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The Use Of Neutron Reflectivity To Study Degradative Processes At An Epoxy/Solid Interface

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Abstract

Neutron reflection is used to examine the structure of an epoxy near an interface. Variations in both the density and the crosslink density within the interphase region are examined. The density is increased near the interface relative to that in the bulk of the film, but the crosslink density over the same region is reduced relative to that in the bulk of the film. These observations are interpreted via packing of the resin oligamers next to the wall, which leads to an increased density and also inhibits the crosslinking reaction. The effect is more pronounced the more slowly the resin is cured. Significant variations in reflectivity are observed with thermal cycling, which indicate an increase in the size of the interfacial layer of excess toluene. However, data for samples with greater number of thermal cycles are required to determine the relation of this effect to the fracture process.

1. Introduction

Predicting failure in adhesive joints is of great importance to many industries. However, a fundamental theory of fracture is not yet possible. Fracture models typically follow one of two approaches: consideration of the energy balance and mechanics involved in crack propagation, or finite element calculations of stress fields on a very fine scale (stress modeling method). In the former case, parameters such as the critical stress intensity factor must be determined experimentally for each system. Regretably, these parameters are geometry dependent and their relation to the molecular structure of the adhesive is not known. In addition, the initiation processes that lead to the development of a macroscopic crack are not understood. In the stress modeling method, the length scale limitation of the continuum approach has not been established. Furthermore, failure criteria are required for predictive models, yet little progress has been reported on the link between molecular structure, strain/stress fields, and failure initiation processes for engineering polymeric adhesives.[1,2] Thus, there is a need for a nanoscale understanding of polymer fracture.

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Neutron reflection is one of only a few characterization techniques which can be used to study buried interfaces *in-situ*. While restricted to model samples, interfacial density and composition profiles can be obtained with a resolution of ~5 Å using isotopic substitution. We are using neutron reflection to address several problems of fundamental importance to the durability of organic/inorganic interfaces. An important focus of this study is the density and composition of an epoxy in the immediate vicinity of a solid surface. In particular, variations in the crosslink density near an interface may have important implications for stress localization and energy dissipation. Another focus is the development of damage at a thermoset/solid interface subjected to cyclic stress loading. The crosslink density within the interphase region can be probed by swelling with a solvent. The degree of local swelling is assumed to be related to the local crosslink density. From variations in the interfacial profile of the swelling solvent with cycling, the evolution of irreversible damage and the length scale of the damage zone can be determined.

2. Experimental

Materials. The substrates used in this study were polished single crystal silicon wafers (Semiconductor Processing Co.). Toluene (Aldrich) was used as the swelling solvent. A deuterated epoxy resin was specially synthesized for this work. The resin was cured with the crosslinker Jeffamine T-403 (Huntsman Chemical Co.) at 36 phr. For the synthesis of the deuterated resin, a 100 ml flask was charged with 1.0 g NaOH pellets (99.9% purity), 3.0 g deuterated bisphenol A (D_{16}, Cambridge Isotopes Labs.) and 9.6 ml of epichlorohydrin. The mixture was stirred and heated, with the heating rate moderated to control the exotherm to a maximum of 107 °C. After the exotherm subsided, the temperature was maintained at 105 °C for 3 hours. The excess epichlorohydrin was then vacuum distilled (< 1 torr) at 70 - 80 °C. The contents of the flask were then dissolved in benzene and filtered. The benzene was subsequently removed under vacuum to leave a viscous liquid (4.15 g, 95% yield). Proton and carbon NMR were consistent with the expected epoxy product and indicated virtually complete deuteration of the bisphenol A The epoxy equivalent weight was determined by C_{13} NMR[2] to be 198 after correction for the presence of deuterium. The IR spectrum indicated the presence of a slightly higher level of hydroxyl groups than noted in an EPON 828 reference spectrum, although no additional carbon or proton peaks were noted in the NMR spectra.

Procedures. Samples are prepared by either spin-coating or roll-coating a toluene solution of the epoxy resin onto the substrates. The cured spin-coated films were ~ 1 µm thick, while the roll-coated films were ~10 μm thick, both measured using a Dektak profilometer. Two cure schedules were used: 1 hr at 80 °C followed by 2 hrs at 125 °C which we refer to as "fast cure" (FC), or 48 hrs at 50 °C which we will refer to as "slow cure" (SC). The FC samples were roll-coated and the SC samples were spin-coated. Although the samples varied in the method of coating as well as in cure schedule, the differences in structure described below are attributed entirely to the cure schedule, as roll-coated and spin-coated samples with the same cure schedule showed similar interface structures. A cyclic stress was imposed by thermal cycling from 40 °C to -65 °C. The difference in thermal expansion coefficients of the silicon and epoxy gives a maximum stress of ~30 MPa during cycling. The samples were placed into a sealed container along with desiccant during thermal cycling to prevent exposure to condensed water vapor.

The neutron reflection experiments were performed at LANSCE (Los Alamos Nat. Lab.) and IPNS (Argonne Nat. Lab.). The sample geometry was such that the neutron beam passed through the silicon wafer before impinging onto the interface. The samples were first measured in the desiccated state, and then after exposure to toluene. The latter was accomplished by covering the entire surface of the wafer with toluene for at least 1 hour. The excess was then removed and the sample was placed into the reflectometer sample chamber. An open beaker of toluene was included to maintain a saturated atmosphere. For analysis of the reflectivity data, the experimental data were compared to curves calculated using the optical matrix method and model SLD profiles.[3] Single layer profiles were examined first, and increasing complexity (additional layers) was added as required. Best fits were determined by nonlinear least-squares regression (Marquardt).

3. Results

As-prepared samples - 0 thermal cycles. Reflectivity from SC and FC samples, both in the desiccated state, are shown in Figure 1a. The curves through the data are best-fits yielding the model scattering length density (SLD) profiles shown in Figure 1b. The dashed curve corresponds to the calculated reflectivity for a film with uniform density and composition normal to the interface. The significant deviation of the data from this curve indicates substantial variation in density and/or composition within the epoxy near the interface. The peak in Figure 1a is the critical edge for total reflection. The peak occurs at nearly identical q ($=4\pi\sin\theta/\lambda$) values for both samples, which indicates that the density and composition of the bulk films are nearly identical. From the SLD value of 3.5 x 10^{-6} Å^{-2} determined from the critical q for total reflection (q_c), and the known composition of the resin, a density of 1.00 is obtained for the bulk of the film. At higher q values, the deviation of the reflectivity from that for a uniform profile indicates a layer of elevated SLD near the interface. For the SC sample, the data are consistent with a single 25 Å layer at the interface in which the SLD is ~ 1.65 times that of the bulk of the film. The data for the FC sample indicate a similar effect, only somewhat less pronounced. The data are not consistent with a single layer model, but rather require at least two layers to describe the region of elevated SLD. The maximum is only 1.46 times the SLD of the bulk film. The second layer extends further from the surface than for the SC sample. Thus the region of elevated SLD is less pronounced and more graded for the FC sample than for the SC sample.

The region of elevated SLD can in principle be due to either a compositional gradient or a density gradient. A compositional gradient is possible since only the resin is deuterated and the crosslinker is protonated. Moreover, within the deuterated resin, only the bisphenol A precursor is deuterated, whereas the epichlorohydrin is protonated. This further increases the possible sources of variation in atomic composition normal to the interface. Assuming a density of unity, the deuterated resin has a calculated SLD of 3.72 x 10^{-6} Å^{-2} whereas the protonated crosslinker has a calculated SLD of 3.0 x 10^{-6} Å^{-2}. Thus, preferential segregation of the resin to the substrate surface alone cannot account for the observed SLD of 5.75 x 10^{-6} Å^{-2}. It is possible that the deuterated bisphenol A central portion of the resin oligamer (SLD = 5.1 x 10^{-6} Å^{-2}) may segregate to the interface in preference to the protonated epoxide end-groups. This would nearly account for the magnitude of the excess SLD. However, this appears highly unlikely since the epoxide end groups (and the amine groups on the crosslinker) should have a stronger affinity for the native silicon oxide than the bisphenol A portion of the resin. Therefore, we conclude that the elevated SLD is most likely due to elevated density rather than to variation in atomic composition. An elevated density may arise due to packing of the oligamers next to the solid, smooth surface. Such an effect has been observed for hydrocarbon liquids next to a hard wall in MD simulations.[4]

Figure 2a shows the reflectivity from the same samples after exposure to toluene. For the SC sample, the critical edge is shifted to lower q compared to the FC sample, indicating a slightly higher level of toluene swelling in the bulk film. The corresponding SLD profiles are shown in Figure 2b. For both samples, the data indicate an excess of toluene near the interface. However, the excess is more pronounced for the SC sample than for the FC sample. In addition, the profile is more graded for the FC sample. The volume fraction profiles calculated from the SLD profiles are shown in Figure 2c. Toluene swells the bulk of the SC sample to a volume fraction of 0.28, compared to 0.24 for the FC sample. The concentration of toluene in the interfacial region is surprisingly high, reaching 0.89 volume fraction for the SC sample. The excess toluene indicates a much lower crosslink density near the interface than in the bulk of the film.

The SLD profiles in the desiccated and toluene-swollen states are compared in Figure 3a for the SC sample and in Figure 3b for the FC sample. The observations of this portion of the study can be summarized as follows. In the dry state there is an elevated density in the near-surface region. Upon swelling with toluene, a substantial excess of toluene is observed in the near-surface region. Both effects are more pronounced for the SC sample than for the FC sample. The excess SLD at the interface in the desiccated state is believed to be due to packing of the resin oligamers at the interface. This packing effect may also lead to a lower crosslink density, either through exclusion of the crosslinker or from restricted mobility within the packed layer. These effects are more pronounced for the SC sample since the chains have more time to adopt the preferred packed structure before curing than for the FC samples.

Variation with thermal cycling. Reflectivity as a function of number of thermal cycles is shown in Figure 4a for a series of SC samples in the desiccated state. Little variation is seen through the first 88 cycles. However, upon further cycling the critical edge shifts to lower q and the reflectivity at $q > q_c$ decreases. SLD profiles corresponding to samples with 0 cycles and 424 cycles are shown in Figure 4b. The shift of the critical edge to lower q indicates a slight decrease in the density of the film with thermal cycling. More importantly, the decrease in reflectivity at $q > q_c$ indicates a reduction in the magnitude of the layer of elevated SLD. It appears that the stresses which arise during thermal cycling disrupt the densely packed layer at the interface.

Figure 5a shows the reflectivity from the same series of samples after exposure to toluene. Only three curves are shown for clarity. The SLD profiles for samples with 0 cycles and 424 cycles are shown in Figure 5b. In order to fit the dip which occurs at q values slightly greater than q_c, it was necessary to allow the imaginary part of the neutron refractive index to increase in the fits. The origin of this effect not clear, but may indicate an increase in the scattering within the bulk of the film. Such an effect may arise if there is an increase in the heterogeneity of the sample. In addition to this effect, there is an increase in the roughness of the free surface of the film with thermal cycling. However, these two effects only account for a small portion of the difference in reflectivity observed upon thermal cycling. The remaining effect is due to variation in the interfacial profile of toluene. In particular, the layer of excess toluene increases about 40 Å. Surprisingly, there also appears to be a decrease in the level of toluene in the layer adjacent to the interface. This latter observation is counterintuitive. Reflectivity for samples with a greater number of thermal cycles is required to interpret these changes, and make conclusions about their relevance to a failure process.

4. Conclusion

Neutron reflection can be used to examine the structure of an epoxy near an interface. Reflectivity from the sample in the desiccated state gives important information about density variation within the interphase region, while variation in crosslink density can be inferred from the profile of a swelling solvent. The density is increased near the interface but the crosslink density over the same region is reduced relative to that in the bulk of the film. These observations are interpreted via packing of the resin oligamers at the surface which leads to an increase density, but also inhibits the crosslinking reaction. The effect is more pronounced the more slowly the resin is cured. Significant variations in reflectivity are observed with thermal cycling, which indicate an increase in the size of the interfacial layer of excess toluene. However, data for samples with greater number of thermal cycles is required to determine the relation of this effect to the fracture process.

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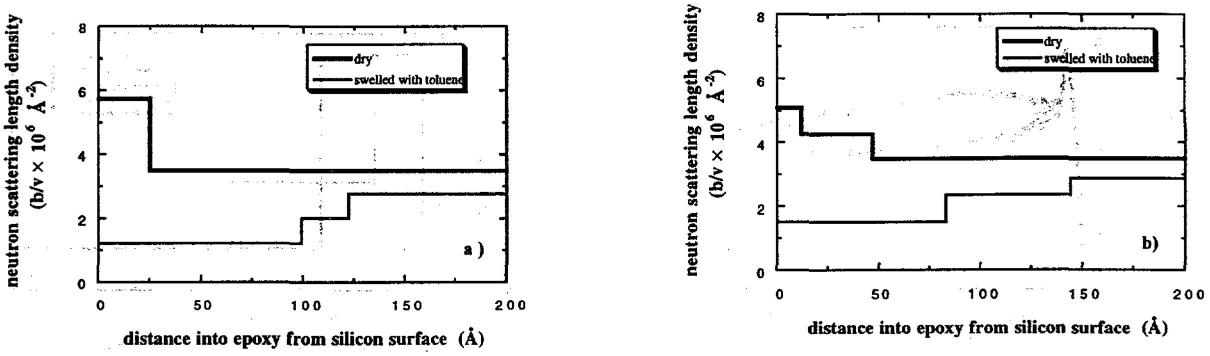

Figure 3. Comparison of SLD profiles in the desiccated and toluene-swollen states for a) SC and b) FC samples.

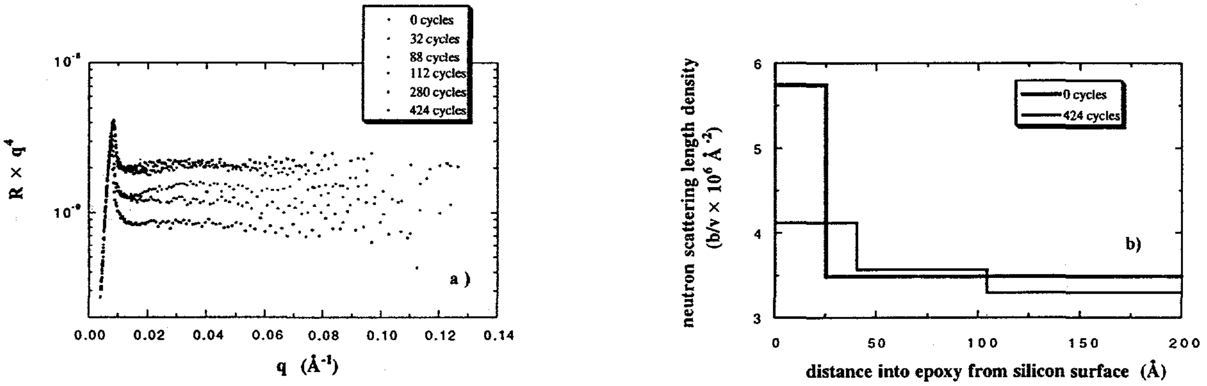

Figure 4. a) Reflectivity for SC samples with 0 to 424 thermal cycles in the desiccated state. b) SLD profiles corresponding to samples with 0 and 424 cycles.

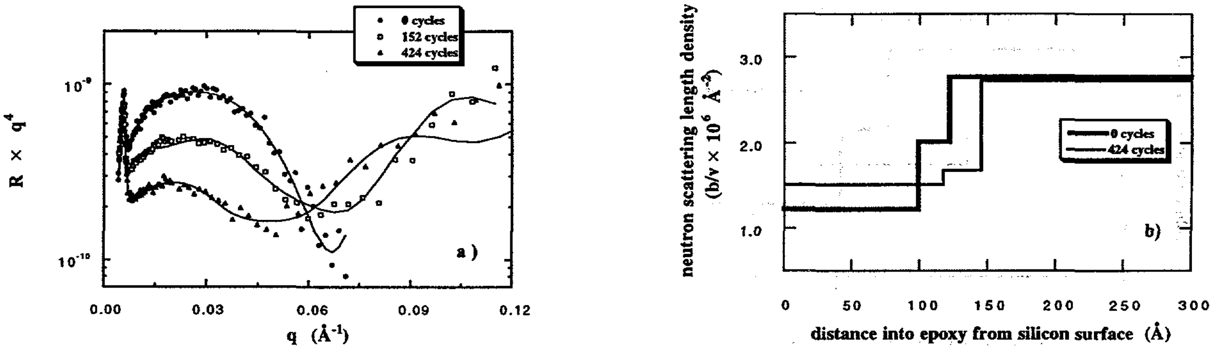

Figure 5. a) Reflectivity for SC samples with 0 to 424 thermal cycles after swelling with toluene. b) SLD profiles corresponding to samples with 0 and 424 cycles.

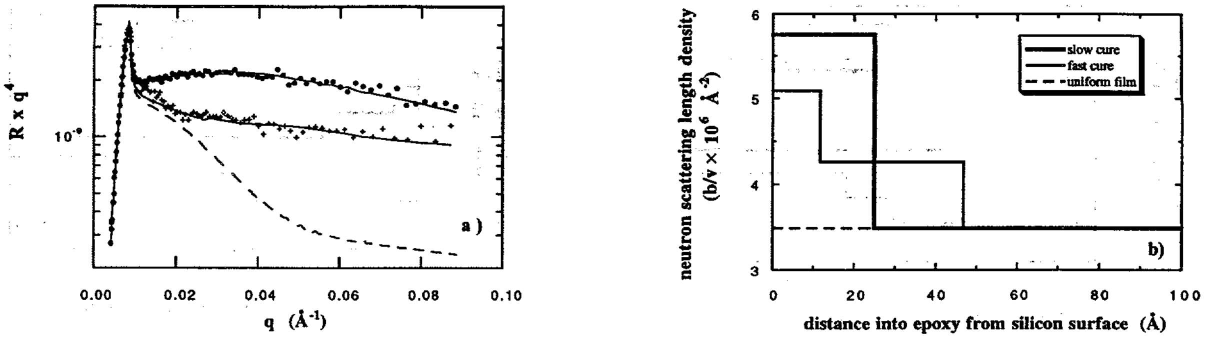

Figure 1. a) Reflectivity for SC (•) and FC (+) samples with 0 thermal cycles in the desiccated state. Dashed line is the calculated reflectivity for a film of uniform SLD. b) Corresponding best-fit SLD profiles.

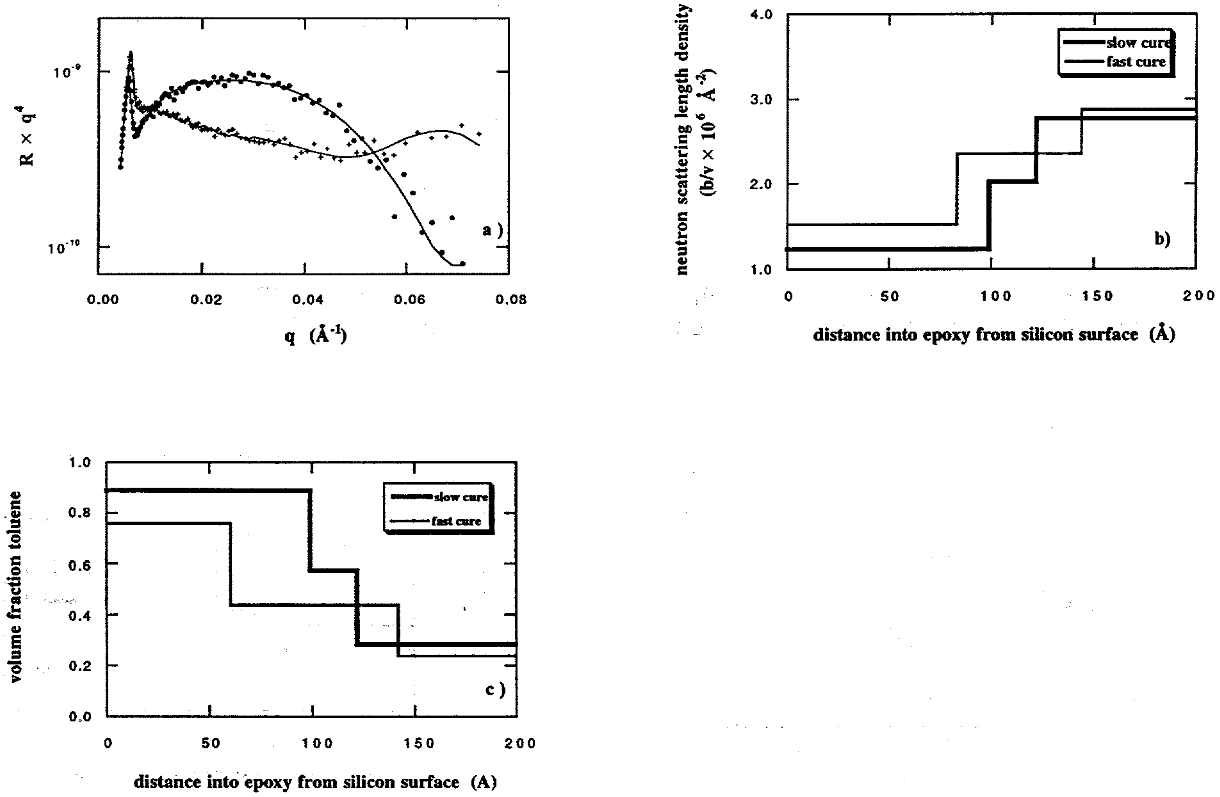

Figure 2. a) Reflectivity for SC (•) and FC (+) samples with 0 thermal cycles after exposure to toluene. b) Corresponding best-fit SLD profiles. c). Toluene volume fraction profiles.