Studying the Buried Interfacial Region with an Immobilized Fluorescence Probe

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Received September 7, 2000; Revised Manuscript Received January 18, 2001

ABSTRACT: The properties of a buried epoxy/glass interfacial region were studied by covalently grafting a fluorescent probe to the glass surface. A (dimethylamino)nitrostilbene (DMANS) fluorophore was tethered to a triethoxysilane coupling agent, generating a fluorescently labeled silane coupling agent (FLSCA). The glass surface was coated with a silane layer that was doped with small amounts of FLSCA. The emission maximum from grafted FLSCA was different than when the dye was dissolved in bulk resin, suggesting a different interfacial structure. When the dye was dissolved in bulk cured resin, a red shift in the emission maximum was detected as the resin temperature was increased. A distinct break in the fluorescence maximum vs temperature slope was detected at the glass transition of the bulk resin. The slope became larger at temperatures above T_g. A similar break was observed from grafted FLSCA, suggesting that the grafted dye was sensitive to an apparent glass transition in the buried interfacial region. The temperature of the apparent interfacial transition measured by grafted FLSCA could be lower or higher than the bulk polymer T_g, depending on the initial structure of the grafted silane layer.

Introduction

The surface and interfacial properties of polymers and polymer films can be different than the properties of the bulk polymer. Thin polymer films on solid substrates have been studied by a variety of techniques including grazing incidence X-ray diffraction,[1] ellipsometry,[2] X-ray[3,4] and neutron reflectivity,[5,6] fluorescence,[7] and optical methods.[8] All results suggest that the surface and interfacial properties of polymers can be different than the bulk polymer.

While many techniques are available to study polymer surfaces and films, studying a buried polymer/substrate interface is more difficult, and few techniques are available. Neutron reflectivity can probe buried polymer interfaces and has been used to study the diffusion of grafted polymer brushes into a cross-linked network[9] and water adsorption at the polymer/silicon wafer interface.[10,11] Neutron reflectivity has the advantage of nanometer scale spatial resolution but requires contrast usually provided by selective dueteration. Sum-frequency vibrational spectroscopy is an emerging technique for studying solid/liquid interfaces[12] with potential to study the buried polymer interface. Various microscopy techniques can be used to study buried interfaces in cross-sectioned samples (i.e., atomic force microscopy[13] or transmission electron microscopy), but these techniques are destructive and can require difficult sample preparation. In general, the current techniques for studying the buried polymer/substrate interface are either expensive or require difficult or destructive analysis or sample preparation. In addition, none of the above techniques can be used for in-situ studies of the buried interface.

An alternative approach to monitoring the buried polymer interface is to use evanescent wave spectroscopy (infrared, near-infrared, Raman, and fluorescence). The technique can be combined with fiber optics to perform in-situ measurements.[14] The major problem is that the penetration depth of the evanescent wave is usually much larger than the critical interfacial region,[15] so interfacial sensitivity is lost in most cases.

Fluorescence spectroscopy has been used to study various properties of polymers including miscibility of polymer blends,[16] polymer mobility,[17] relaxation and physical aging effects,[18] water sorption and diffusion in polymers,[19,20] and polymer reaction kinetics.[21−24] While fluorescence is useful for studying a wide variety of polymer properties, the major disadvantage is that the dye probe is usually dissolved into the bulk polymer, although it may also be chemically bonded to the polymer. When the dye is in bulk polymer (either free or attached), it is difficult to extract interfacial information. 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. The major goal of this paper is to demonstrate an in-situ, fluorescence-based technique to study the properties of the buried polymer/glass interfacial region.

Technique

To obtain true interfacial sensitivity, the dye probe was grafted to the substrate surface by using a (dimethylamino)nitrostilbene (DMANS) fluorophore 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.[25−28] The

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10.1021/ma0015572 CCC: $20.00
Published on Web 02/23/2001

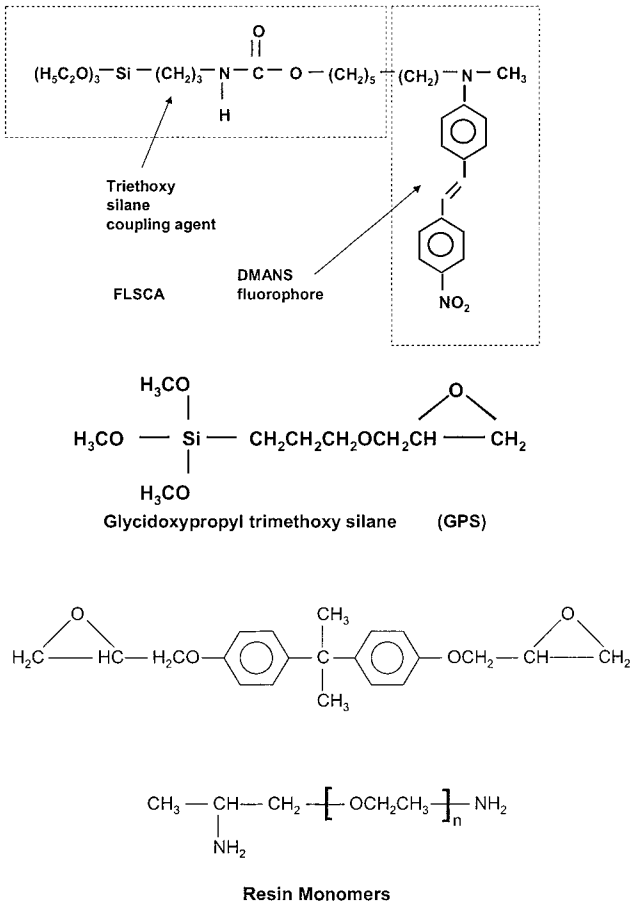

Figure 1. FLSCA coupling agent is made by tethering a (dimethylamino)nitrostilbene (DMANS) fluorescent dye to a triethoxysilane coupling agent, shown on top. FLSCA is diluted on the glass surface with glycidoxypropyltrimethoxysilane (GPS), shown second from top. The amine hardened epoxy resin system is also shown above. Third from the top is the DGEBA monomer. The bottom structure is the diamine hardener. The "*n*" can be adjusted so that the number-average molecular weight of the hardener is 230, 400, or 2000 g/mol.

FLSCA coupling agent can then be grafted to the glass surface using typical silane coupling agent chemistry.[29] For application to process monitoring, FLSCA can be grafted to a glass fiber optic and inserted into a composite mold to perform in-situ measurements.[30]

A pure FLSCA layer was not grafted to the glass surface. Instead, the FLSCA dye was diluted in the deposition solution to low levels with another coupling agent. This FLSCA/diluting coupling agent mixture was then grafted to the glass, generating a model interfacial region. An epoxy/coupling agent/glass interfacial region is a useful model because coupling agents are commonly used to coat fiber reinforcements in glass reinforced composite parts. Coupling agents can also be useful for preventing water adsorption at metal/polymer interfaces.[10] The diluting silane coupling agent used in this study was glycidoxypropyltrimethoxysilane (GPS) (see Figure 1).

After the silane layer was deposited, the FLSCA/GPS coated glass surface was immersed in epoxy resin. As the epoxy resin cures, the fluorescence response from the grafted FLSCA was measured. To test the sensitivity of the dye to polymer mobility, the fluorescence emission was monitored as the cured sample temperature was varied.

Experimental Section

The uncertainty given in the experimental procedure description or shown in the experimental results represents a range of values. For some of the experimental results the uncertainty is shown as a standard deviation based on measurements taken on at least three samples and multiple measurements per sample. When a standard deviation is used, the symbol, (sd), will appear after the number to indicate that a standard deviation is being used.

Unless otherwise stated, all chemicals were used as obtained from Aldrich Chemical Co. (Milwaukee, WI). FLSCA was synthesized by a method described previously in the literature.[25−28] Glycidoxypropyltrimethoxysilane (GPS) was used as received from Gelest (Tulleytown, PA).[31]

The resin system used in this study was an amine hardened epoxy system, composed of a stoichiometric mixture of diglycidyl ether of bisphenol A (Tactix 123, Dow Chemical Co.) and poly(propylene glycol) bis(2-aminopropyl ether) (Jeffamine D2000, D400, or D230; Aldrich Chemical Co.). The resin monomers are also shown in Figure 1. For the amine hardener, "*n*" was varied so the number-average molecular mass was 2000 g/mol (D2000), 400 g/mol (D400), or 230 g/mol (D230). These hardeners were used as received from Aldrich Chemical Co. (Milwaukee, WI). The two components were mixed together with a mechanical stirrer and then degassed under vacuum for 10 min prior to use.

Coupling agent layers were grafted to glass microscope coverslips (Fisher Scientific, Pittsburgh, PA) using an ethanol-based deposition procedure as described previously.[25,32] GPS and FLSCA were added to an ethanol/water mixture with the volume fraction of ethanol equal to 95%, under slightly acidic conditions. The total silane concentration in the deposition solution was 5 vol %. The molar ratio of FLSCA to GPS in the deposition solution was 0.005 ± 0.001. After 5 h hydrolysis of the coupling agents, clean glass microscope coverslips were added to the deposition solution. The coupling agents adsorb to the glass surface for 10 min. The coated coverslips were then cured at 100 ± 2 °C for 1.5 ± 0.2 h. After this cure, some of the coverslips were washed by two successive dips in clean ethanol for 30 ± 5 s. During the ethanol dip, the coated coverslips were vigorously shaken. The purpose of this wash was to remove excess dye and weakly adsorbed coupling agent that had deposited on the surface during solvent evaporation. The remaining coated coverslips were not washed. Both the washed and unwashed coverslips were further cured for 1 ± 0.1 h at 100 ± 2 °C. The samples were sealed in a glass vial and stored in the dark until the sandwich samples and the fluorescence measurements were made the following day.

Scanning electron microscopy measurements on cross sections of the coated coverslips showed that the washed layers were ∼400 nm thick and the unwashed layers were ∼800 nm thick. This is very thick for a silane coupling agent layer used in glass fiber reinforced composites but not an unusual thickness for actual sizing packages used to coat fiber reinforcements.[33] In addition to the coupling agent, a sizing package may also contain lubricants, antistatic agents, or a resin compatible film former. The deposition procedure used in this study is similar to most procedures used for academic research with silane coupling agents. Much of that work, however, does not report the actual thickness or amount of adsorbed material. To demonstrate the potential of this technique, we used coupling agent layers as a model-sizing package. In the future we plan to study silane layers as thin as a monolayer but need to make improvements in the collection efficiency of our fluorimeter. This is not a severe technical obstacle, since single molecule fluorescence measurements have been established.[34] Also, we plan to develop chemistry for attaching the dye to the film former component of the sizing layer to study dissolution of the sizing into the polymer resin.

After the FLSCA/GPS layers were grafted to the glass coverslips, each coated coverslip was sandwiched with uncured epoxy resin between two uncoated glass coverslips. The range of the thickness of the epoxy resin in the sandwich was 25−

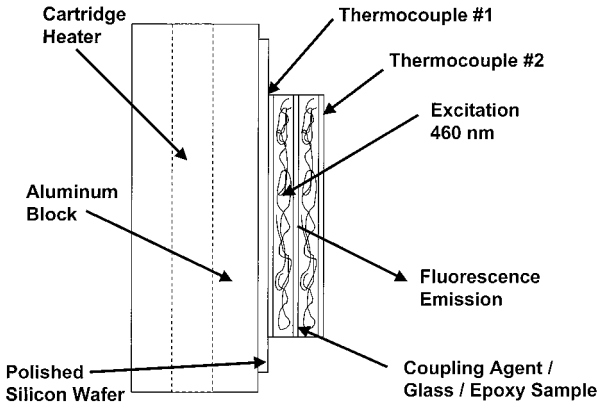

Figure 2. Temperature dependence of the fluorescence emission was monitored by mounting a cured sandwich sample to an aluminum block and heating with a cartridge heater. A polished silicon wafer was put between the sample and the aluminum block to prevent the excitation light from scattering off the aluminum surface and into the detector.

100 μm. This thickness is large enough that the epoxy in the sandwich is similar to bulk resin. Excitation light was sent through the uncoated coverslip and the epoxy resin. The fluorescence was collected from the FLSCA/GPS layer, buried under the thick epoxy sandwich. The fluorescence from grafted FLSCA was measured in uncured resin and cured resin. The sandwich sample was cured in an oven. When DGEBA/D2000 or DGEBA/D400 was used, the sandwich was cured for 4 ± 0.1 h at 100 ± 2 °C. When DGEBA/D230 was used, the sandwich was cured for 4 ± 0.1 h at 100 ± 2 °C, followed by a 1 ± 0.1 h postcure at 130 ± 5 °C. For samples of DMANS or FLSCA in bulk epoxy, the center coverslip in the sandwich was not coated with a FLSCA/GPS coupling agent layer, but the dye was dissolved into the epoxy resin used in the sandwich structure.

After the resin was cured, the sandwich sample was mounted to an aluminum block as is shown by Figure 2. The block was heated with a cartridge heater, and the fluorescence from grafted FLSCA/GPS layers in the cured sandwich was measured as a function of the sample temperature. Thermocouples were placed on both the inside and the outside of the sandwich sample. The sample temperature was taken as the average of the two thermocouple readings. The temperature uncertainty was estimated as one-half the difference between the two thermocouples and is shown in Figures 4 and 5 as an error bar. During these fluorescence experiments, the temperature was varied between 0 and 130 °C. The fluorescence was measured approximately every 10 °C. The temperature was controlled by a feedback control loop through the outside thermocouple. When the set point was increased by 10 °C, it took only a few minutes to reach the set point, but 15 ± 5 min was allowed for the sample temperature to equilibrate around the set point. Control experiments were conducted with no dye grafted to the glass surface or in the epoxy resin. The fluorescence from these control sandwich samples was negligible.

Fluorescence data were 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 sandwich samples were placed at a 60 ± 5° angle relative to the incidence light.

Differential scanning calorimetry (DSC) was conducted on the resins using a Perkin-Elmer model DSC 7. The scan rate was 10 °C/min. The T_g values were similar at a scan rate of 5 °C/min.

Results

Figure 3 shows the change in fluorescence emission during resin cure, when DMANS or FLSCA was dissolved into bulk DGEBA/D400. The emission maximum

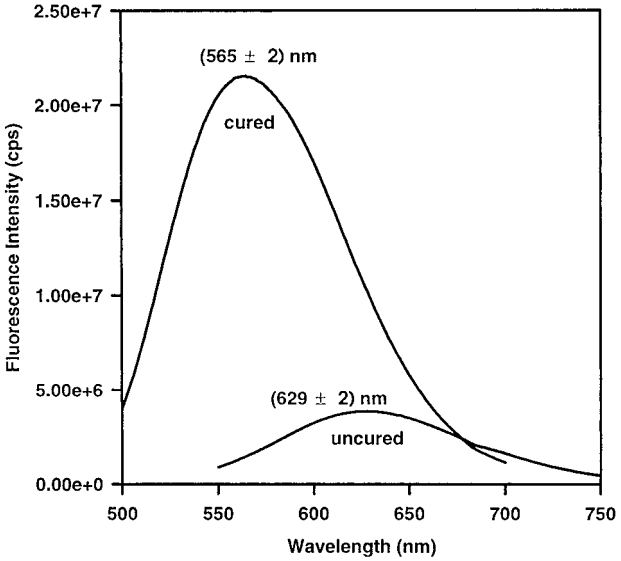

Figure 3. When DMANS or FLSCA was dissolved in bulk resin, a blue shift in the emission maximum and an increase in the fluorescence intensity could be followed during resin cure. Since no internal standard was present to normalize the intensity, it is more practical to monitor the wavelength shift.

for DMANS in bulk epoxy was the same as for FLSCA in the bulk resin. Both a blue shift in the emission maximum and an increase in intensity can be followed during resin cure. These changes in fluorescence emission were due to the combined effects of a decrease in the dielectric constant and an increase in resin viscosity during cure. These effects are discussed in detail in a previous publication.[25,32] The fluorescence in both cured and uncured epoxy was measured at room temperature (24 ± 1 °C). The relative standard uncertainty in the intensity was 10%.

Similar fluorescence changes were observed during resin cure, when washed and unwashed FLSCA/GPS layers were grafted to glass microscope coverslips and the coated coverslips immersed in epoxy resin sandwich samples. The total shift for the dye in bulk resins was largest ranging from 59 to 66 nm. For the washed layers the shift was smallest, ranging from 39 to 50 nm. For the unwashed layers the shift was intermediate between the two. The magnitude of the fluorescence shift can be used to study the buried interfacial chemistry.[32]

To test the sensitivity of the dye to resin mobility, the fluorescence emission was measured as the temperature of the cured sandwich sample was varied. Samples were mounted to an aluminum block with a cartridge heater as shown in Figure 2. The position of the emission maximum can be plotted against temperature. This is shown in Figure 4 for DMANS in both DGEBA/D400 and DGEBA/D230. A distinct break in the slope of the fluorescence maximum vs temperature curve occurred at 41.7 ± 3.1 sd °C for the DGEBA/D400 resin and at 82.2 ± 3.4 sd °C for the DGEBA/D230 resin. These breaks correspond to the onset of the glass transition as measured by differential scanning calorimetry (DSC), shown by the arrows in Figure 4. In Figure 4, horizontal error bars show the range of the sample temperature, as described in the Experimental Section. Three curves are shown for each resin to illustrate the sample-to-sample reproducibility. The inset in Figure 4b shows the fluorescence emission for DMANS in bulk DGEBA/D230 at various temperatures. At low temperatures (low T) the intensity is larger. As the temperature was

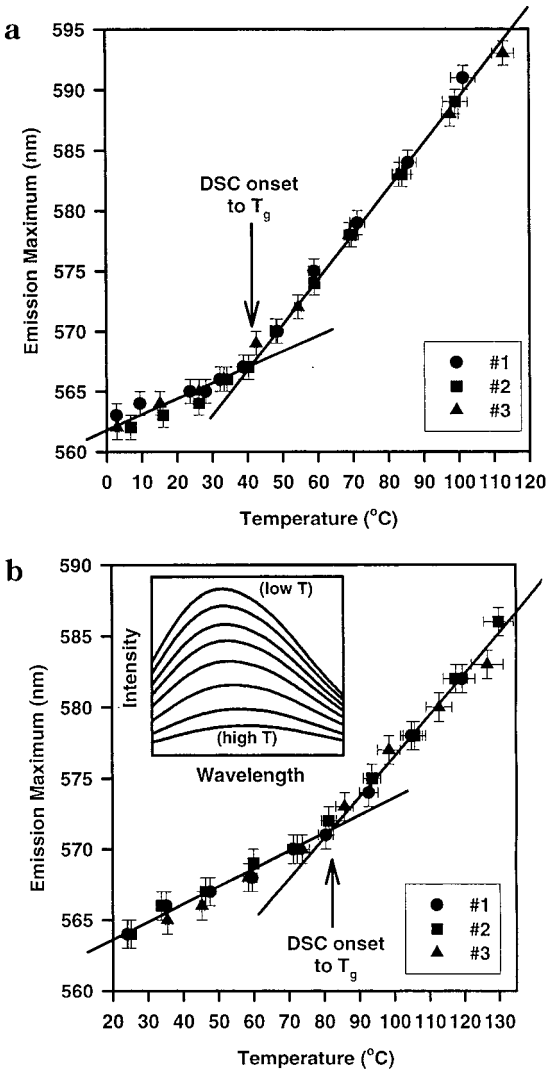

Figure 4. Fluorescence emission maximum vs temperature for (a) DMANS in bulk DGEBA/D400 and (b) DMANS in bulk DGEBA/D230. The break in the slope of the curves corresponds with the onset of the bulk resin glass transition, as measured by DSC (shown by the arrows). The same curves were obtained for FLSCA dissolved in the bulk resins. The inset in (b) shows the fluorescence emission for DMANS in cured DGEBA/D230 at various temperatures.

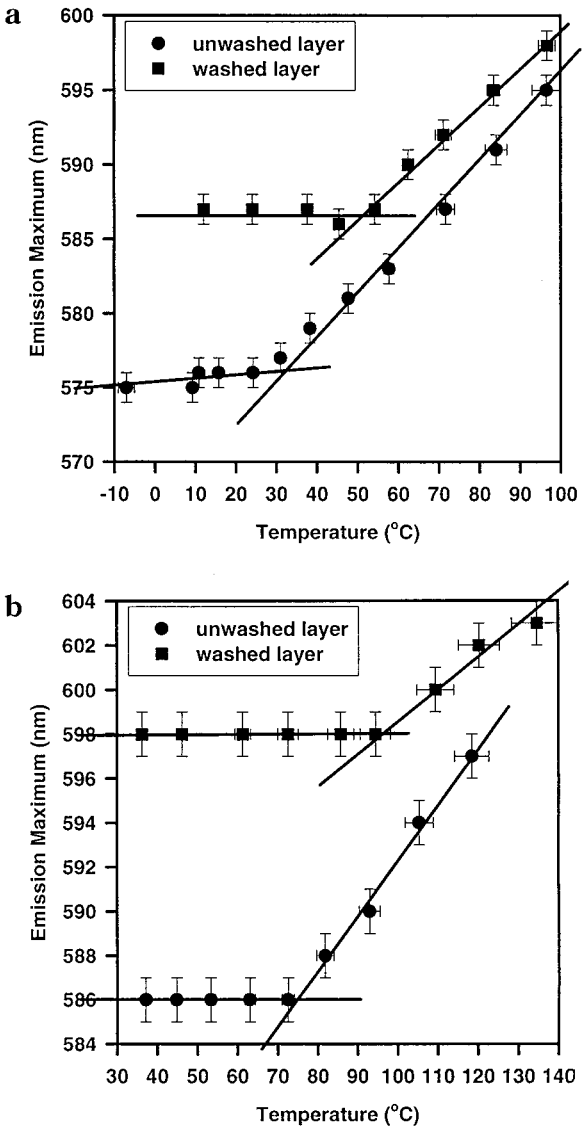

Figure 5. Fluorescence emission maximum vs temperature plots for washed and unwashed FLSCA/GPS layers immersed in (a) DGEBA/D400 or (b) DGEBA/D230. The interfacial transition is dependent on the initial structure of the silane layer.

increased (high *T*), the intensity decreased and the emission maximum shifted to longer wavelengths. The spectra have a high signal-to-noise ratio, and the emission maximum can be measured to ±1 nm.

Figure 5a,b shows the corresponding experiments for both washed and unwashed FLSCA/GPS layers grafted to a glass microscope coverslip and immersed in DGEBA/D400 (Figure 5a) or DGEBA/D230 (Figure 5b). The temperature of the interfacial fluorescence break from grafted FLSCA was different than when the dye was dissolved in bulk epoxy, suggesting a different interfacial structure. In addition, the temperature of the interfacial transition was dependent on the initial structure of the silane layer. Washed layers showed an interfacial transition ranging from 15 to 25 °C higher in temperature than the unwashed layers.

Discussion

After resin cure, an increase in fluorescence intensity and a blue shift in the emission maximum were observed for the dye in bulk resin and FLSCA grafted to the glass surface. These emission changes are due to three factors: a change in the dielectric properties, an increase in refractive index, and an increase in resin viscosity during cure. These effects are discussed in detail in a previous publication.[25,32] No internal standard exists in these samples to normalize the intensity, so intensity measurements are only qualitative. Since the fluorescence spectra have high signal-to-noise ratio, it is more practical to monitor the emission shift rather than intensity.

Comparing the position of the emission maximum from grafted FLSCA/GPS layers (Figure 5) with DMANS in bulk resin (Figure 4) shows that the interfacial properties are different than the properties of the bulk resin. The emission maximum from the grafted FLSCA is offset toward longer wavelengths relative to the dye in bulk polymer. In a previous paper we showed that the fluorescence difference (between grafted FLSCA and DMANS in bulk cured epoxy) was not due to dye concentration effects, tethering a silane coupling agent tail on DMANS to make FLSCA, or covalently grafting the dye into the silane layer.[32] In the absence of these

artifacts, the emission offset could be caused by two factors: a difference in the chemistry near the glass surface relative to the bulk resin and/or enhanced polymer mobility near the glass surface.

To study the mobility dependence, λ_{max} was monitored as a function of temperature. Chemical changes were minimized by making the measurements on the cured sandwich sample, where the chemistry is no longer rapidly changing due to the curing reaction. To understand the dependence of λ_{max} on the polymer mobility, it is important to consider the interaction between the dye and the polymer.

The Lippert equation[35] (eq 1) describes how general solvent effects can cause shifts in fluorescence emission.

$$\nu_a - \nu_f \cong \frac{2}{hc}\left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)\frac{(\Delta\mu)^2}{a^3} + \text{const} \quad (1)$$

where ϵ is the solvent dielectric constant, n is the refractive index of the solvent, c is the speed of light, h is Planck'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 wavenumbers (cm^{-1}) of the absorption and emission intensity maxima, respectively. The Stokes shift is defined as the difference between the absorption and emission 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 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. Equation 1 is derived assuming that all solvent relaxation occurs before the excited dye releases a fluorescence emission. This may not be true for a fully cross-linked network. But eq 1 can still qualitatively show how changes in refractive index and dielectric properties can cause shifts in the emission maximum.

The dielectric mobility of the surrounding solvent can alter the dielectric constant that is observed by the excited dye molecule. In general, we might expect the fluorescence emission to be sensitive to the polymer dielectric relaxation, when the distribution of fluorescence lifetimes overlaps with the distribution of polymer relaxation times. The fluorescence lifetime of DMANS in the cured DGEBA/D400 system was near 5 ns. The α relaxation time is on the order of 100 s. Because of the large difference between the fluorescence lifetime and the polymer α relaxation time, it is unlikely this relaxation is the cause of the fluorescence shift near the polymer T_g. Coupling between short- and long-range chain motion might exist. This could change the local dielectric environment around the excited dye, but from the fluorescence data we cannot determine whether this cooperative motion occurs. Nevertheless, the data in this paper clearly illustrate this sensitivity.

Figure 4 shows that the fluorescence vs temperature slope changes at the temperature corresponding to the α transition. The α transition is associated with large-scale mobility of the polymer backbone and the glass transition. Smaller scale relaxation can also occur in the polymer, such as β and γ relaxations associated with mobility of the cross-links and segmental rotations, respectively. The β and γ transitions will occur at temperatures much lower than the α transition, and we could not go to low enough temperatures to test the dye sensitivity to these transitions. We speculate that the position of the fluorescence maximum will be less sensitive to these smaller scale transitions than to the glass transition. Analyzing the slopes of the fluorescence vs temperature curves, below the apparent T_g, supports this conclusion. When the dye is in bulk DGEBA/D230, the slope of the fluorescence maximum vs temperature curve before the transition was 0.127 ± 0.011 sd nm/°C. For the dye in DGEBA/D400 the slope was 0.150 ± 0.028 sd nm/°C before the transition. Despite a 40 °C difference in the glass transition of these resins, the λ_{max} vs temperature slope was nearly indistinguishable for the two resins in the glassy state. These data suggest that the dye is more sensitive to larger scale network mobility rather than smaller scale relaxation of the glassy state.

To further illustrate the lack of mobility sensitivity with a dye in a glassy polymer, DMANS was dissolved in DGEBA/D230, DGEBA/D400, and DGEBA/D2000. The resins were completely cured. After cure, the DMANS fluorescence was measured at room temperature (24 ± 1 °C). Both DGEBA/D230 and DGEBA/D400 are glasses at room temperature. The room-temperature emission maximum from DMANS in both these glassy resins was 565 ± 2 nm, despite the 40 °C difference in T_g. DGEBA/D2000 has a transition well below room temperature and had an emission maximum at 575 ± 2 nm. Since the chemistry of these resins is very similar (differing only by the molecular mass of the hardener), the different emission from DGEBA/D2000 is due the enhanced mobility of the rubbery polymer. These experiments further illustrate that the fluorescence emission is detecting larger scale motion of the network and is less sensitive to smaller scale dynamics.

Another possible explanation for the dye sensitivity to the α transition is a refractive index change of the polymer. As the temperature is increased, the polymer thermally expands. This will cause a decrease in refractive index. Equation 1 shows that a decrease in refractive index will lead to a red shift in fluorescence. During the transition between the ground and excited states, the electron clouds of the surrounding polarizable molecules can reorient to stabilize both states. The polymer refractive index is related to the density of polarizable molecules. When the refractive index is large, the electronic reorientation is more effective at stabilizing both the ground and excited states. This leads to a smaller Stokes shift and emission from higher energy levels.[35] As the temperature increases, the polymer refractive index decreases due to thermal expansion, causing a red shift in emission. The red shift due to thermal expansion can be estimated by using the Lippert equation (eq 1).[35] Assuming a refractive index change over the glass transition[36] of the polymer is ≈0.04, a refractive index change from 1.60 to 1.56 due to resin expansion will cause a red shift of ∼8 nm. (The parameters used in the Lippert equation for DMANS are discussed in a previous publication.[25]) We are seeing red shifts of 5−20 nm after the polymer glass transition. The red shift we observed over the transitions in Figure 4 and Figure 5 is reasonable considering thermal expansion.

Figure 4 clearly shows the correlation between the fluorescence break and the onset to the glass transition as measured by DSC. Looking at Figure 5, it is tempting to state that we are measuring the glass transition in the buried interfacial region. The grafted dye is obviously measuring an interfacial transition. The temperature of the transition is dependent on the initial structure of the silane layer and is associated with enhanced polymer mobility. But a number of factors need to be considered further before labeling the interfacial transition as the T_g. These factors include (1) a possible gradient of properties, both chemical and mobility, in the buried interfacial region and (2) the possibility of orientation near the glass surface.

First, the interfacial region most likely has a gradient of both chemical and physical properties. It is difficult to define a T_g when a gradient in mobility may exist. The fluorescence spectra suggest that the interfacial gradient is smooth rather than abrupt. If an abrupt change in the interfacial properties existed, then the dye would be in distinct environments. In that case we might see multiple maxima or humps in the emission spectra of FLSCA. Analyzing the width of the emission spectra could provide information about the distribution of local environments surrounding the dye, but this requires accurate measurements of intensity. Since we do not have an internal standard, we have chosen not to focus on intensity-based measurements at this time.

Since the fluorescence is collected over the entire region, the response will represent the averaged properties of the buried interfacial region. Although each dye molecule responds to its local environment, we measure fluorescence from many molecules. The total emission will represent the average environment. This is why fluorescence, a local measurement, can be sensitive to bulk properties. Analyzing the emission maximum vs temperature slopes suggests that the interfacial region has a gradient of properties. The slopes both before and after the transition in the washed FLSCA/GPS layers were smaller than the slopes for both the unwashed layer and the dye in bulk resin. This makes sense, since the washed layers had a higher apparent transition than both the bulk resin and the unwashed layers and since a smaller slope suggests hindered mobility. It is more interesting to compare the slopes of the unwashed layer with the slopes of the dye in bulk resin. The apparent transition temperature in the unwashed layer occurs at a lower temperature than the bulk resin glass transition, suggesting enhanced mobility in the unwashed interfacial region. But, the slopes of the fluorescence maximum vs temperature curves were less for the unwashed layer than for the dye in bulk resin, suggesting an interfacial region with hindered mobility.

Although we do not completely understand the slopes of the λ_{max} vs temperature curves, we will propose an interfacial model that explains the difference in the interfacial transition temperatures and the small slopes from the unwashed layers. Close to the glass surface, the coupling agent layer will be more tightly bound. When the resin reacts with the tightly bound layer, the polymer mobility will be hindered. In addition, the immobile glass surface can potentially restrict the polymer mobility. (This explains the higher interfacial transition temperature from the washed layers.) Further from the glass surface, the coupling agent layer will be less tightly bound and can contain a region of weakly adsorbed coupling agent molecules. When the resin reacts with these weakly bound molecules, the polymer is more mobile. In addition, coupling agents are known to plasticize epoxy resins.[37] (This explains the lower temperature transition from the unwashed layers.) If both factors are present in the unwashed layers, the relative contribution of these two competing effects will determine the averaged interfacial fluorescence response. Since the fluorescence response was collected from the entire interfacial region, with the unwashed layers it may be possible to observe the fluorescence break at lower temperatures (due to a region of plasticized or mobile resin) and still have the slopes being smaller than expected (due to the fluorescence contribution from the less mobile layer near the glass surface).

We did not study the effect of polarized excitation. Fluorescence anisotropy would give information about the orientation of the dye molecules in the interfacial region. If significant orientation exists in the interfacial region, then relaxation of the molecular orientation could contribute to the shift in the emission maximum with temperature because the local dielectric environment surrounding the dye could change. We expect orientation to become increasingly important with thinner layers. The layers used in this study are fairly thick and most likely have a random orientation. Still, the effect could be important very near the glass surface. As we push the technique to probe thinner interfacial regions, we plan to incorporate anisotropy measurements into the analysis to probe molecular orientation near the glass.

In addition to studying mobility, the magnitude of the fluorescence shift can provide information about the chemical composition of the interfacial region. To study the chemistry of the interfacial region, the mobility dependence of the fluorescence emission must be minimized. To do this, the emission can be monitored in the glassy polymer, where the dye is less sensitive to polymer mobility. Figure 5a,b shows that λ_{max} (in cured sandwich samples) for the washed layers was red-shifted relative to the emission from the unwashed layers. Emission from both the washed and unwashed layers was also red-shifted relative to the dye in bulk resin (Figure 4). When the spectra are measured in the glassy state, the offset in the emission must be due to differences in the chemistry of these regions. At this point we do not know the specific chemical differences in the interfacial region, only that the grafted dye can be used to detect chemical differences. This is a focus of ongoing research.

Conclusion

By covalently grafting a dye probe (FLSCA) to glass surfaces, the properties of the submicron buried polymer/glass interfacial region can be studied. Grafted FLSCA can be used to detect both chemical and mobility differences in the interfacial region. By measuring the fluorescence in the glassy polymer, where the mobility sensitivity of the dye is small, the interfacial chemistry can be probed. By monitoring the temperature dependence of the fluorescence emission, mobility transitions in the buried interface were measured. Changing the initial structure of the silane layer alters the transition temperature of the buried interface. Washed layers showed higher transition temperatures than the unwashed layers. The technique is a simple, inexpensive tool to study the interfacial behavior in situ.

References and Notes

(1) Factor, B. J.; Russell, T. P.; Toney, M. F. *Macromolecules* **1993**, *26*, 2847.
(2) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59.
(3) Van Zanten, J. H.; Wallace, W. E.; Wu, W.-L. *Phys. Rev. E* **1996**, *53*, R2053.
(4) Reiter, G. *Macromolecules* **1994**, *27*, 3046.
(5) Wu, W.-L.; Satija, S. K.; Majkrzak, C. F. *Polym. Commun.* **1991**, *32*, 363.
(6) Wu, W. L.; van Zanten, J. H.; Orts, W. J. *Macromolecules* **1995**, *28*, 771.
(7) Hall, D. B.; Miller, R. D.; Torkelson, J. M. *J. Polym. Sci., Part B* **1997**, *35*, 2795.
(8) Prucker, O.; Christian, S.; Bock, H.; Ruhe, J.; Frank, C.; Knoll, W. *Macromol. Chem. Phys.* **1998**, *199*, 1435.
(9) Geoghegan, M.; Clarke, C. J.; Boue, F.; Menelle, A.; Russ, T.; Bucknall, D. G. *Macromolecules* **1999**, *32*, 5106.
(10) Wu, W.-L.; Orts, W. J.; Majkrzak, C. J.; Hunston, D. L. *Polym. Eng. Sci.* **1995**, *35*, 1000.
(11) Kent, M. S.; McNamara, W. F.; Baca, P. M.; Wright, W.; Domeier, L. A.; Wong, A. P. Y.; Wu, W.-L. *J. Adhes.* **1999**, *69*, 139.
(12) Bain, C. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1281.
(13) VanLandingham, M. R.; Dagastin, R. R.; Eduljee, R. F.; McCullough, R. L.; Gillespie, J. W. *Composites, Part A* **1999**, *30*, 75.
(14) Woerdeman, D. L.; Spoerre, J. K.; Flynn, K. M.; Parnas, R. S. *Polym. Compos.* **1997**, *18*, 133.
(15) Woerdeman, D. L.; Parnas, R. S. *Appl. Spectrosc.*, in press.
(16) Semerak, S. N.; Frank, C. W. *Macromolecules* **1981**, *14*, 443.
(17) Bokobza, L.; Pham-Van-Cang, C.; Monnerie, L.; Vandendriessche, J.; De Schryver, F. C. *Polymer* **1989**, *30*, 45.
(18) Royal, J. S.; Torkelson, J. M. *Macromolecules* **1993**, *26*, 5331.
(19) Sung, C. S. P.; Sung, N. H. *Mater. Sci. Eng.* **1993**, *A162*, 241.
(20) Miller, D. E.; Krueger, R. H.; Torkelson, J. M. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 2343.
(21) Sung, C. S. P.; Sun, H. L. *Macromolecules* **1986**, *19*, 2922.
(22) Sung, C. S. P.; Song, J. C. *Macromolecules* **1993**, *26*, 4818.
(23) Loutfy, R. O. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *20*, 825.
(24) Pekcan, O.; Yilmaz, Y.; Okay, O. *Polymer* **1997**, *38*, 1693.
(25) 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.
(26) Robello, D. R. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 1.
(27) Chaput, F.; Riehl, D.; Lévy, Y.; Boilot, J.-P. *Chem. Mater.* **1993**, *5*, 589.
(28) Chaput, F.; Riehl, D.; Boilot, J.-P.; Cargnelli, K.; Canva; Lévy, Y.; Brun, A. *Chem. Mater.* **1996**, *8*, 312.
(29) Plueddemann, E. P. *Silane Coupling Agents*; Plenum Press: New York, 1982.
(30) Lenhart, J. L.; van Zanten, J. H.; Dunkers, J. P.; Parnas, R. S. *Proc. Soc. Plastics Eng. ANTEC* **2000**, *1*, 827.
(31) NIST does not endorse any products. Identification of a commercial product is made only to facilitate experimental reproducibility and to describe experimental procedure.
(32) Lenhart, J. L.; van Zanten, J. H.; Dunkers, J. P.; Parnas, R. S. *Langmuir* **2000**, *16*, 8145.
(33) Thomason, J. L.; Dwight, D. W. *Composites, Part A* **1999**, *30*, 1401.
(34) Farrer, R. A.; Previte, M. J. R.; Olson, C. E.; Peyser, L. A.; Fourkas, J. T.; So, P. T. C. *Opt. Lett.* **1999**, *24*, 1832.
(35) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983; Chapters 7 and 8.
(36) Bock, H.; Christian, S.; Knoll, W.; Vydra, J. *Appl. Phys. Lett.* **1997**, *71*, 3643.
(37) Moussawi, H. A.; Drown, E. K.; Drzal, L. T. *Polym. Compos.* **1993**, *14*, 195.

MA0015572