolecules* **1994**, *27*, 3114.
(2) Brown, H. R.; Russell, T. P. *Macromolecules* **1996**, *29*, 798.
(3) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59.
(4) Reiter, G. *Macromolecules* **1994**, *27*, 3046.
(5) Wallace, W. E.; van Zanten, J. H.; Wu, W. L. *Phys. Rev. E.* **1995**, *52*, R3329.
(6) Wu, W. L.; van Zanten, J. H.; Orts, W. J. *Macromolecules* **1995**, *28*, 771.
(7) Drzal, L. T. The Interphase in Epoxy Composites. In *Advances in Polymer Science*; Dusek, K., Ed.; Springer-Verlag: Berlin, 1986; p 1.
(8) Morris, C. E. M.; Pearce, P. J.; Davidson, R. G. *J. Adhes.* **1982**, *15*, 1.
(9) Plueddemann, E. P. *Composite Materials: Interfaces in Polymer Matrix Composites*; Academic Press: New York, 1974; Vol. 6.
(10) Larson, B. K.; Drzal, L. T. *Composites* **1994**, *25*, 711.
(11) Thomason, J. L. *Composites* **1995**, *26*, 487.
(12) Palmese, G. R.; McCullough, R. L. *J. Appl. Polym. Sci.* **1992**, *46*, 1863.

10.1021/la000553n CCC: $19.00 © 2000 American Chemical Society
Published on Web 09/15/2000

affect the adhesive quality and durability of the resin/substrate bond.

Studying a buried interface is more difficult than studying polymer films or surfaces, and few techniques are available. Neutron reflectivity has potential for monitoring buried polymer interfaces with nanometer-scale resolution. Neutron reflectivity was used to study the diffusion of grafted polymer brushes into a cross-linked network[13] and water adsorption at the polymer/silicon wafer interface.[14−16] Neutron reflectivity was also used to study diffusion between a thin *d*-PMMA layer buried near a silicon wafer by bulk PMMA. As the thickness of the buried *d*-PMMA layer decreased, the interdiffusion slowed significantly, suggesting reduced polymer mobility near the wafer surface.[17,18] Sum-frequency vibrational spectroscopy is a newly developing in situ technique for studying solid/liquid interfaces[19] and has the potential to study the buried polymer interface. A variety of destructive techniques such as X-ray photoelectron spectroscopy[20] and secondary ion mass spectrometry[21] can potentially be used to depth profile the chemistry changes from the polymer surface to the buried interfacial region. Various microscopy techniques can be used to study buried interfaces in cross-sectioned samples, but these techniques are destructive and can require difficult sample preparation. Atomic-force microscopy was used to probe the modulus of an epoxy resin near glass fibers[22] in a cross-sectioned and polished sample. Scanning and transmission electron microscopies also have potential to view the buried polymer/substrate interface if the sample is cross-sectioned. The current techniques, available to study a buried interface, are powerful because of their high-resolution capability. But in general, the expense, difficult or destructive analysis, and difficult sample preparation make them nearly impossible for general usage in the industrial polymer community.

Another approach to in situ monitoring of the buried polymer interface is to use evanescent wave spectroscopy (infrared, near-infrared, Raman, and fluorescence). The advantage of evanescent wave spectroscopy is that the technique can be made practical by wave guiding the radiation down a fiber optic. The major problem is that the evanescent wave can penetrate several microns from the surface, depending on the wavelength.[23] Even though the evanescent power decays rapidly from the surface, a significant portion of the response can come from a micron or more away from the surface. Because the critical area near the surface where the polymer properties are different from the bulk resin is usually less than a micron, the evanescent wave technique does not have true interfacial sensitivity in most cases. Neff et al. used evanescent wave fiber-optic fluorescence with a fluorophore dissolved in epoxy resin to monitor the epoxy cure near the fiber surface.[24] No difference in interfacial cure was observed relative to cure of the bulk resin. They concluded that this was because the penetration depth of the evanescent wave was much larger than the critical interfacial region. Other groups have used evanescent wave near-infrared spectroscopy to probe the reaction between an aminopropylsilane coupling agent coating on the fiber surface and the epoxy monomer.[25] But, for epoxy cured with an amine hardener, it is difficult if not impossible to distinguish between the amine group on the coupling agent and the amine in the hardener, especially because the thickness of the silane layer was not known.

Fluorescence spectroscopy has been used to study various properties of polymer and composite materials. Excimer-forming probes have been used to study miscibility of polymer blends,[26−28] polymer mobility,[29] and the glass transition of thin polymer films.[30] Mobility-sensitive molecules have been used to study polymer relaxation and physical aging effects.[31,32] Fluorescence monitoring has also been used to study water sorption and diffusion in polymers,[33,34] polymer reaction kinetics,[35−38] and the onset of gelation during cure of thermosetting resins.[24,39] Fluorescence lifetime measurements were used to study cross-linking of epoxy resins.[40] Anisotropy decay was used to study the mobility of different molecular-weight polybutadienes.[41] Nonradiative energy transfer was used to study small molecule diffusion in rubbery polymers near the glass transition.[42] Many groups have combined fluorescence spectroscopy with fiber-optic technology to make practical sensor devices to monitor resin cure.[23,24,43−46]

For most of these fluorescence techniques, the dye probe must be dissolved into the bulk resin. This approach can create significant problems. When the dye is in bulk polymer, the molecules are free to diffuse throughout the polymer, making studies of the buried interface difficult. Even if evanescent wave techniques are used, the region of resin sampled by the evanescent wave can still extend into the bulk resin. For industrial usage, other problems exist when dissolving the fluorescent probe in the polymer. First, the probe molecules are often only slightly soluble

(13) Geoghegan, M.; Clarke, C. J.; Boue, F.; Menelle, A.; Russ, T.; Bucknall, D. G. *Macromolecules* **1999**, *32*, 5106.
(14) Kent, M. S.; McNamara, W. F.; Baca, P. M.; Wright, W.; Domeier, L. A.; Wong, A. P. Y.; Wu, W.-L. *J. Adhesion.* **1999**, *69*, 139.
(15) Wu, W.-L.; Orts, W. J.; Majkrzak, C. J.; Hunston, D. L. *Polym. Eng. Sci.* **1995**, *35*, 1000.
(16) Kent, M. S.; Smith, G. S.; Baker, S. M.; Nyitray, A.; Browning, J.; Moore, G.; Hua, D.-W. *J. Mater. Sci.* **1996**, *34*, 927.
(17) Lin, E. K.; Wu W.-L.; Satija S. K. *Macromolecules* **1997**, *30*, 7224.
(18) Lin, E. K.; Kolb, R.; Satija, S. K.; Wu, W. L. *Macromolecules* **1999**, *32*, 3753.
(19) Bain, C. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1281.
(20) Ho-Kei Lo, H.; Chan, C.-M.; Zhu, S.-H. *Polym. Engineer. Sci.* **1999**, *39*, 721.
(21) Spool, A. M. *IBM J. Res. Dev.* **1994**, *38*, 391.
(22) VanLandingham, M. R.; Dagastine, R. R.; Eduljee, R. F.; McCullough, R. L.; Gillespie, J. W. *Composites A* **1999**, *30A*, 75.
(23) Parnas, R. S.; Woerdeman, D. L. *Proceedings of the ASME International Mechanical Engineering Congress & Exposition*, Dallas, Texas, 1997.
(24) Neff, R. A.; Woerdeman, D. L.; Parnas, R. S. *Polym. Compos.* **1997**, *18*, 518.
(25) Connell, M. E.; Cross, W. M.; Snyder, T. G.; Winter, R. M.; Kellar, J. J. *Composites A* **1998**, *29A*, 495.
(26) Semerak, S. N.; Frank, C. W. *Macromolecules* **1981**, *14*, 443.
(27) Gashgari, M. A.; Frank, C. W. *Macromolecules* **1981**, *14*, 1558.
(28) Semerak, S. N.; Frank, C. W. *Macromolecules* **1984**, *17*, 1148.
(29) Bokobza, L.; Pham-Van-Cang, C.; Monnerie, L.; Vandendriessche, J.; De Schryver, F. C. *Polymer* **1989**, *30*, 45.
(30) White, C. C.; Wu, W. L. Unpublished results.
(31) Schwab, S. D.; Levy, R. L. In *Polymer Characterization*; Advances in Chemistry Series 227; American Chemical Society: Washington, DC, 1990; p 397.
(32) Royal, S. J.; Torkelson, J. M. *Macromolecules* **1993**, *26*, 5331.
(33) Sung, C. S. P.; Sung, N. H. *Mater. Sci. Eng.* **1993**, *A162*, 241.
(34) Miller, D. E.; Krueger, R. H.; Torkelson, J. M. *J. Polym. Sci. Part B: Polym. Phys.* **1995**, *33*, 2343.
(35) Sung, C. S. P.; Sun, H. L. *Macromolecules* **1986**, *19*, 2922.
(36) Sung, C. S. P.; Song, J. C. *Macromolecules* **1993**, *26*, 4818.
(37) Loutfy, R. O. *J. Polym. Sci. Part B: Polym. Phys.* **1992**, *20*, 825.
(38) Pekcan, O.; Yilmaz, Y.; Okay, O. *Polymer* **1997**, *38*, 1693.
(39) Lin, K. F.; Wang, F. W. *Polymer* **1994**, *35*, 687.
(40) Strehmel, B.; Strehmel, V.; Younes, M. *J. Polym. Sci. Part B: Polym. Phys.* **1999**, *37*, 1367.
(41) Fofana, M.; Veissier, V.; Viovy, J. L.; Monnerie, L. *Polymer* **1989**, *30*, 51.
(42) Deppe, D. D.; Miller, R. D.; Torkelson, J. M. *J. Polym. Sci. Part B: Polym. Phys.* **1996**, *34*, 2987.
(43) Woerdeman, D. L.; Spoerre, J. K.; Flynn, K. M.; Parnas, R. S, *Polym. Compos.* **1997**, *18*, 133.
(44) Paik, H.-J.; Sung, N. H. *Polym. Eng. Sci.* **1994**, *34*, 1025.
(45) Dang, W.; Sung, N. H. *Polym. Eng. Sci.* **1994**, *34*, 709.
(46) Fuchs, A.; Sung, N. H. In *Polymer Surfaces and Interphases: Characterization, Modification and Application*; SPE Symposium ANTEC 1995; VSP: Boston, 1997; p 345.

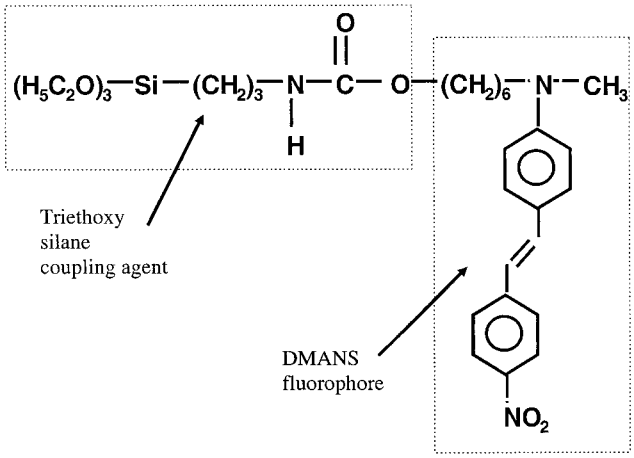

Figure 1. DMANS fluorophore is tethered to a triethoxysilane coupling agent, giving the FLSCA molecule shown here. This entire molecule is then grafted to the glass surface, immobilizing the DMANS fluorophore at the interface.

in the resin systems, so extensive mixing may be required before processing. Second, small amounts of the dye can change the resin color. To overcome these difficulties, we propose immobilizing the fluorescent probe directly to the substrate surface. Then the fluorescence response can only come from the interfacial region.

Technique

Two major goals are the focus of our work: the first is to develop an in situ, fluorescence-based sensor to monitor the properties of the critical buried interfacial region near the glass surface, and the second is to make the technique practical as a process control tool for composite manufacturing. This paper will demonstrate the interfacial sensitivity of the technique.

To obtain true interfacial sensitivity, the dye probe must be grafted to the substrate surface. Then the fluorescence response can only come from the interfacial region. In this work, a dimethylaminonitrostilbene (DMANS) fluorophore was tethered to a triethoxysilane coupling agent, generating the fluorescently labeled silane coupling agent molecule (FLSCA) shown in Figure 1. The chemistry of this tethering reaction is shown in the literature.[47−50] The FLSCA coupling agent can then be grafted to the glass surface using typical silane coupling agent chemistry.[51] To make the technique practical for sensor applications, FLSCA can be grafted to a glass fiber optic and inserted into a composite mold to perform in situ measurements during processing.[52]

A pure FLSCA layer is not grafted to the glass surface. Instead, the FLSCA dye is diluted in the deposition solution to trace levels with another coupling agent. This FLSCA/diluting coupling agent mixture is then grafted to glass to generate a model interfacial region. An epoxy/coupling agent/glass interfacial region is a useful model, because coupling agents are commonly used to coat fiber

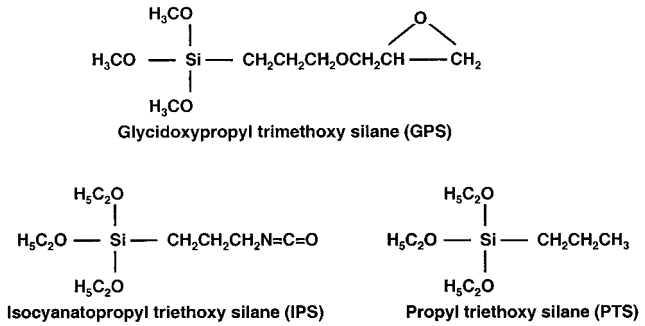

Figure 2. FLSCA dye is diluted to trace levels with one of these coupling agents, to generate a model glass/resin interface and test the effects of the grafting procedure on the FLSCA fluorescence response.

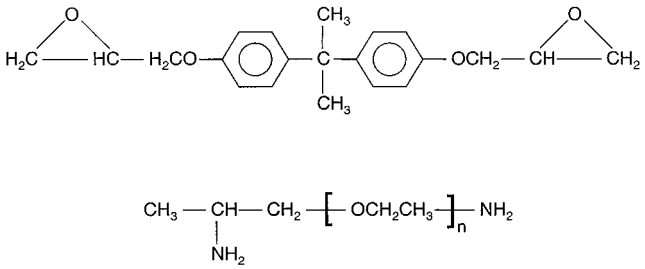

Figure 3. Amine-hardened epoxy resin system. Top structure is Tactix 123; bottom structure is Jeffamine D400.

reinforcements in glass-reinforced composite parts. Coupling agents are also useful for preventing water adsorption at the silicon wafer/resin interface for semiconductor chips.

After the FLSCA is grafted, the coated glass surface is immersed in epoxy resin. As the epoxy resin cures, the fluorescence response from the grafted FLSCA is measured. The goal of this work is to demonstrate that this technique can be used to monitor cure of the epoxy resin, and that the grafted FLSCA is sensitive to the buried interfacial region. To demonstrate interfacial sensitivity, the fluorescence behavior of grafted FLSCA was shown to be clearly different than fluorescence from the dye in bulk epoxy.

Experimental Section

Unless otherwise stated, all chemicals were used as obtained from Aldrich Chemical Co. (Milwaukee, WI). FLSCA was synthesized by a method described in a previous paper[47] and the literature.[48−50] Silane coupling agents were used as received from Gelest (Tulleytown, PA). The silane coupling agents that are used to dilute FLSCA are glycidoxypropyltrimethoxysilane (GPS), isocyanatopropyltriethoxysilane (IPS), and propyltriethoxysilane (PTS). The chemical structures of these coupling agents are shown by Figure 2.

The resin system used in this study was an amine-hardened epoxy system. The resin system was composed of a stoichiometric ratio of diglycidyl ether of bisphenol A (Tactix 123, Dow Chemical Co.) mixed with poly(propylene glycol) bis(2-amino propyl ether), (Jeffamine D400, Aldrich). The resin monomers are shown in Figure 3. The two components were mixed together with a mechanical stirrer and then degassed under vacuum for 10 min before use. At room temperature, this resin system reacts slowly, so a negligible amount of reaction occurs during mixing and degassing. The Tactix resin was not purified.

When the DMANS or FLSCA fluorescent molecules were mixed in the resin system, a stock solution of either DMANS or FLSCA in Tactix 123 was made. This stock solution was stirred overnight to allow the dye to dissolve in the resin. Occasionally, the stock solution was gently heated with air during the stirring to prevent crystallization of the Tactix 123 monomer. Before being used, part of the stock solution was diluted with more Tactix 123

(47) Lenhart, J. L.; van Zanten, J. H.; Dunkers, J. P.; Zimba, C. G.; James, C. A.; Pollack, S. K.; Parnas, R. S. *J. Colloid Interface Sci.* **2000**, *221*, 75.
(48) Robello, D. R. *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 1.
(49) Chaput, F.; Riehl, D.; Lévy, Y.; Boilot, J.-P. *Chem. Mater.* **1993**, *5*, 589.
(50) Chaput, F.; Riehl, D.; Boilot, J.-P.; Cargnelli, K.; Canva, Lévy Y.; Brun, A. *Chem. Mater.* **1996**, *8*, 312.
(51) Plueddemann, E. P. *Silane Coupling Agents*; Plenum Press: New York, 1982.
(52) Lenhart, J. L.; van Zanten, J. H.; Dunkers, J. P.; Parnas, R. S. SPE ANTEC 2000 Proceedings, May 7, Orlando, FL; in press.

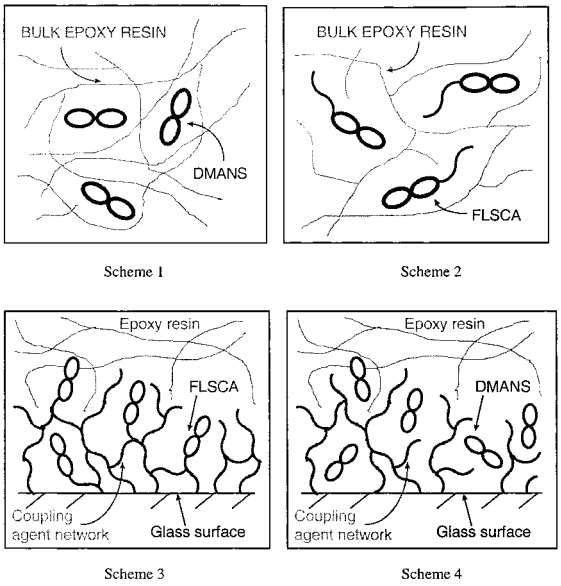

Figure 4. Illustrations of the four experimental schemes.

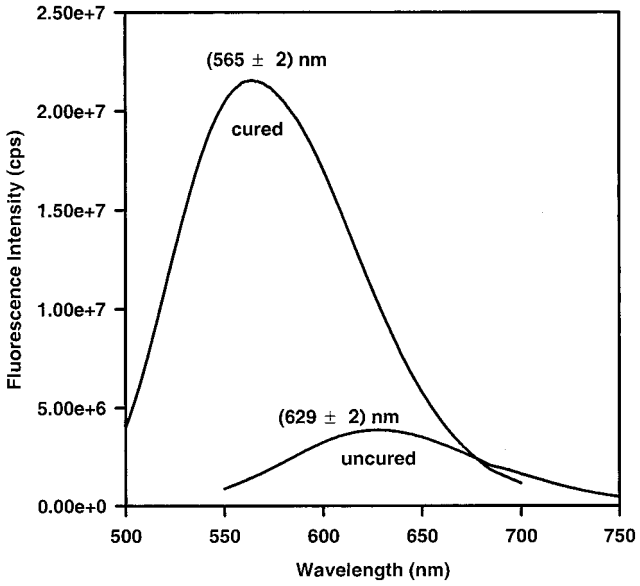

Figure 5. Fluorescence change from DMANS in bulk epoxy (Scheme 1), when the epoxy resin is cured. Three samples were measured for DMANS in uncured epoxy. All the samples had an emission maximum at 629 nm in uncured epoxy and 565 nm in cured epoxy. The position of the maximum was determined visually by estimating where a line tangent to the fluorescence emission had a slope of zero. The uncertainty in the position of λ_{max} is ±2 nm relative to the value displayed in the figure. This uncertainty was estimated from the uncertainty associated with visually determining the maximum of the emission. The relative standard uncertainty of the intensity given in the figure is ±15%.

monomer to achieve the fluorescent dye concentration desired for the particular experiment. The relative amount of D400 to total amount of Tactix 123 always remained the same for each experiment. Only the ratio of the fluorescent dye to Tactix 123 was changed by the dilution. These solutions were then added to a 1 × 1 cm glass cuvette. Absorption and fluorescence measurements were performed on the unreacted epoxy/dye samples at room temperature. The cuvettes were then put in an oven for 4 ± 0.1 h at 100 ± 2 °C to allow the epoxy resin to cure. Absorption and fluorescence measurements were then performed on the cured epoxy/dye samples after being cooled to room temperature.

Coupling agent layers were grafted to glass microscope coverslips (Fisher Scientific, Pittsburgh, PA) using an ethanol-based deposition procedure as described in a previous paper.[47] The coupling agents and FLSCA were added to an ethanol/water mixture with the volume fraction of ethanol equal to 95% under slightly acidic conditions. After hydrolysis of the coupling agents, clean glass microscope coverslips were added to the deposition solution. The coupling agents adsorb to the glass surface. The coated coverslips were then cured at 100 °C for 1.5 h. The coverslips were then dipped in clean ethanol for 15 ± 5 s to remove excess dye and coupling agent that had deposited on the surface during solvent evaporation. The samples were further dried for 1 h at 100 °C. After drying, the samples were sealed in a glass vial and stored in the dark until fluorescence measurements were made about 12 h later.

Fluorescence measurements were first made on the individual coverslips that were exposed only to air. Then, the samples were immersed in the uncured epoxy resin, and fluorescence measurements were again collected. These samples were then put in an oven for 4 h at 100 °C to allow the epoxy resin to cure over the grafted coupling agent coatings. The coverslips were removed from the oven and cooled to room temperature. Fluorescence measurements were then made on the coverslips immersed in cured epoxy.

Fluorescence data was measured using a Spex Fluorolog fluorimeter (Edison, NJ) in the right-angle geometry collection mode. The excitation wavelength was 460 ± 5 nm. To minimize the amount of excitation light that was reflected into the detector, the microscope coverslips were placed at a 60 ± 5° angle relative to the incidence light. For samples of DMANS or FLSCA in bulk epoxy, the cuvettes were placed in a standard holder and fluorescence was measured in the right-angle geometry collection mode.

Absorption measurements were made using a Perkin-Elmer Lambda 9 UV−Vis−NIR spectrophotometer. (Norwalk, CT) A deuterium lamp was the UV source and a tungsten−halogen lamp was the visible source. The detector was a photomultiplier tube. A bandpass of 1 nm and a scan rate of 240 nm/min were used to make the absorption measurements.

Four basic experiments were performed for this paper. These experiments are illustrated in Figure 4. For each experiment either the DMANS or FLSCA fluorescent dye is used. In each experiment the dye molecules are in a slightly different environment. To interpret the fluorescence data it is important to understand which experimental scheme is represented. Scheme 1 shows DMANS dissolved in the bulk epoxy resin. Scheme 2 shows FLSCA in the bulk resin. Scheme 3 shows FLSCA grafted onto a glass microscope coverslip with a diluting coupling agent. The coated coverslip is immersed in the epoxy resin. In this experimental scheme, the FLSCA molecule can covalently bond with the glass surface or the neighboring coupling agent molecules. Scheme 4 shows DMANS dissolved into a diluting coupling agent coating on the glass microscope coverslip. The coated coverslip is immersed in epoxy resin. Unlike FLSCA, the DMANS fluorophores in Scheme 4 cannot covalently bond with the glass or the coupling agent molecules. The DMANS is not constrained by covalent bonding and is free to diffuse away from the surface into the bulk epoxy resin.

Results

The data in Figure 5 shows the fluorescence emission from DMANS when dissolved into the bulk epoxy resin (Scheme 1). The mole ratio of DMANS to Tactix 123 was 1.0×10^{-5} in the resin mixture. In bulk uncured epoxy, the fluorescence emission from DMANS occurs with an intensity maximum, λ_{max}, at 629 nm. After measuring the fluorescence in uncured epoxy, the solution was heated for 4 h at 100 °C to allow the epoxy resin to cure. Then, the solution was cooled to room temperature, and the DMANS fluorescence was measured in the cured epoxy. In cured epoxy, the fluorescence intensity from DMANS increased and λ_{max} shifted to 565 nm. The blue shift in λ_{max} and the increase in fluorescence intensity are due to

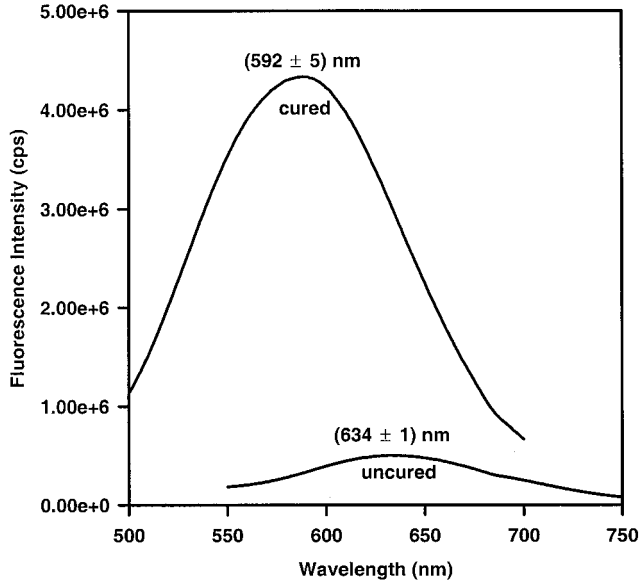

Figure 6. Fluorescence change from grafted FLSCA (Scheme 3) during epoxy cure. The FLSCA dye is diluted on a glass microscope coverslip with the GPS coupling agent. The coated coverslip is immersed in epoxy. The mole ratio of FLSCA to GPS in the deposition solution was 0.2%. The uncertainty is given as a standard deviation from measurements performed on eight samples. The background fluorescence from the control (a coverslip coated only with GPS and immersed in epoxy resin) was small when compared with the fluorescence from the grafted FLSCA layer. The relative standard uncertainty of the intensity given in the figure is ±15%.

both an increase in the resin viscosity and a decrease in the resin dielectric constant during cure.[47,53−56]

Figure 6 shows fluorescence data when the dye molecule is immobilized at the glass/resin interface via the FLSCA coupling agent (Scheme 3). For this experiment, FLSCA was diluted with GPS and grafted to the glass microscope coverslip using the ethanol/water based deposition procedure that is described in the experimental section. The molar ratio of FLSCA to GPS in the deposition solution was 0.2 ± 0.02%. The thickness of the coupling agent coating was 0.8 ± 0.3 μm, as measured by scanning electron microscopy. When the FLSCA/GPS-coated coverslip is immersed in uncured epoxy resin, the grafted FLSCA fluoresces with a maximum intensity at 634 nm. This is similar to the DMANS fluorescence in bulk uncured epoxy. In the cured epoxy, λ_{max} from the grafted FLSCA occurs at 592 nm, which is red-shifted compared with the 565-nm fluorescence of DMANS in bulk cured epoxy. The fluorescence difference between the dye probe in bulk resin and grafted to the glass surface indicates that the mobility and chemistry of the bulk resin are different from those of the buried interfacial region. This could occur if cure differences exist between the bulk resin and the interfacial region.

For the fluorescence to truly represent the polymer structure, the absorption behavior of DMANS must be in the linear concentration range or the fluorescence emission will be distorted. Inner filtering often occurs when the dye concentration is large and the solution absorption deviates from the linear Beer−Lambert regime. Figure 7

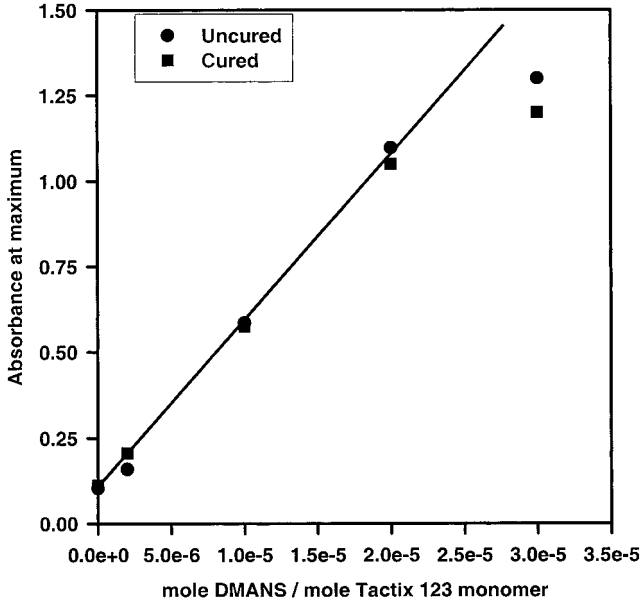

Figure 7. Beer−Lambert plot of the absorption of DMANS in bulk epoxy versus the DMANS concentration. The relative standard uncertainty in the absorption measurement given in the figure is ±0.01 absorption units. The primary uncertainty in the data is due to accurate knowledge of the DMANS concentration in the resin. The DMANS concentration had a relative standard uncertainty in the displayed value of ±10%, on the basis of how accurately the Tactix 123 resin and DMANS dye could be weighed.

Table 1. Fluorescence Shift from DMANS or FLSCA in a Variety of Experimental Schemes

		position of fluorescence maximum	
sample	scheme	uncured epoxy	cured epoxy
DMANS in bulk epoxy	1	629 ± 2	565 ± 2
FLSCA/GPS layer			
large FLSCA concentration	3	634 ± 1	592 ± 5
small FLSCA concentration	3	632 ± 3	590 ± 5
FLSCA in bulk epoxy	2	629 ± 2	566 ± 2
DMANS/GPS layer	4	629 ± 2	566 ± 2

shows the absorption of the DMANS/epoxy solutions (Scheme 1) as a function of the DMANS concentration in the solution. The absorption data was taken at the maximum of the absorption peak, which occurs at 445 nm for DMANS in the epoxy. The DMANS concentration is given as moles of DMANS per mole of Tactix 123 monomer. Figure 7 shows that both cured and uncured solutions maintain absorption in the linear regime until the mole ratio of DMANS to Tactix 123 is 2.0×10^{-5}. At mole ratios above this, the fluorescence emission in epoxy will be red-shifted because of the presence of inner filter effects. At mole ratios below 2.0×10^{-5}, the DMANS fluorescence is not distorted, and occurs with λ_{max} at 565 nm in cured epoxy.

It is also important to demonstrate that fluorescence from the grafted FLSCA is not distorted because of a high FLSCA surface concentration. In addition to previous data, Table 1 shows the fluorescence shift from a FLSCA/GPS layer (Scheme 3) where the FLSCA/GPS mole ratio is very small (≈0.03%). As the resin cures, the fluorescence shifts from 632 nm in uncured epoxy to 590 nm in cured epoxy. The uncertainty is given as a standard deviation on the basis of measurements made from seven samples. A similar FLSCA/GPS layer was made with a molar ratio of ≈1% in the deposition solution. Again the fluorescence

(53) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983.
(54) Lapouyade, R.; Kuhn, A.; Letard, J.-F.; Rettig, W. *Chem. Phys. Lett.* **1993**, *208*, 48.
(55) Gruen, H.; Gorner, H. *J. Phys. Chem.* **1989**, *93*, 7144.
(56) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 12.

shift occurred from ~635 nm in uncured epoxy to ~590 nm in cured resin. Comparing this data with Figure 6 shows that the FLSCA surface concentration, over a broad range (0.03 to 1.0 mol %), does not effect the position of the fluorescence emission, although the fluorescence intensity decreases as the FLSCA concentration is lowered.

A large FLSCA/GPS mole ratio of 0.2% (Figure 6) does not generate an inner filter effect in the grafted layer. But the same DMANS/Tactix ratio (Figure 7) will generate severe inner filtering in the bulk epoxy. This is due to the path length dependence of an inner filter effect. For Figure 7, with DMANS in the bulk epoxy (Scheme 1), a 1×1 cm cuvette was used to measure the fluorescence changes during resin cure. The fluorescence was collected at a right-angle geometry, relative to the excitation beam. For the fluorescence to escape from the cuvette, the photons must travel ≈0.5 cm. In a highly concentrated solution this generates a very high probability that an emission photon will be absorbed by another molecule before it can travel 0.5 cm and escape the cuvette. But for Figure 6, FLSCA was grafted to the glass surface in a thin (≈0.8 μm) layer. At the same dye concentration, the emission photons have a much higher probability of escaping from the 0.8-μm-thick layer before being absorbed. When FLSCA is immobilized in a coupling agent layer, the FLSCA concentration can be much higher than that of DMANS in bulk epoxy and still not cause inner filter effects.

Table 1 also shows the fluorescence shift of FLSCA in bulk epoxy resin (Scheme 2). The uncertainty of λ_{max} is ±2 nm relative to the displayed value was due to the inaccuracy of determining the fluorescence maximum visually. For this experiment, the FLSCA molecule was not grafted to the glass surface, but instead dissolved into the epoxy resin. The fluorescence of FLSCA in bulk epoxy is similar to that of its DMANS precursor (see Figure 5). The λ_{max} of DMANS and FLSCA are the same in the case where the epoxy is cured as well as for the case of uncured epoxy. Because the fluorescence behavior of DMANS and FLSCA are similar in bulk epoxy, this demonstrates that the fluorescence emission of DMANS is not significantly affected by tethering the molecule to a silane coupling agent to make FLSCA. The exact concentration of FLSCA in the epoxy resin could only be estimated, because an unknown amount of the FLSCA powder did not dissolve in the Tactix 123 resin. Inner filter effects were avoided by diluting the resin until the absorption was 0.3. The FLSCA concentration was then estimated by assuming that the absorption behavior of FLSCA in epoxy is similar to the absorption of DMANS in epoxy as shown by Figure 7. For an absorption value of 0.3, Figure 7 shows that the FLSCA concentration would be 6.0×10^{-6}, and is within the linear range of the Beer−Lambert law.

To test whether FLSCA is bound in the coupling agent layer, the grafted GPS layer was doped with the DMANS fluorophore (Scheme 4), instead of FLSCA. Because DMANS does not have a coupling agent tail to covalently attach to the surface layer, the molecule will be free to diffuse away from the glass surface and into the bulk epoxy resin. Table 1 shows the fluorescence response from the DMANS/GPS layer when immersed in the epoxy resin. In uncured epoxy the DMANS/GPS layer fluoresces with a maximum of 629 nm. In cured epoxy the fluorescence maximum occurs at 566 nm. During the 4 h, 100 °C cure, DMANS has significant time and mobility to diffuse away from the glass. DMANS has a λ_{max} at 565 nm in cured epoxy, suggesting that most of the DMANS molecules in the GPS layer diffused away from the surface and into a bulk resin environment. The uncertainty is given as a standard deviation on the basis of measurements taken from five samples. Because fluorescence from the FLSCA/GPS layer in cured epoxy occurs at 592 nm, this data suggests that the FLSCA molecules are bound to the glass surface by the coupling agent layer.

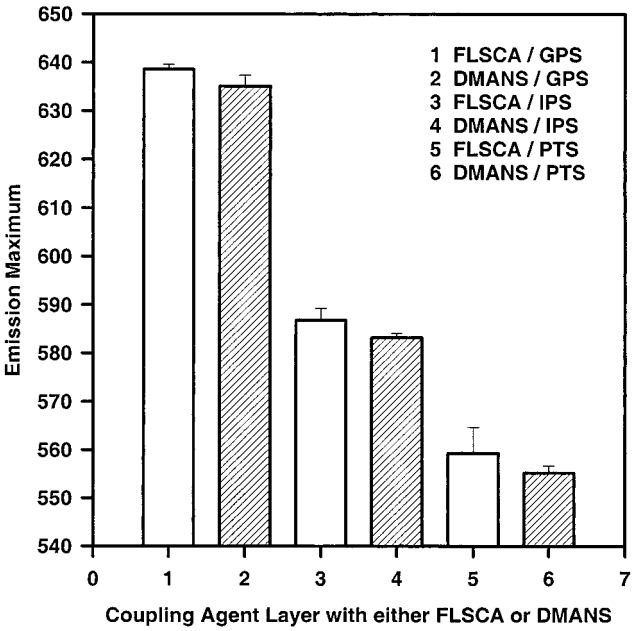

Figure 8. Position of λ_{max} for a coupling agent layer on the glass surface doped with either FLSCA or DMANS. The coupling agent layers were not immersed in epoxy resin. The similar fluorescence behavior shows that grafting FLSCA covalently into a coupling agent layer does not significantly affect the position of the fluorescence emission. The uncertainty is given as a standard deviation. Measurements were taken on at least five samples for each layer type.

Can covalently grafting FLSCA to the glass surface affect its fluorescence response? To test this, the fluorescence of DMANS in a coupling agent layer was compared with that of covalently bound FLSCA in a similar layer. In these experiments FLSCA was deposited with a diluting coupling agent onto the glass microscope coverslip (Scheme 3). A similar deposition procedure was used to deposit a coupling agent layer doped with DMANS (Scheme 4) instead of FLSCA. For these experiments the coated coverslips were not immersed in the epoxy resin. The fluorescence response was completely due to the effects of the coupling agent layer. Figure 8 shows the position of the fluorescence maximum and standard deviations from coupling agent layers containing either DMANS or FLSCA. This data shows that the fluorescence response from the dye is not significantly affected by covalent grafting into the coupling agent layer. This demonstrates that the fluorescence difference between DMANS in bulk cured epoxy (565 nm) and the grafted FLSCA layer immersed in cured epoxy (592 nm) was not due to the effect of constraining FLSCA in the layer.

Discussion

As the epoxy resin cures, a fluorescence intensity increase and blue shift in λ_{max} was observed from DMANS, whether free in the bulk epoxy, free in the coupling agent layer, or bound in the layer by the FLSCA coupling agent. These changes in fluorescence emission are discussed in detail in a previous paper.[47] They are due to both an increase in the resin viscosity during cure and a decrease in the resin dielectric constant during cure. Although the fluorescence intensity change is large during resin cure, it is more practical to monitor the fluorescence shift. The

difficulty associated with an intensity-based sensor is also discussed in the previous paper.[47] For this paper, only the fluorescence shift is discussed. The intensity increase during cure is real, but the magnitude of the increase is obscured by the different geometry between the bulk fluorescence and the grafted FLSCA fluorescence experiments.

A statistically significant difference exists between fluorescence from DMANS in bulk cured epoxy and the grafted FLSCA. This difference suggests a difference in the interfacial properties, which could be caused by cure differences between the interfacial region and bulk resin. A cure variation could occur because of a number of closely related factors. For example, the epoxy functionality of the GPS coating on the glass can potentially react with the amine hardener in the resin. Water adsorption in the interfacial region can accelerate the epoxy amine reaction. The structure of the coupling agent layer will affect the ability of the resin to penetrate the layer. The preferential diffusion of resin monomers into the coupling agent coating could lead to differences in the concentration of reactive groups between the bulk resin and the interfacial region. Finally, the constraint imposed by the solid glass interface could perturb the structure of this region.

To obtain interfacial sensitivity, the FLSCA probe must be bound in the interfacial region. Table 1 shows that λ_{max} for FLSCA occurs at 566 nm in bulk cured epoxy. If most of the FLSCA molecules diffused away from the glass surface, then λ_{max} from the layer would also occur near 566 nm, because the diffused FLSCA will be surrounded primarily by the resin environment. Because λ_{max} from these FLSCA/GPS layers actually occurs near 592 nm, this suggests that the FLSCA molecules remain in the interfacial region during cure. In addition, when DMANS was used in the coupling agent layer instead of FLSCA, Table 1 shows that λ_{max} occurs at 566 nm in cured epoxy. Because DMANS cannot covalently bond with the layer, this shows that the coupling agent tail on FLSCA is able to bind with the layer, and immobilize the dye at the interface.

The blue shift in λ_{max} from grafted FLSCA during resin cure can potentially offer information about the structure of the interfacial region, and how this structure changes during cure. The blue shift indicates that the epoxy is able to penetrate the silane layer. If no interpenetration occurred, then little or no fluorescence shift would be observed from the grafted dye. The extent of interpenetration was not studied in this paper, and would depend on the ratio of the resin reaction kinetics to the kinetics of interpenetration, and on the structure of the initial sizing layer. This dependence is currently being studied. During the epoxy cure at 100 °C, the resin penetrates the silane coating. The resin monomers can react with each other, and with the epoxy functionality in the GPS layer. As polymerization occurs the resin may form an interpenetrating network (IPN) with the coupling agent layer, leading to an interfacial region with a gradient of properties between the glass surface and the bulk resin. As the resin reacts, the chemistry and viscosity of the interfacial region change, causing changes in the fluorescence emission from the grafted FLSCA. The extent of the fluorescence shift from grafted FLSCA may relate directly to the extent of interpenetration between the silane layer and epoxy. This could dramatically affect the adhesion and durability of the interfacial bond.

If this technique is truly sensitive to interfacial formation, then the grafted FLSCA has potential to measure the physical properties of the buried interface. As was mentioned in the introduction, fluorescence has been used to measure the glass transition of thin polymer films. DMANS was used to measure the glass transition of epoxy resins.[31] This suggests that the grafted FLSCA be used to measure the glass transition of the buried interface.

The red-shifted emission from the grafted FLSCA in cured epoxy (Figure 6) relative to DMANS in bulk cured epoxy (Figure 5) could be caused by two factors or a combination of both: (a) a difference in the chemistry or (b) a difference in mobility in the interfacial region. Red-shifted emission indicates that the fluorophore is releasing photons from a lower-energy excited state. For DMANS the emission red-shifts as the polarity of the solvent cage increases.[47,53−56] This suggests that the interfacial region is a more polar environment than the bulk resin. The emission can also be influenced by the mobility of the polymer around the dye. In a mobile environment the emission can be red-shifted relative to a highly constrained environment.[47,53−56] This suggests that mobility in the interfacial region is enhanced. At this point, we cannot separate the chemical and mobility effects. This is the major focus of our current research efforts. The GPS layer is initially more polar than the bulk epoxy (emission from a FLSCA/GPS layer ≈640 nm, emission from DMANS in bulk uncured epoxy ≈629 nm). This is due to the large number of polar oxygen molecules in the silane layer (present in the epoxy functionality on GPS, as covalent bridges between the silane molecules, and potentially as free, uncondensed hydroxyl groups). Even if the resin completely penetrates the silane layer and reacts with all the epoxy functional groups in the layer, the layer would remain more polar than the bulk resin because of the excess oxygen. Silane coupling agents are known to plasticize epoxy resins,[57] so it is reasonable that the IPN between the silane coating on the glass and the resin could have higher mobility than the bulk epoxy. This could lead to a lower glass transition in the interfacial region. Other work has suggested that the glass transition of the interfacial region is lower than in the bulk resin. A lower T_g can be caused by the presence of a sizing package,[57] or by nonstoichiometric monomer concentration[12] due to preferential adsorption of monomers to the interfacial region. Again, these topics are a focus of ongoing work.

An interaction between the glass surface and the FLSCA dye could influence the emission, but because the layers were ≈1 μm thick, it is unlikely that this interaction caused the fluorescence differences observed in Figures 5 and 6. Because the dye can only "see" its surrounding solvent cage, the effects of the glass surface on the FLSCA behavior would only become important in thin silane layers (1−5 monolayers thick). The effect of the layer thickness on fluorescence from the grafted FLSCA was not studied in this paper. Because the structure of the silane layer is dependent on its thickness, the silane thickness could influence the interpenetration between the epoxy and silane. The thickness effect is currently being studied and much thinner layers will be made (less than 100 nm thick).

One final possibility that could influence the fluorescence of grafted FLSCA is phase separation of FLSCA and GPS on the glass surface. If FLSCA agglomerated into high surface concentration areas, inner-filter effects could occur if these phase domains were large. The solubility parameter of the organic functionality on GPS is 19.0 $MPa^{1/2}$.[58] The solubility parameter of the organic end of FLSCA is estimated to be 21.8 $MPa^{1/2}$ by group

(57) Moussawi, H. A.; Drown, E. K.; Drzal, L. T. *Polym. Compos.* **1993**, *14*, 195.
(58) Plueddemann, E. P. *J. Adhes.* **1970**, *2*, 184.

contribution theory.[59] Because the solubility parameters are close, and the FLSCA mole fraction is small, it is unlikely that phase separation occurs on the glass surface.

Summary

We have proposed a general technique for studying the buried polymer layer near a solid surface by immobilizing a fluorescent probe to the solid substrate. An epoxy/silane/glass interfacial region was chosen as a model for this study, but the technique can potentially be used to study other polymer−substrate interfaces. Our results have shown that grafted FLSCA can detect a difference between the interfacial and bulk resin properties. The results suggest a higher polarity or enhanced mobility in the interfacial region. To support this conclusion, we demonstrated that the red-shifted emission from grafted FLSCA relative to bulk epoxy was not due to dye concentration effects, or to covalent binding of the dye in the silane layer. Three key points were shown:

(1) Inner-filter effects do not distort the fluorescence spectrum of DMANS in bulk epoxy, or in the grafted FLSCA layers.

(2) The emission maximum from the dye is not changed by the silane coupling agent tail on FLSCA. In addition, covalently grafting FLSCA with the coupling agent layer on the glass surface does not alter the position of the fluorescence emission.

(3) The FLSCA molecules are actually bound in the coupling agent layer, and in general are not free to diffuse away from the interface and into the bulk resin.

Figure 9 is a graph that summarizes the key points of this paper. First, fluorescence from the FLSCA/GPS layer occurs at 592 nm when the layer is immersed in cured resin. Because DMANS in bulk cured epoxy has a fluorescence maximum at 565 nm, this suggests a cure difference between the bulk resin and the interfacial region. FLSCA in bulk cured epoxy has a maximum at 566 nm. This suggests that the fluorescence from DMANS is not affected by tethering the molecule to a silane coupling agent. It also suggests that the FLSCA molecules remain bound in the interfacial region and do not diffuse into the bulk epoxy. If most of the grafted FLSCA molecules broke from the layer and diffused into the bulk resin, then the fluorescence maximum from the grafted FLSCA/GPS layer would occur at 566 nm instead of 592 nm. The fluorescence maximum from a GPS layer doped with DMANS occurs at 565 nm in cured epoxy. This further verifies that most of the FLSCA molecules are bound in the interphase region by the coupling agent layer. Because DMANS cannot covalently bind with the diluting coupling agent or the glass surface, the molecules are free to diffuse into the bulk resin. The coupling agent tail on FLSCA allows the dye to be immobilized near the glass surface, and remain immobilized in the interphase region during cure. Finally, the data from Figure 8 shows that the DMANS fluorescence emission is not affected by tethering the molecule to a silane coupling agent tail or by grafting the molecule covalently into the coupling agent layer via FLSCA. The curves in Figure 9 were scaled to similar fluorescence intensities to put all curves on the same graph. The scaling factor was the same at all wavelengths, so the scaling process does not affect the position of the fluorescence maximum.

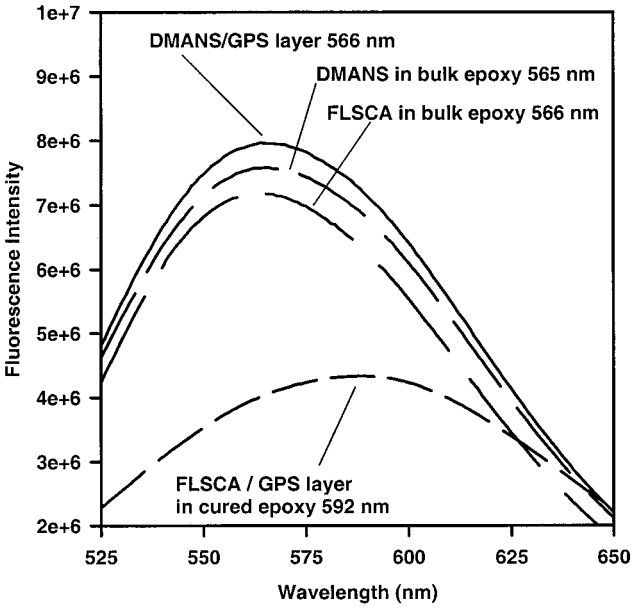

Figure 9. Summary of key results that suggest the grafted FLSCA layer has interfacial sensitivity. The curves are scaled to similar intensities to put all the curves on the same graph.

Acknowledgment. Special thanks to Kwame Griffith, Ashebir Fiseha, Ryan Cameron, Steve Pollack, and Calvin James for aid in the synthesis of the FLSCA dye; also to Douglas Robello for useful discussions about the synthesis and supplying the HMANS molecule, and to William Birch for suggestions about the deposition procedure.

LA000553N

(59) Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC Press: Boca Raton, FL, 1983.