Localizing a Fluorescent Dye to Probe the Buried Interfacial Chemistry

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ABSTRACT

Silane coupling agent multi-layers on glass were doped with small levels of a fluorescently labeled silane coupling agent molecule (FLSCA). When immersed in epoxy resin, a blue shift in the emission from FLSCA could be followed during resin cure. The magnitude of the fluorescence shift was dependent on the thickness of the silane layer. Thicker layers showed smaller shifts, suggesting incomplete resin penetration into the thicker silane layers. External Reflection Fourier Transform Infrared Spectroscopy (FTIR) and angle-resolved X-ray Photoelectron Spectroscopy (XPS) were used to verify penetration between the silane layers and the resin hardener.

INTRODUCTION

The interfacial properties of polymers are known to be different than the bulk polymer. While many techniques are available to study polymer surfaces and thin films, few are available to probe a truly buried polymer / substrate interface. The properties of this buried interfacial region will determine the adhesive strength and durability of the bond, and have technical implications in many areas including composites, electronics, coatings, biomaterials, and adhesives.

In this work, a dimethyl-amino-nitro-stilbene (DMANS) fluorophore was tethered to a triethoxy silane coupling agent tail, generating a fluorescently labeled silane coupling agent, FLSCA (shown in Figure 1). FLSCA can be grafted to the glass surface using typical silane chemistry. Pure FLSCA was not grafted to the surface. Instead FLSCA is diluted in the deposition solution to small levels with another silane coupling agent. The FLSCA / diluting silane mixture is then grafted to a glass microscope cover slip. The diluting coupling agent used in this study was glycidoxypropyl triethoxy silane (GPS), also shown in Figure 1. After deposition, the silane-coated cover slip was immersed in epoxy resin. The fluorescence was measured before and after epoxy cure. Since FLSCA is grafted with the silane layer, the fluorescence response is isolated to the buried interfacial region.

EXPERIMENTAL

Synthesis of the FLSCA dye and the coupling agent deposition procedure was described previously [1]. Varying the total silane concentration of the deposition solution from (0 to 0.2) mmol/mL controls silane layer thickness. The molar ratio of FLSCA to GPS in the deposition solution ranged from 0.002 to 0.005. Layer thickness was determined by scanning electron microscopy on cross-sectioned glass cover slips. The epoxy resin was a stochiometric mixture of diglycidyl-ether-of bisphenol A (DGEBA) [2] cured with a linear diamine hardener, Jeffamine D230 (Figure 1). Fluorescence measurements were made using a Spex Fluorlog fluorimeter [3]. The data uncertainty is given as a standard deviation from measurements made on at least 5 samples.

External reflection FTIR experiments were conducted on the silane coupling agent layers using a 60 ° angle of incidence on a Nicolet FTIR with 1200 scans at a resolution of 4 cm^{-1} and a mercury-cadmium-telluride detector. The XPS analysis was carried out using a SPECS spectrometer equipped with a standard Al Kα ($h\nu$ = 1486.6 eV) x-ray source (anode voltage 15 kV, filament current 20 mA, power 250 W). For the survey-scan spectra, a pass energy of 30 eV, a step size of 0.2 eV, a dwell time of 50 ms, and a scan total of 1 were selected. Spectra were collected with the sample surface oriented either 90° or 40° relative to the analyzer lens. The sampling depths at the 90° and 40° electron take-off angles were estimated to be 5-10 nm and 3-7 nm, respectively [4]. Signal collection utilized a 180° hemispherical analyzer in the constant energy mode. The aliphatic component of the C 1*s* peak (285 eV) was used as a binding energy reference.

RESULTS AND DISCUSSION

The inset in Figure 2 shows typical fluorescence emission from the FLSCA / GPS layers before and after resin cure. A blue shift in the emission maximum and an increase in the fluorescence intensity occur during cure. Since no internal standard exists in this system to normalize the intensity, the emission maximum will be monitored. The emission spectra have a high signal to noise ratio and the emission maximum can be measured to ± 1 nm. Figure 2 plots the total fluorescence shift during resin cure for FLSCA / GPS layers of different thickness and immersed in the epoxy resin. Also shown is the total shift for FLSCA dissolved in the bulk resin.

The blue shift in fluorescence is due to the epoxy-amine reaction during cure. The dye does not respond directly to this reaction but is sensitive to two factors that change with resin cure: a) a decrease in the resin dielectric constant and b) an increase in the resin refractive index. These factors are discussed in detail elsewhere [1,3]. The magnitude of the fluorescence shift during cure can provide information about the buried interfacial structure. Figure 2 shows that the shift from FLSCA in bulk resin was larger than the shift from the grafted FLSCA / GPS layers. This difference in the shift shows that the structure of the buried interfacial region is different than the bulk

resin. In a previous publication we showed that the dye emission maximum was not distorted due to dye concentration, covalent bonding with the silane layer, or tethering the dye to the silane-coupling agent tail [1]. In the absence of these artifacts, changes in the fluorescence shift suggest differences in the interfacial chemistry. The shift from grafted FLSCA/GPS layers shows that the resin molecules are able to penetrate and react with the silane layer. If no inter-penetration occurred, then the local environment surrounding FLSCA would not change and no shift would be observed. The smaller shift from thicker layers suggests that the resin does not completely penetrate or react with the thickest layers. The incomplete penetration is likely caused by a competition between monomer diffusion into the layer, and the resin reaction, which slows the diffusion process. In thick layers the resin gels before complete inter-penetration. We do not expect the shift from FLSCA/GPS layers thinner than 0.1 μm to approach the total shift of the dye in bulk resin. The total shift from extremely thin layers will approach a limiting value near 50 nm as will be discussed below.

Since fluorescence is an indirect measure of the cure reaction, external techniques are needed to relate the FLSCA emission to interfacial chemistry. To verify that the resin monomers are able to penetrate the silane layer, external reflection FTIR experiments were conducted on the thickest FLSCA/GPS layers before and after 20 h immersion in the D230 hardener at 100 °C. In this experiment, the layer was immersed only in the hardener, allowing for equilibrium penetration without diffusion limitations due to gelation. If the layers were immersed in both DGEBA and D230, we can not separate the bulk resin reactions and the interfacial chemistry. The FTIR data is shown in Figure 3. The bottom curve is for FLSCA/GPS layer before immersion in the hardener. The broad band near 3500 cm^{-1} is due to the Si-OH absorption [5]. The peaks at (3050 and 3000) cm^{-1} are due to the CH and CH_2 stretching modes, strained in the epoxide ring on GPS [5]. The top spectrum displays the layer after immersion in the hardener. The two peaks at (3050 and 3000) cm^{-1} are gone, indicating near complete opening of the epoxide groups on GPS. A large broad absorption also occurs at 3450 cm^{-1}, due to the NH stretching of the amine [5].

Figure 3 verifies that the hardener is able to penetrate into the silane layer. After the layer was immersed in D230, the surface was rinsed with clean acetone to remove the excess hardener before the FTIR spectrum was collected. The amine absorption must be due to hardener molecules that have diffused into the FLSCA/GPS layer. The disappearance of the strained CH stretching modes suggests the reaction between the amine on the hardener and the epoxide on GPS. The fluorescence shift during resin cure also suggests this reaction.

The strained CH stretching modes in Figure 3 are not detected after immersion in the hardener, suggesting nearly complete epoxy reaction within the GPS layer. Some epoxy groups, buried in the GPS layer may be inaccessible, but these comprise only a small portion of the layer and were not be detected by the FTIR. Fluorescence measurements on the FLSCA/GPS layer before and after immersion in D230 showed a (50 ± 2) nm shift. This represents the maximum expected shift due to complete reaction of the GPS groups in the silane layer, and is shown in Figure 2 by the dotted line. Since the total shift from the thickest silane layers was less than 50 nm, we propose that an excess of unreacted epoxides exist in the thickest silane layers due to incomplete resin penetration. It is interesting that even with complete epoxide reaction in the silane layer, the total shift is still less than with the dye in bulk resin. This indicates that the interfacial chemistry is different even with complete resin cure. At this time we do not know the specific differences in chemistry.

To further verify inter-penetration between the hardener and the silane layer, an XPS survey scan at a 90° electron take-off angle (Figure 4) was acquired on a FLSCA/ GPS film after immersion in D230. Most of the physically adsorbed diamine was removed by the acetone rinse since discernible Si 2*s* and Si 2*p* peaks (GPS signatures) were present in the spectrum (Figure 4). The spectrum suggests that GPS is dispersed with the diamine molecules, as the relative atomic concentrations of both N (D230 signature) and Si were significantly present. The lower amine concentration at the 90 ° electron take-off angle relative to the 40 ° angle suggest that an amine gradient may be present in the silane layer, with less hardener penetration further into the layer. The relative uncertainty in the atomic concentrations is less than 0.05.

Summary

A fluorescent probe (FLSCA), localized in silane layers on a glass surface, provides a useful technique for studying interfacial chemistry and formation during resin cure. A blue shift in the emission from grafted FLSCA occurs during cure. A smaller shift from thicker FLSCA/GPS layers suggest that the interfacial width is dictated by the competition between the diffusion rate of monomers into the silane layer and the resin reaction kinetics. External reflection FTIR and angle resolved XPS on FLSCA/GPS layers, immersed in hardener, verified the hardener penetration and reaction with the GPS layer. The FTIR and XPS experiments can not provide information about the buried interfacial chemistry for layers immersed in the full resin, because of the similar functionality between the DGEBA monomer and the GPS layer. But FTIR and XPS on model systems can be used to relate the FLSCA emission with the interfacial chemistry.

1. J. Lenhart, J. van Zanten, J. Dunkers, R. Parnas, Langmuir, 16, 8145 (2000).
2. NIST does not endorse any products.
3. J. Lenhart, J. van Zanten, J. Dunkers, C. Zimba, C. James, S. Pollack, R. Parnas, J. Coll. Interface Sci. 221, 75 (2000).
4. D. Briggs and M. Seah, Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, (John Wiley & Sons, 1983).
5. N. Colthup, L. Daly, S. Wiberley, Introduction to Infrared and Raman Spectroscopy, (Academic Press Inc., CA, 1990).

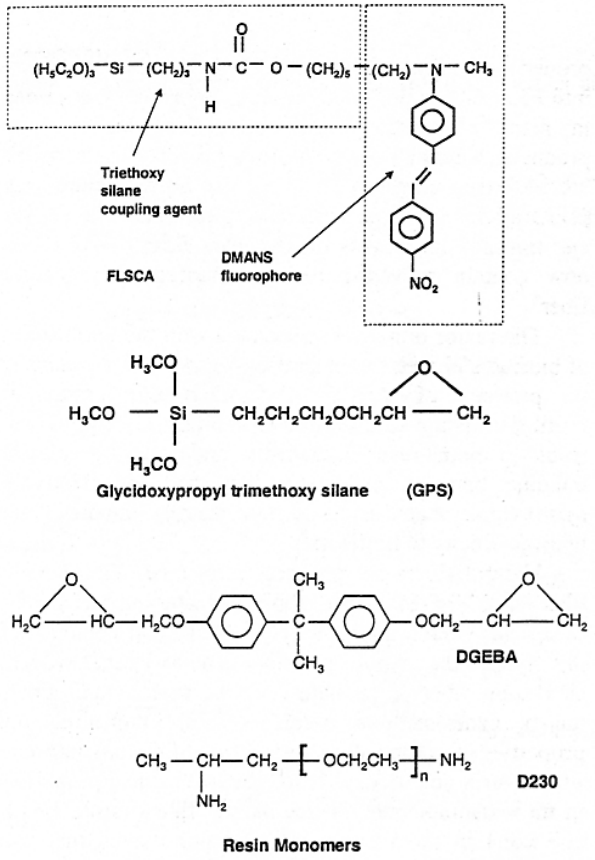

Figure 1. The structure of FLSCA, GPS and the resin.

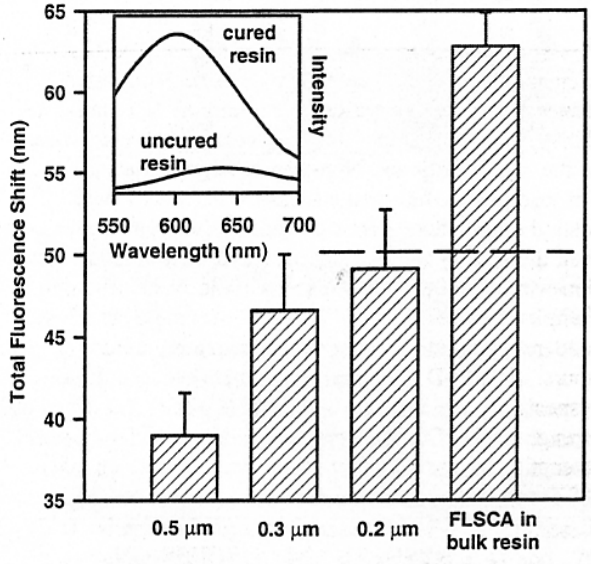

Figure 2. The fluorescence shift during cure for FLSCA / GPS layers of varied thickness. The inset shows typical emission from grafted FLSCA before and after resin cure. The standard deviation in thickness was 50% of the total thickness.

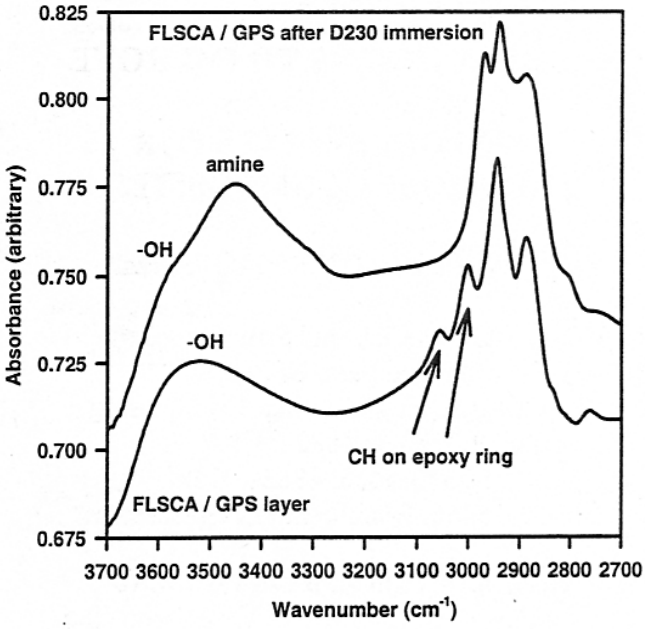

Figure 3. FTIR spectra of FLSCA / GPS layers before (bottom) and after (top) immersion in D230 hardener.

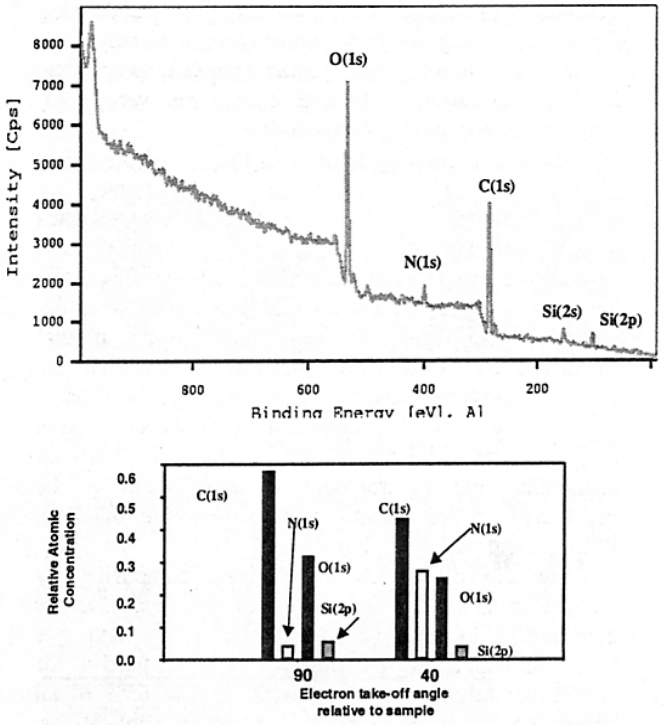

Figure 4. XPS survey scan (top) of the FLSCA / GPS layer after immersion in the hardener. The bottom shows the atomic concentrations at different electron take-off angles. The 90-degree angle probes deeper into the sample.