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Molecular-to-Continuum Fracture Analysis of Thermosetting Polymer / Solid Interfaces

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Molecular-To-Continuum Fracture Analysis of Thermosetting Polymer / Solid Interfaces

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Interface Reliability - Adhesion, Corrosion, Tribology

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Abstract

This report focuses on the relationship between the fundamental interactions acting across an interface and macroscopic engineering observables such as fracture toughness or fracture stress. The work encompasses experiment, theory, and simulation. The model experimental system is epoxy on polished silicon. The interfacial interactions between the substrate and the adhesive are varied continuously using self-assembling monolayers. Fracture is studied in two specimen geometries: a napkin-ring torsion geometry and a double cantilevered beam specimen. Analysis and modeling involves molecular dynamics simulations and continuum mechanics calculations. Further insight is gained from analysis of measurements in the literature of direct force measurements for various fundamental interactions. In the napkin-ring test, the data indicate a nonlinear relationship between interface strength and fracture stress. In particular, there is an abrupt transition in fracture stress which corresponds to an adhesive-to-cohesive transition. Such nonlinearity is not present in the MD simulations on the tens-of-nanometer scale, which suggests that the nonlinearity comes from bulk material deformation occurring on much larger length scales. We postulate that the transition occurs when the interface strength becomes comparable to the yield stress of the material. This postulate is supported by variation observed in the fracture stress curve with test temperature. Detailed modeling of the stress within the sample has not yet been attempted. In the DCB test, the relationship between interface strength and fracture toughness is also nonlinear, but the fracture mechanisms are quite different. The fracture does not transition from adhesive to cohesive, but remains adhesive over the entire range of interface strength. This specimen is modeled quantitatively by combining i) continuum calculations relating fracture toughness to the stress at 90 Å from the crack tip, and ii) a relationship from molecular simulations between fracture stress on a ~ 90 Å scale and the fraction of surface sites which chemically bond. The resulting relationship between G_c and fraction of bonding sites is then compared to the experimental

data. This first order model captures the nonlinearity in the experimentally-determined relationship. A much more extensive comparison is needed (calculations extending to higher G_c values, experimental data extending to lower G_c values) to guide further model development.

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Appendix 1 Manipulating Polymer Connectivity to Control Interfacial Fracture

Appendix 2. Structure within Thin Epoxy Films Revealed by Solvent Swelling: A Neutron Reflectivity Study

I. Introduction

Fractures between polymeric adhesives and solid surfaces are an important factor affecting component viability in an aging stockpile. This work focuses on understanding the factors that control fracture at structural adhesive/solid interfaces, and incorporating such information into increasingly complex predictive models. Our present goal is to determine the dependence of joint strength and fracture toughness on interfacial chemical bonding, stress field (mode of loading), and the presence of flaws of various sizes. This information will provide the basis for a fundamental understanding of failure criteria in such systems. Indeed, the goal of adhesion science is to predict adhesive bond strength from first principles (Pocius, 1997).

The relationship between the intermolecular forces across the interface and joint strength or fracture energy is important from the standpoint of designing interfacial chemistry sufficient to provide the level of mechanical strength required for a particular application. In addition, it is also important for understanding the effects of surface contamination. Different types of contamination, or different levels of contamination, likely impact bond strength in different ways. A fundamental understanding of the relationship between joint strength and interface bonding will give insight into these issues. Furthermore, the relationship is also important from the standpoint of aging. If interfacial chemical bonds scission over time due to the presence of a contaminant such as water, or exposure to UV, etc, the relationship between joint strength/fracture toughness and interface strength is important for predicting reliability with time.

The detailed dependence of the interfacial fracture energy on the fundamental interfacial interactions has not yet been established. An interfacial molecular potential $\Psi(x,y,z)$ is illustrated in Figure I-1, which represents only the fundamental interactions acting across the interface. Note that in general the energy versus distance relationship normal to the surface will vary in the x-y plane. This is due to the fact that nearly all interfaces have some degree of chemical heterogeneity on a molecular scale. The maximum force required to separate two molecules is obtained as the peak in the derivative of the potential. A molecular scale force-distance relationship for an interface is also illustrated in Figure I-1. Most work thus far has emphasized the energy of separation, or the area under the force-distance curve. This is the thermodynamic work of adhesion $W_a = \gamma_1 + \gamma_2 - \gamma_{12}$ where γ_i are the surface energies and γ_{12} is the interfacial energy. It is well known that the energy needed to fracture an adhesive joint (practical work of adhesion, W_p) is nearly always far greater than W_a . This is due to energy dissipation processes. An important goal in adhesion science today is to understand the relationship between W_a and W_p . This

relationship depends upon the material properties of the adhesive and adherend, as well as the type of interactions acting across the interface. The following postulate has been proposed in the literature (Pocius, 1997)

$$W_p = W_a + f(W_a) \zeta \quad (I.1)$$

where ζ is a rate-dependent function, and $f(W_a)\zeta$ describes how mechanical energy is dissipated within the adhesive.

In general, the function $f(W_a) \zeta$ varies with material type, the type of interactions acting across the interface, the rate of the fracture process, and the mode of loading. For elastomeric materials, the relationship between W_a and W_p is described by (Gent and Shultz, 1972)

$$W_p = W_a + W_a \zeta \quad (I.2)$$

The dependence of ζ on rate is very strong for elastomeric materials. In principle, at very low rates $\zeta = 0$ and $W_p = W_a$. Since the deformation of elastomers is continuous with stress, the limit of $\zeta = 0$ can be approached in carefully designed experiments. For interfaces between brittle materials such as metal-ceramic interfaces, there is a relatively abrupt onset of deformation in the vicinity of the yield stress. The relationship between W_p and W_a has been shown to be quite different in this case, with most of the increase in W_p occurring over a small range of interface strength (Lipkin and Beltz, 1996). In principle, for perfectly brittle solids no dissipation occurs ($\zeta = 0$) and $W_p = W_a$. However, this limit may not be realizable in practice due to that fact that some degree of yielding occurs on a very local scale in most cases, i.e. materials are not perfectly brittle on all length scales.

The function $f(W_a) \zeta$ has also been examined for interfaces between thermoplastic polymers reinforced with block copolymers. In this case the function was found to depend upon the areal chain density and molecular weight of the copolymer, as the energy dissipation and fracture mechanisms vary depending upon these factors (Brown, 1991, Creton and Kramer, 1992, Washiyama et al, 1993, Washiyama et al 1994). Finally, for glassy adhesives on low surface energy substrates such as polyethylene and Teflon, much data supports a linear relationship between the joint strength measured in various geometries and W_a [Mittal, 1975].

The goal of the present work is to discover and model the relationship between W_p and the type and spatial distribution of fundamental interfacial interactions for structural adhesives on solid substrates. This is an important step toward the larger goal of

determining the complete relationship between W_p and the interfacial interaction potential. Eq I.1 tacitly assumes that energy dissipation depends upon the area under the molecular force-distance curve, rather than on the shape of the curve or, in particular, the maximum force required for separation. This assumption is critical to modeling fracture, and remains to be confirmed or disproved. In the present work we focus on high surface energy solid substrates for which there can be strong chemical interactions with the adhesive. We postulate that interface strength (maximum force) is the key parameter for glassy adhesives which possess yield behavior. The basis of this assumption is that the amount of energy dissipation depends upon the extent of yielding, which in turn is determined by local stress levels.

To guide the development of a fracture model and for validation, a model experimental system has been developed. The system is composed of an epoxy bonded to polished silicon. An epoxy was chosen as a typical glassy structural adhesive. Polished silicon wafers were used as substrates in order to i) remove the effects of roughness, and ii) allow the interfacial chemical bonding to be varied continuously via self-assembling monolayer techniques. This model system covers a wide range of the independent variables, and thus represents a range of engineering materials. We determined the fracture energy as a function of the interface strength experimentally, and compared these data to the theoretical model.

When a crack is present on an interface, the general criteria for propagation are well understood. For an interfacial crack to propagate, the strain energy released must equal the energy to separate the materials, or the fracture toughness. It is also true that for a crack to propagate, the stress at the crack tip must reach values sufficient to break interfacial bonds. The magnitude of the crack tip stresses which the interface can support, and the mode mixity, determine the degree of plastic deformation and the fracture toughness. However, when a joint without a macroscopic crack in the bond-line is loaded, the factors which control stress concentrations, material deformation, and fracture are less clear. In the experimental portion of this work, two fracture tests are employed, a napkin-ring (NR) torsion test and a double cantilevered beam (DCB) test, which correspond to these two situations. In addition, the NR test provides a shear loading which contrasts with the nearly purely tensile loading in the DCB test. Both tests provide important new insights that add to our predictive capability. However, our detailed quantitative modeling work to date has focused exclusively on the DCB geometry.

The quantitative model for the DCB specimen focuses on the dependence of the fracture toughness G_c (here equivalent to W_p) on the nature and extent of the interfacial interactions. The model begins with a continuum mechanics calculation of the stress/strain

fields near a crack tip in a double cantilevered beam (DCB) test geometry. The calculated results becomes increasingly suspect as the crack tip is approached because the behavior of the material within high stress/strain fields is not easily measured or modeled. In particular, nonlinear viscoelasticity and plasticity must be modeled for very high stress/strain fields. The goal is to determine a relationship between G_c and the stress at roughly 100 Å from the crack tip. Ultimately, the molecular details of the fracture process at the crack tip are beyond the continuum limit. Therefore, the molecular-scale fracture events are investigated using molecular simulations covering length scales up to a few hundred Ångstroms. The contribution of the MD simulations to the fracture model is the relationship between fracture stress (on a 100 Å length scale) and the fraction of surface sites that chemically bond. The two relationships are then combined to provide the relationship between G_c and the fraction of surface sites that chemically bond. This can then be compared directly to the experimental data. The model is illustrated in Figure I-2.

The work is described below in five sections. Section II describes the experimental work, in which self-assembling monolayers were used to continuously vary the interface strength for the NR and DCB test specimens. Section III describes the continuum calculations for the stress/strain fields near the crack tip in the DCB geometry for the materials in the experimental system. Section IV describes the molecular simulations of fracture. In Section V we estimate the intrinsic interface strength for the present experimental systems from direct measurements of the force–distance relationships for fundamental interactions reported in the literature. This plays a key role in the interpretation of the experimental data and analysis of the model. Section VI is a summary of the results, which includes a postulated new criterion for the transition from adhesive-to-cohesive failure in the NR test, and comparison of the G_c versus fraction of bonding sites relationship from the combined continuum and MD calculations to the experimental data. The section concludes with a discussion of the significance of this work, and suggested future work.

II. Experimental work

The primary variable in this study is the extent of interface bonding. Strong adhesive joints require that a high degree of energy be dissipated within the adhesive. In glassy polymers, plastic deformation is the major contribution. The degree of plastic deformation in glassy polymers is a strong function of the local stress level. When an interface is sufficiently weak, local stresses remain low prior to interfacial separation, and little energy is dissipated within the adhesive. On the other hand, for a sufficiently strong interface, local stresses exceed the yield stress (σ_y) and plastic deformation and energy dissipation occurs. However, the extent of interfacial bonding needed to promote yielding locally within the adhesive in various loading geometries is not understood quantitatively. Furthermore, the relationship between the size of the yield zone at a crack tip and the interface strength is not understood quantitatively. Likewise, the conditions which determine when a failure will change from adhesive to cohesive are not understood. In the case where such a transition does occur, the relationship between interface strength and the transition is not established. These are important topics addressed in this study.

II.a Use of self-assembling monolayers to vary interface bonding.

We have used self-assembling monolayers (SAMs) of organosilane molecules to systematically vary the degree of bonding between the epoxy adhesive and the silicon substrate. Three methods of accomplishing this have been used, each providing complementary information. These methods are illustrated in Figure II-1

The first method was to coat the substrate surface to varying degrees with octadecyltrichlorosilane (ODTS). The epoxy interacts strongly with the bare silicon oxide surface, likely through interactions between the silanol groups on the substrate and the amine groups on the crosslinker, but the epoxy interacts only weakly with the methylated tails of the ODTS monolayer. A substrate fully coated with ODTS presents a completely methylated surface to the epoxy, and the interactions are limited to the van der Waals type. By only partially coating the substrate with ODTS, some sites are left available to bond strongly to the epoxy. Partial coverage is achieved by limiting the exposure time of the substrate to the coating solution.

The second method was to use lithography to pattern domains into which the ODTS monolayers are deposited. All work to date has involved photolithography. After deposition of the ODTS, the photoresist was removed, leaving a bare silicon surface except where the ODTS was deposited. Within the domains, the ODTS was at full close packed

density, and thus interactions with the epoxy were limited to the van der Waals type. In this work, the ODTS has been deposited in square domains in a grid pattern. By varying the spacing between the domains, the coverage was varied from 0 to 100% as in the first method, but in this case using domains of specified size (50 μm and 5 μm).

The third method involved mixed monolayers composed of methyl-terminated molecules with either amine-terminated or bromine-terminated molecules. The latter two functional groups react with the epoxide groups. In this case the coverage was maintained at full close-packed density, but the composition was varied. In this way the surface was varied from a fully methylated surface to a surface entirely covered with reactive sites. This method allows the most precise quantification of the extent of interfacial bonding, and largely eliminates uncertainty about heterogeneity in the plane of the surface (although the distribution of the two components in the mixed monolayer may still be distributed nonrandomly).

II.b. Napkin ring torsion test

II.b.1. Materials and Methods.

The substrates used in this study were polished single crystal silicon wafers (type P, orientation 100) from SilicaTek and Monsanto. The substrate thickness was 600-650 μm . ODTS was obtained from Akros. Anhydrous hexadecane and anhydrous carbon tetrachloride were obtained from Aldrich. Research grade EPON 828 resin was obtained from Shell. The crosslinker Jeffamine T-403 was obtained from Huntsman Chemical Co. All materials were used as received. Deuterated epoxy resin was synthesized using deuterated bisphenol A and epichlorohydrin. The synthesis and purification procedures have been described in detail elsewhere. (Kent, et al, 1999)

For Method 1 (variable coverage of ODTS), the wafers were cleaned in a UV-ozone chamber and then submerged in a hexadecane / carbon tetrachloride solution containing ODTS. The coverage of ODTS was varied by controlling the time of exposure to the solution. The SAM-coated wafers were sonicated in toluene to remove nonbonded material, and then dried.

For Method 2 (patterned domains of ODTS), the wafers were cleaned in a UV-ozone chamber and then a photoresist was spin-coated onto the bare wafer. Several resists were used throughout the course of this work (Shipley positive photoresists AZ 4330, AZ 5214, and AZ 4110). The pattern was exposed in the photoresist on a Suss MA6 contact

aligner in vacuum contact with exposure times appropriate for each resist. In early work, hexamethyl disilazane (HMDS) was used to promote adhesion of the photoresist to the silicon wafer. However, it was discovered that the HMDS could not be easily removed, and the final wafer contained HMDS in the regions between the ODTS domains. Further processing was done without HMDS, and all the data reported here are for wafers processed without HMDS. In the absence of HMDS, adhesion of the photoresist to the silicon substrates was accomplished by heating the wafers to 400 °C in a N₂ overpressure box oven to remove adsorbed water. Surprisingly, the fracture strength of the silicon decreased with the heat treatment, and interfacial fracture stresses greater than 20 MPa could not be measured due to fracture of the silicon. This effect is currently under investigation. The wafers with patterned photoresist were placed in a UV-ozone cleaner for 15 minutes to clean organic contamination out of the square holes, leaving bare silicon. The wafers were then submerged immediately into an ODTS solution and left for 24 hours to deposit ODTS at full density into the square holes. The photoresist and nonbonded ODTS were then removed by repeated sonication in toluene and acetone.

For Method 3 (mixed monolayers), the wafers were cleaned in a UV-ozone chamber and then submerged in a hexadecane solution containing a mixture of 1-bromo-11-undecyltrichlorosilane and dodecyltrichlorosilane at the desired proportions at 60 °C for 5 hrs. The conversion from bromine to amine was done by a multi-step process. The bromine was converted first to azide by reacting with sodium azide in dimethylformamide (DMF) for 48 hrs. After the mixed SAMs were cleaned with distilled water and acetone, azide was then converted to NH₃⁺ in a three step process of a reaction with lithium aluminum hydride in tetrahydrofuran (THF) for 24 hrs, followed by an overnight soak in pure THF, concluded by a 5 hr soak in 5% HCl. Finally, the mixed SAMs were placed in triethyl amine for 24 hr to convert the NH₃⁺ to amine groups. This results in a dense packed monolayer with a controlled concentration of terminal NH₂ groups.

All contact angle measurements were made with an Advanced Surface Technology, Inc. VCA 2500 Video Contact Angle System. Advancing (receding) contact angles were measured by slowly adding (removing) liquid from the drop with a syringe and recording the maximum (minimum) contact angle. For the epoxy contact angles, it was necessary to coat the tip of the syringe needle with a fluorinated material so that the epoxy did not wet the needle. A 3% solution of Teflon AF in FC-77 was used to coat the needle. The coating was cured at 108°C for at least 40 minutes prior to use.

The mass coverage of ODTS was determined by X-ray reflectivity using a Scintag X_i powder diffractometer equipped with Cu K α radiation, an incident beam mirror, and a peltier-cooled solid-state Ge detector. The incident beam mirror was used to generate a

parallel beam (in the height dimension) from the divergent x-ray source. A variable slit system at the exit port of the mirror housing was dialed to create a beam of 50 microns in height; the beam width in the non-parallel direction was 10 mm. The technique and data analysis have been reviewed elsewhere. (Russell, 1990)

The majority of the fracture tests were performed with steel rings having an I.D. of 20.98 mm and an O.D. of 23.19 mm (± 0.03 mm). One set of tests was performed using rings with an I.D. of 10.43 mm and an O.D. of 12.21 mm. To remove machine oil, the rings were sonicated in an acetone bath for 30 min. The rings were then sandblasted to roughen the surface and soaked in isopropyl alcohol. After cleaning, the sandblasted rings were coated with A1100 coupling agent solution: 250 ml DI Water, 0.20 ml Formic Acid 94%, and 1.25 ml A1100. The solution was stirred for 10 minutes prior to application. The rings were dip coated and then heated for one hour at 90°C.

The two epoxy components were mixed for 5 minutes using a metal spatula. The mixture was then placed in an oven at 60°C for 10 minutes to release any air bubbles caused from mixing. The epoxy was then applied to the rings as uniformly as possible. To avoid smearing the epoxy, the rings were lowered just above the silicon surface and then dropped onto the silicon. The bond thickness as measured by Dektak profilometer was 50-60 μm . The ring/wafer sets were then placed in an oven at 50°C and allowed to cure for 2 days.

Most samples were fractured in a torsion geometry using a Mitutoyo Datatorq digital torque wrench mounted in a home-made goniometer. In these experiments the rate was not precisely controlled, but was roughly 60 deg/min. One series of tests were performed with an INSTRON using a range of precisely controlled rates. The applied shear stress at fracture (σ) is obtained from the maximum torque value (T) using the relation (Adams and Wake, 1984)

$$\sigma = T / (2\pi r^2 h) \quad (\text{II.1})$$

where r is the radius of the ring and h is the wall thickness.

AFM images were obtained using a Park Scientific Autoprobe LF in either noncontact or lateral force tapping mode. SEM images were obtained using a JEOL JSM 6400XV electron microscope. Optical micrographs were obtained using a Leitz Orthoplan optical microscope (50 to 500x magnification) using interference contrast reflected light illumination.

The surface energy of the uncured epoxy mixture was measured by the Wilhelmy plate technique using a sand-blasted platinum plate and a Q11 force transducer from

Hottinger Baldwin Measurements. Measurements were made at room temperature, and were taken within 30 minutes after the components were mixed to ensure that the extent of the crosslinking reaction was negligible.

II.b.2. Results

II.b.2.a. Method 1: Variable coverage of ODTS

II.b.2.a.1. Characterization of ODTS layers

A number of techniques have been used to characterize the ODTS monolayers prior to applying the epoxy. These include atomic force microscopy, advancing and receding contact angles with both water and uncured epoxy, and X-ray reflectivity. Our goals were to determine fractional mass coverage and the degree of in-plane heterogeneity. These features are related to the molecular interface potential $\Psi(x,y,z)$ which describes the fundamental interactions between the epoxy and the silicon oxide.

Atomic force Microscopy (AFM). AFM was used to examine the degree of lateral heterogeneity within the incomplete monolayers. Previous reports have indicated island formation can occur under certain conditions of temperature and chain length due to a lateral phase transition (Carraro et al, 1998, Huang, et al, 1997, Bierbaum, et al, 1995, Banga, et al, 1995). Our concern was to determine the conditions for which island formation occurred in our samples, and whether island formation has any effect on the fracture behavior. We examined ODTS layers at varying coverage for depositions at room temperature ($\sim 24^\circ\text{C}$) from a hexadecane/carbon tetrachloride solution (4/1 by vol) containing 0.058 vol % ODTS, and also for depositions at 10°C from a hexadecane/carbon tetrachloride solution (2.3/1 by vol) containing 0.050 vol % ODTS. AFM images in Figures II-2 and II-3 obtained at 24°C and 10°C , respectively, are representative of this study. Over the entire range of coverage examined, island formation is clearly observed at 10°C , but is entirely absent for depositions at room temperature.

Contact Angles. Figure II-4 shows equilibrium water contact angle as a function of exposure time for the silicon wafer pieces in the ODTS solution at room temperature ($\sim 24^\circ\text{C}$, same solution as described above). The form of this curve remained constant throughout our study, but the numerical values varied slightly from day to day. The variation is likely due to variable amounts of water on the wafer surfaces or in the

solutions. To obtain multiple samples with the same coverage for the fracture study, trays containing at least ten wafer pieces were immersed into the treating solution and removed at the desired times. The equilibrium water contact angle was measured on each piece. The mean and standard deviation of the equilibrium water contact angle for the ten samples are reported along with the fracture stresses in the following section.

Advancing and receding water contact angles are given as a function of the equilibrium water contact angle in Figure II-5 and II-6 for depositions at room temperature ($\sim 24^\circ\text{C}$) and 10°C , respectively. We focus on the regime of relatively high contact angles where a strong variation in the fracture behavior occurs. For deposition at room temperature, the difference between advancing and receding contact angle (Δ) varies from roughly 15° at full coverage to 31° at the lower end of the range examined. Most of the variation in Δ occurs over the narrow range of equilibrium contact angle from $\sim 103^\circ$ to $\sim 95^\circ$. This increase in the value of Δ with decreasing ODTS coverage indicates an increase in the degree of heterogeneity or roughness of the surface layer. For deposition at 10°C , the difference between advancing and receding contact angle (Δ) varies from roughly 5° at full coverage (equilibrium contact angle of 115°) to 9° at an equilibrium contact angle of 107° to 29° at an equilibrium contact angle of 82° .

Advancing and receding epoxy contact angles as a function of ODTS coverage for depositions at 24°C are shown in Figure II-7, where again the ODTS coverage is reflected in the equilibrium water contact angle. Data were again obtained only for the range of relatively high ODTS coverage. The epoxy is nonwetting over the entire range examined. On the other hand, apparent complete wetting (contact angle $\leq 5^\circ$) was observed for the epoxy on the native oxide of silicon in the absence of ODTS. In contrast to the results obtained with water, no variation in the difference between the advancing and receding contact angles was detected with the epoxy.

X-ray reflectivity. For depositions at room temperature, mass coverage of ODTS was determined by X-ray reflectivity over the range of coverage corresponding to the strong variation in fracture behavior. Representative X-ray reflectivity data are shown in Figure II-8 for depositions at room temperature. The mass coverage obtained from integrating the fitted electron density profiles is shown in Figure II-9 for a range of coverage corresponding to equilibrium contact angles from 95° to 115° (full coverage). No island formation was observed by AFM for depositions at room temperature, and therefore in the analysis of the reflectivity a laterally uniform layer was assumed. Full coverage corresponds to a surface density of 1.9 mg/m^2 or $1\text{ molecule}/24.6\text{ \AA}^2$. This is a slightly lower density than reported by Wasserman et al. (Wasserman et al, 1989).

II.b.2.a.2. Measurements of fracture stress

In order to establish that the napkin-ring test measures a critical stress state, the ring diameter was varied by roughly a factor of 2. Load to failure was determined for rings bonded to bare silicon wafers (no ODTs). The data shown in Figure II-10 indeed demonstrate that fracture occurs at a constant stress level independent of ring diameter according to eq. II.1.

The fracture stress for an epoxy composition of 46 phr (parts crosslinker per hundred parts resin by weight) is plotted in Figure II-11 as a function of ODTs coverage where the latter is reflected in the equilibrium water contact angle. We note that for the case of full ODTs coverage, the joint did not fracture, but rather the ring could be rotated on the substrate indefinitely and yet remain attached. The stress level indicated in the figure is that required to rotate the ring. We also note that the observed stress value at full ODTs coverage (≤ 3 MPa) is consistent with the value reported for shearing CH_3 terminated SAMs using the surface forces apparatus (Yoshizawa, et al, 1993, Yamada, et al, 1998). The data are replotted in Figure II-12 where the abscissa has been converted to relative ODTs mass coverage using the data of Figure II-9. A third representation is given in Figure II-13, where the abscissa has been converted to work of adhesion using the epoxy advancing contact angle data of Figure II-7 and the Young-Dupre equation:

$$W_a = \gamma_{lv} (1 + \cos \theta) \quad (\text{II.2})$$

where γ_{lv} is the surface tension of the epoxy and θ is the contact angle of the uncured epoxy on the substrate. The surface tension of the uncured epoxy was determined to be 34.3 mJ/m^2 by the Wilhelmy plate technique. We note that W_a in eq II.2 represents the work to separate the uncured epoxy from the substrate, and does not account for chemical bonds formed during cure. The work to separate chemically bonded surfaces is calculated to be $\sim 40 \text{ J/m}^2$ for covalent bonds assuming 1 bond per $25 \text{ \AA}^2$ (Pocius, 1997). As will be discussed in section IV, the areal density of interfacial bonds between the epoxy and the substrate is far less than $1/25 \text{ \AA}^2$. We estimate the areal bond density to be reduced from $1/25 \text{ \AA}^2$ by a factor between 21 and 6.5, leading to an estimate of the work of separation which ranges from 2 to 6 J/m^2 . Experimentally, a value of $\sim 1 \text{ J/m}^2$ has been reported for the fracture of crosslinked polybutadiene at very low rates (Gent and Lai, 1994). In any event, the work to fracture surfaces with covalent bonds can be considered to be of magnitude 1 J/m^2 or greater, far above that calculated using contact angles. The latter only

measures the work due to the physical interaction forces across the interface prior to curing. We note that much data in the literature for adhesives on low surface energy solids (such as polytetrafluoroethylene and polyethylene) shows a linear relationship between fracture strength and $W_a = \gamma_{iv} (1 + \cos \theta)$, which contrasts sharply with the present data for epoxy on silicon. This dramatic difference is due to the presence of chemical bonds in the latter case.

Figure II-11 also shows fracture data for samples in which ODTS was deposited at 10 °C, where island formation is observed by AFM. The fracture behavior is indistinguishable from that for depositions at room temperature when plotted versus the equilibrium water contact angle. We also note that the fracture behavior was unchanged from that in Figure II-11 following extensive filtration to remove dust particles.

Several other characteristics of the system were varied to determine the sensitivity of the fracture stress curve to these parameters. Figure II-14 compares fracture data for samples with epoxy compositions of 36, 46, and 56 phr. The stoichiometric composition is 46 phr. Little change in the fracture stress curve is observed for the three different compositions. Temperature and rate are important variables for materials which have a viscoelastic response. Figure II-15 shows fracture stress data as a function of angular velocity (rate) at a fixed composition of 46 phr crosslinker for a bare silicon surface and for an ODTS coverage corresponding to an equilibrium contact angle of 95°. The range in which the rate of the torque test can be varied is only limited to two orders of magnitude. The difference between the fracture stress for the two coverages appears to increase with increasing rate. The same effect can be investigated over a much wider range by varying the temperature of the fracture test rather than the rate. Figure II-16 shows fracture stress data as a function of temperature at a fixed composition of 46 phr crosslinker. Indeed, a strong dependence of the fracture stress curves upon temperature is observed. The shift in the curve with decreasing temperature in Figure II-16 is consistent with the trend observed with increasing rate in Figure II-15.

II.b.2.a.3. Characterization of fracture surfaces

Visual examination of the fracture surfaces suggests a complete absence of epoxy on the substrates for ODTS coverages corresponding to equilibrium water contact angles from 115° down to roughly 98°. Furthermore, no epoxy could be detected on the substrate by AFM, SEM, or optical microscopy over this range as well. In order to further examine the substrate surface, additional samples were prepared with a deuterated epoxy resin and TOF-SIMS analysis was performed following fracture. Deuterium labelling allowed the

presence of the epoxy resin to be distinguished from adventitious hydrocarbon material. Calibration was performed using a ~ 30 Å film of deuterated epoxy, (thickness measured by X-ray reflectivity). The data are shown in Figure II-17, expressed as the ratio of the intensity of D⁺ ions to Si ions, and divided by the integrated signal resulting from the 30 Å d-epoxy film. While the level of deuterium on the substrate was significantly above the background level, the level is far below that for the 30 Å d-epoxy film. In fact, the quantity of deuterium observed corresponds to only a very small fraction of a monolayer of deuterated epoxy. Several areas on the substrate surfaces were examined with essentially the same result. This indicates that the fracture remains truly interfacial in this range of ODTS coverage.

Examination of the surfaces of the rings by optical microscopy revealed the extent of deformation on the epoxy surfaces. No deformation was detected for the water contact angle range $104^\circ - 115^\circ$, but rather the epoxy surface retained the smooth character of the polished silicon substrate. On the other hand, substantial deformation was observed for the range $98^\circ - 103^\circ$, the amount of deformation increasing with decreasing water contact angle. Representative images are shown in Figures II-18 – II-20. This is the only significant observation coincident with the strong increase in the fracture stress. The length scale of the deformation is macroscopic, and the deformation patterns do not appear to be derived from the propagation of the crack (no wake lines).

For ODTS coverages corresponding to water contact angles less than 98° , macroscopic quantities of epoxy were observed visually on the substrates. Near 98° , typically only one small spot of epoxy remained on the substrate surface. With decreasing ODTS coverage, the amount of epoxy remaining on the substrate surface increased. For bare silicon wafers (no ODTS), epoxy was observed over nearly the entire surface of the substrate which was in contact with the ring.

II.b.2.b. Method 2: Patterned domains of ODTS

AFM images of substrates prior to bonding were obtained to verify that the desired pattern was reproduced in the ODTS monolayer. A representative image is shown in Figure II-21. AFM investigation indicates that the SAM patterns were very well reproduced, and very few defects were observed.

Two domain sizes have been used: squares of $50\text{ }\mu\text{m}$ on a side, and squares of 5 microns on a side. The fracture stress data are shown in Figure II-22, where the fracture stress is plotted as a function of the relative mass coverage of ODTS. Data for Method 1

are also included for comparison. The effect of depositing the ODTS in domains is dramatic, in sharp contrast to the lack of change observed in Figure II-11 for incomplete monolayers with or without a lateral phase transition.

II.b.2.c. Method 3: Mixed monolayers

Two types of mixed monolayers have been used: mixtures of dodecyltrichlorosilane with 1-bromo-11-undecyltrichlorosilane, and mixtures of dodecyltrichlorosilane with aminoundecyltrichlorosilane. Both bromine-terminated SAMs and amine-terminated SAMs were found to react with the epoxy. The chemical reactivity of bromine with epoxide rings has been reported recently in the literature (Sharghi, et al., 1998). The fracture stress data are shown in Figure II-23, where the fracture stress is plotted as a function of the percentage (by mole) of methyl-terminated molecules in the treating solution. A sharp transition in fracture stress with interface bonding sites is observed, as was the case with the incomplete monolayers of Method 1. A significant shift in the fracture stress curve is observed for bromine and amine terminated molecules. This could either be due to differences in the extent of reaction with the epoxide groups, or a difference in the strength of the bond.

II.b.3. Discussion

The data in Figure II-11 – Figure II-13 (Method 1) and Figure II-23 (Method 3) seem to indicate that at the transition a sharp increase in fracture stress occurs for a very small increase in the extent of interfacial bonding. However, before reaching that conclusion, another possibility must also be considered. An alternative explanation for the sharp transition is that for high ODTS coverage (or high methyl content of the mixed SAMs) the epoxy dewets upon curing on some length scale such that the actual contact area between epoxy and substrate is reduced. If that were the case, the sharp transition in fracture stress could be due to a transition from partial to complete wetting. In other words, the transition would coincide with the difference between an interface containing many defects (voids or dewetted regions) and thus a low contact area, and an interface with few defects (fully wetted case) and thus a high contact area. However, several observations argue against this interpretation. First, the contact angle of the (uncured) epoxy is finite over the entire range of coverage where the transition occurs, and varies smoothly with ODTS coverage. No evidence of a wetting transition is observed over the

relevant range of coverage. Indeed, the observation that a strong bond can be formed even when the adhesive does not wet the substrate is important to note. However, there could possibly be a dewetting effect due to curing of the epoxy, such that the curing epoxy pulls away from the substrate. In other words, a transition from wetting to nonwetting may exist in the cured sample, even though none is indicated from the data in Figure I-7. Second, and more importantly, the strong variation in the fracture curves with temperature in Figure II-16 indicates that the fracture transition is related to deformation within the epoxy, rather than the presence or absence of defects on the interface. If the transition were related to the presence or absence of defects formed during curing, the transition would remain the same when the fracture test is performed at different temperatures. The strong shift that is observed with test temperature is strong evidence that the transition is not determined by a wetting/dewetting transition, but by material deformation.

Having eliminated the explanation based on partial dewetting, we conclude that the sharp increase in fracture stress does indeed correspond to a small increase in the extent of interfacial bonding. In Figure II-11, a ≥ 10 -fold increase in fracture stress occurs for a $\sim 10\%$ increase in the number of available bonding sites on the surface. In Figure II-23, again a ≥ 10 -fold increase in fracture stress occurs for a $\sim 10\%$ increase in the number of functional groups per area. This strong dependence appears to be due to the onset of significant yielding over a narrow range of stress, as the only observation coinciding with the transition in fracture stress is the onset of significant deformation within the epoxy. Moreover, the observed deformation is over macroscopic portions of the rings. There appears to be a critical value of interface strength which corresponds to the onset of macroscopic deformation in the epoxy. At this critical value of interface strength, stress within some macroscopic portion of the material has apparently attained σ_y either before or during unstable crack propagation to produce the yielding that is observed. Thus, the nonlinearity between interface strength and fracture stress appears to come from the nonlinear response of the material.

The simple picture arrived at from these observations is that the transition in fracture stress occurs when the interface strength is able to support stresses sufficient to cause plastic deformation within the epoxy. This simple picture is further supported by the variation of fracture stress with rate and temperature shown in Figures II-15 and II-16. As the temperature of the test is decreased (or the rate is increased), the epoxy becomes stiffer or more resistant to deformation while the interface bond strength is relatively unaffected. Higher stresses are required for deformation to occur within the epoxy. Therefore, by the postulated criterion the transition in fracture stress should occur at higher values of interface strength. While this simple idea captures the basic trend, a more detailed description of the

material deformation is likely required to describe the precise change in the curves with temperature, notably the change in slope.

The fact that the relation between interface bonding and fracture stress is not sensitive to epoxy composition (Figure II-14) is a little surprising given the above interpretation, in that the macroscopic yield stress reported in the literature varies roughly 20% over this range of composition. (Morgan et al, 1984). Measurements of the yield stress values for each composition under the present cure conditions are needed for an accurate comparison, and will be obtained in future work. Further work will focus on other methods to vary material stiffness such as the introduction of glass microbeads into the epoxy.

When the interface strength reaches a sufficiently high value, we assume that crack initiation occurs within the bulk epoxy. This is inferred from the plateau in Figure II-11, where the fracture stress is independent of the ODTs coverage, and is consistent with the observation that epoxy is left on the substrate surface. However, we note that in our analysis of the fracture surfaces we were not able to identify the specific location where the crack initiated. Somewhat surprisingly, we find that only a small degree of interface bonding is required for fracture to initiate within the bulk epoxy rather than on the interface. In particular, from Figure II-12 we find that up to 65% of the reactive sites on the substrate surface can be occupied/blocked by ODTs and yet the fracture still initiates cohesively. In Figure II-23 we find that up to 70% (Br termination) - 80% (amine termination) of the surface sites can be nonbonding methyl groups and yet the fracture still initiates cohesively. Also, in Figure II-11 we find that the surface can be changed from hydrophilic (completely wet by water) to substantially hydrophobic (equilibrium water contact angle of 98°) before any change in the fracture stress is observed. Apparently strong epoxy-substrate interactions are required over only a small fraction of the surface area for the fracture to initiate cohesively within the epoxy. We return to this in section VI, as further insight has is provided by the MD simulations (section IV) and calculations of the intrinsic interface strength (section V).

An important unanswered question in the above interpretation is the origin of stress concentration. The postulate for the transition in fracture stress described above suggests that significant stress concentrations must occur, as the measured stress levels (≤ 30 MPa) are always lower than the yield stress in shear (~ 46 MPa). Such stress concentrations could arise due to slight misalignment of the ring and substrate, or possibly due to flaws. A full stress analysis has not yet been attempted for this system. This issue must be resolved in future work.

Another important observation of this work is that the presence of phase separated domains within the incomplete monolayers doesn't effect the fracture behavior, while a large change in the fracture curves results when the ODTS is deposited at full density into well-defined domains. Figure II-11 shows that with Method 1, the same catastrophic relationship is obtained for relatively uniform incomplete monolayers and for highly nonuniform incomplete monolayers. However, Figure II-22 shows a dramatic change when the ODTS is deposited in domains using Method 2 relative to that obtained with Method 1. We interpret this as indicating that the ODTS domains observed for the 10 °C depositions using Method 1 are not at full density. Rather, the packing density of ODTS within the domains is such that the epoxy can still bond strongly to the substrate. This needs to be examined by X-ray reflectivity measurement of the density when the domains just begin to meet for the 10 °C depositions. The strong effect observed between Method 1 and Method 2 is believed to be due to the fact that in Method 2, the ODTS in the domains is at close-packed density. In that case, the domains act as flaws or disbonded regions. We find for the case of 50 μm domains that the fracture stress is nearly proportional to the area fraction occupied by the disbonded regions. For 5 μm domains the fracture stresses are slightly higher than those for 50 μm domains at the same mass coverage. An important extension of this work is to investigate smaller domain sizes to determine the size below which flaws have no impact on the fracture behavior.

Summary. Over a large range, the interface strength has little effect on the fracture stress because failure apparently initiates cohesively. (We reiterate that the initiation site cannot be directly determined in this test, but rather cohesive initiation is inferred from the plateau in fracture stress in Figures II-11 – II-14 and Figure II-23 along with observations of the fracture surfaces.) Only a low level of interface bonding is sufficient to achieve cohesive crack initiation. The transition from cohesive (high critical stress) to adhesive (low critical stress) crack initiation occurs over a narrow range of interface strength for methods I and III. The transition apparently occurs when the interface strength is sufficient to support stresses high enough to cause plastic deformation within the epoxy. The sharpness of the transition is consistent with the bulk material response where the onset of material deformation occurs over a narrow range of stress. The observed catastrophic relationship indicates that one cannot use joint strength as a measure of aging, since no change is observed until catastrophic failure occurs.

The data imply that interfacial flaws greater than a certain size (not yet identified but less than 5 μm) have a strong impact on the fracture behavior. This provides insight into the importance of various types of contamination or defects. Contamination will have a

strong impact if it is distributed in domains greater than a critical size (not yet identified but less than 5 μm). If it is uniformly distributed, contamination will be important only if enough surface sites are occupied that the number of bonding sites left available for the adhesive is insufficient to support stresses comparable to σ_y . We will return to this point in section VI.

II.c Double cantilevered beam (DCB) test

A Sandwiched Double Cantilevered Beam (SDCB) specimen has been used to measure the toughness of a silicon/epoxy interface as a function of the extent of interfacial bonding. Interfacial toughness is a macro-scale material property that characterizes when an existing interfacial crack will advance. A detailed discussion of interfacial fracture mechanics theory is found in Rice (1988) and Hutchinson and Suo (1992). One aspect of interfacial fracture mechanics that distinguishes it from traditional linear elastic fracture mechanics is the role of mode mixity. Asymmetries with respect to the interface are responsible for the inherently mixed mode condition found at the tip of an interfacial crack. Both normal and shear stresses are present on the interface ahead of the crack tip, and in general the ratio of these stresses changes with distance from the crack tip. The level of mode mixity (defined as the arctangent of the ratio of shear stress to normal stress at a fixed distance $\hat{l}$ in front of the crack tip in the region dominated by the stress singularity) depends on the elastic properties and the body's overall geometry and loading. According to current thought, resistance to interfacial crack propagation is most conveniently specified in terms of critical energy release rate G_c versus the mode mixity $\hat{\psi}$. The fracture criterion for interfacial cracking is then defined by

$$G = G_c(\hat{\psi}) \quad (\text{II.3})$$

where $G_c(\hat{\psi})$ is the mode mixity dependent interfacial toughness. An interface crack that is subjected to mode mixity $\hat{\psi}$ advances when the energy release rate for crack extension G equals the critical value associated with that mode mixity, $G_c(\hat{\psi})$. There is experimental evidence, at least for relatively weak interfaces, that G_c increases substantially with increasing $\hat{\psi}$ (Liechti and Chai 1992 and Liang and Liechti 1995).

II.c.1. Materials and Methods.

As in the Napkin Ring tests, the epoxy adhesive is EPON 828/T-403. A 100:46 weight ratio was used and the system was cured for 48 hours at 50°C. The extent of interfacial bonding was varied using ODTS incomplete monolayers (Method 1). The method of ODTS deposition and the characterization of the incomplete monolayers are as given in Section II.b.

The toughness of a silicon/epoxy interface was measured with a variant of the double cantilevered beam specimen, the SDCB. Measuring the toughness of a silicon/epoxy interface proved to be a challenge since an interfacial crack tends to kink into the relatively brittle silicon. The successful design is 125 mm long, 12.7 mm wide and made from a 19.4 mm thick sandwich composed of 9.1 mm aluminum / 0.6 mm silicon / 0.6 mm epoxy / 9.1 mm aluminum. This design minimizes the axial in-plane strain within the silicon layer and subjects it to a nearly uniaxial stress state when remote from the crack tip. Note that for a given toughness level, the maximum arm strain developed in a DCB specimen scales as the reciprocal of the square root of the product of the arm's thickness times its Young's modulus. This motivates the use of the relatively thick and stiff aluminum outer layers. Furthermore, the silicon is cut so that the (100) orientation is along the beam axis. In this orientation the silicon is orthotropic (e.g., no shear coupling), Young's modulus (130 MPa) is minimized, and the Poisson's ratio (0.28) is a reasonable match to that of the adjacent epoxy and aluminum layers. This ensures that the relatively thin silicon is in an essentially uniaxial stress state when the beam arm is bent. Detailed finite element analysis of this SDCB showed the crack tip mixity to be about positive 8 degrees at a reference length of 10 μm (the estimated epoxy plastic zone length). This mixity tends to push the crack away from the silicon and into the epoxy. The toughest silicon/epoxy interface measured was 20 J/m², and in this case the in-plane strain in the silicon is estimated to be only 300 $\mu\epsilon$.

Some details in the method used to fabricate the SDCB evolved with time. Described below is the current approach. First a silicon strip of the same length and width as the 6061 T6 aluminum adherends is bonded to one of the adherends. The unpolished side of the silicon is the side bonded (i.e. toughness measurements are made on the polished side) to the aluminum. The integrity of this bond is crucial. The aluminum surface is lightly sandblasted and then cleaned. The silicon surface is plasma treated. A structural epoxy adhesive is used to bond the materials together. Next, the polished silicon surface is cleaned and an OTDS SAM coating is applied when desired. At one end of the adherend a 40 mm long section of the silicon surface is fully coated with the OTDS SAM. This

provides a poorly bonded region from which interfacial cracking is easily initiated. The final step bonds two adherends together with an approximately 0.6 mm thick epoxy adhesive layer. This is done in an open cavity RTV mold that confines the epoxy. The adherend with the silicon layer is placed at the bottom of the cavity with the silicon side up. Small spacers are bonded to the ends of this adherend to define the epoxy layer thickness, and the second adherend is then positioned on top. The upper adherend contains injection and exit holes for the epoxy through its thickness. These holes are at opposite ends of the adherend. After the epoxy is injected, the mold is placed in an oven to cure the epoxy.

The specimen is pinned into a load train that utilizes a chain linkage and is loaded by pulling the ends apart at a crosshead displacement rate of one mm/s to propagate a crack along the interface. The crack grows stably with increasing end displacement allowing several G_c measurements to be made while testing a single specimen. G_c depends on the load to propagate a previously arrested crack and the associated crack length (inferred from the measured specimen compliance). The calibration used to determine G_c from the measured load and crack length is based upon results published by Bao et al (1992) for a single material DCB. A finite element analysis indicates that their results can be applied to the present SDCB if plane strain G is scaled by a factor of 1.05 while the associated plane stress specimen compliance is scaled by 0.93. Note that the presence of the silicon layer on the one aluminum adherend is accounted for in the calibration by replacing that two-material adherend with a slightly thicker aluminum adherend with the same bending stiffness. As indicated above, this SDCB specimen has $\hat{\psi}_{r=0.01\text{mm}} = 8^\circ$.

II.c.2. Results

The measured silicon/epoxy interfacial toughness is plotted in Figure II-24 and summarized in Table II.1. Results from three separate test series are shown. The toughness results are presented as a function of ODTS coverage as indicated by equilibrium water contact angle. As discussed in Section II.b.2.a, equilibrium water contact angle can be related to mass coverage of ODTS. For the fully ODTS-coated surface, the fracture toughness was below the level that could be measured ($\sim 2 \text{ J/m}^2$), as the crack ran the entire length of the sample upon initiation. A visual inspection of the failed samples suggests adhesive failure with no signs of cohesive failure in the epoxy, even for the bare silicon/epoxy interface. This has been confirmed by TOF-SIMS analysis of samples fabricated with a deuterated epoxy resin, which indicated only a very small amount of deuterium (less than the maximum values shown in Figure II-17) remains on the substrate surface after fracture. This indicates that the failure remains adhesive in this loading

geometry even in the absence of the ODTS monolayer. In some tests the crack kinked into the silicon after substantial interfacial crack growth. In such cases only the data corresponding to interfacial cracking is presented. The measured interfacial toughness for EPON 828/T403 epoxy on a native oxide silicon surface is about 20 J/m².

Table II.1 Interfacial toughness ($\hat{\psi}_{r=0.01\text{mm}} = 8^\circ$) of an EPON828/T403 epoxy adhesive on an OTDS-coated silicon substrate.

Series Number	Equilibrium Water Contact Angle (degrees)	Number of Measurements	G_c (J/m ²)	Standard Deviation (J/m ²)
1	0	6	20.8	3.4
1	95	10	4.2	0.9
1	101	14	1.6	0.6
2	82	7	16.4	3.2
3	0	10	22.0	2.7
3	97	13	7.8	2.9

II.c.3. Discussion

Although the data are limited, interfacial toughness appears to vary in a nonlinear fashion with interface strength. The dependence is very strong over a narrow range of ODTS coverage, and then appears to level off at lower ODTS coverage. A similar nonlinear trend was observed in the NR strength measurements. However, there are some very important differences in the results of these two tests, and the apparent similarity in the shape of the curves is only superficial. First, the rise in fracture toughness occurs at noticeably lower values of ODTS coverage (equilibrium water contact angle) in the DCB test than in the NR test. Second, while more data are needed, the form of the curve appears to be different. In the NR test the onset of the plateau in fracture stress appears to occur very abruptly, whereas the data in Figure II-24 show a smoother or more gradual leveling off. Thirdly, in the DCB test the failure remains interfacial for all values of interface strength, whereas a transition from interfacial to cohesive failure occurs in the NR test. The leveling off of the fracture toughness in the DCB test is likely due instead to the number of substrate bonding sites exceeding the bonding sites of the epoxy. These observations indicate that the fracture mechanisms are very different. We will return to this point in section VI.

III. Continuum Analysis of Interfacial Cracking

The solid mechanics community continues to devote considerable effort towards developing improved methods for modeling interfacial fracture. Much of this work involves extending linear elastic fracture mechanics to include interfacial cracking (Rice, 1988, Hutchinson and Suo, 1991). Other notable work includes efforts to understand the effect of material yielding (Shih and Asaro, 1988; Bose et al., 1999) and the relationship between cleavage cracking and atomic-scale interfacial decohesion (Suo et al., 1993, Lipkin and Beltz, 1996). Still other work has pursued an embedded process zone approach that uses a traction-separation relation to incorporate crack extension in a natural way (Needleman, 1987; Tvergaard and Hutchinson, 1992; and Hutchinson, 1997). Here we will analyze polymer/solid interfaces with the goal of establishing the relationship between fracture toughness and the stress field a few nanometers from the crack tip. This will allow connection with the results of MD simulations described in the following section. To achieve this goal, a material model is needed which is valid down to this very small length scale. The question can be raised as to whether the epoxy structure is uniform down to such small length scales. However, some support for this has been obtained recently in the swelling of thin ($\sim 600 \text{ \AA}$) epoxy films where the concentration profile of the swelling solvent was measured through the film by neutron reflectivity (Yim et al., 1999).

The sandwiched aluminum/silicon/epoxy/aluminum DCB test is analyzed as in the fracture experiments discussed in Section II.c. Although the results we present are for this one specific specimen configuration, they should apply in a broader sense. The analysis proceeds as follows. First a traditional linear elastic interfacial fracture analysis is performed to determine the specimen's energy release rate and mode mixity. Next the effect of epoxy yielding is considered. The sandwiched DCB is analyzed using a pressure-dependent Drucker-Prager epoxy yield model. Here stresses are resolved on the micron scale, and plastic zone size and crack-tip blunting are quantified. Since this analysis indicates the yield zone is small compared to the region dominated by the elastic stress singularity, an asymptotic small-scale yielding analysis is performed next. This analysis considers the crack to be semi-infinite with the remote boundary loads specified by the elastic singularity solution. Here a highly refined finite element mesh is used to investigate the stress state down to the nanometer scale. This pushes the continuum analysis beyond its rigorous limits of applicability. Nevertheless these results, which include the effect of rapid work hardening at large strain, should provide useful insights into the fundamental failure process.

III.a. Linear Elastic Interfacial Fracture Mechanics Analysis

Figure III-1 shows the finite element mesh used to carry out the linear elastic fracture mechanics analysis of the sandwiched aluminum/silicon/epoxy/aluminum specimen. The mesh is composed of eight-noded, reduced integration, plane strain quadrilateral elements. The wedge-shaped elements that surround the crack tip are formed by collapsing one side of quadrilateral elements. The collapsed, crack tip nodes are constrained to have the same displacement, whereas the mid-side nodes closest to the crack tip are moved to the quarter-point position to incorporate a square root singularity. The length of the smallest elements is 0.5 μm (0.0008 of the adhesive bond thickness). All materials are modeled as isotropic and linear elastic. Silicon has a Young's modulus $E=130$ GPa and Poisson's ratio $\nu=0.28$, aluminum has $E=69$ GPa and $\nu=0.33$, while the epoxy has $E=3.5$ GPa and $\nu=0.35$.

A highly refined crack-tip mesh is used in the analysis so that the parameters defining the asymptotic stress state can be evaluated. The form of the singular stress state at the tip of a crack lying on the interface between two dissimilar, linear-elastic, isotropic materials is well known (Rice 1988, Hutchinson and Suo, 1992). Figure III-2 shows the plane strain interfacial crack problem considered. Material 1 is above the interface and material 2 is below, and μ_i , E_i , and ν_i ($i=1,2$) are the shear modulus, Young's modulus, and Poisson's ratio of the respective materials. Note that for a wide class of plane elasticity problems for bimetals with prescribed tractions, the stress state depends only on two non-dimensional material parameters α and β (Dundurs, 1969), and these constants are used in the solutions presented below. For plane strain

$$\alpha = \frac{(\bar{E}_1 - \bar{E}_2)}{(\bar{E}_1 + \bar{E}_2)} \quad \text{where} \quad \bar{E}_i = \frac{E_i}{1 - \nu_i^2} \quad \text{for } i = 1, 2 \quad (\text{III-1})$$

$$\beta = \frac{1}{2} \frac{\mu_1(1 - 2\nu_2) - \mu_2(1 - 2\nu_1)}{\mu_1(1 - \nu_2) + \mu_2(1 - \nu_1)} \quad (\text{III-2})$$

The asymptotic solution for in-plane stress at the tip of an interface crack between two dissimilar, linear elastic, isotropic materials is

$$\sigma_{jk} = \frac{1}{\sqrt{2\pi r}} \left[\text{Re}(Kr^{i\varepsilon}) \tilde{\sigma}_{jk}^I(\theta, \varepsilon) + \text{Im}(Kr^{i\varepsilon}) \tilde{\sigma}_{jk}^{II}(\theta, \varepsilon) \right] \quad (j, k = r, \theta) \quad (\text{III-3})$$

where

$$K = K_1 + iK_2, \quad i \equiv \sqrt{-1} \quad (\text{III-4})$$

$$\varepsilon = \frac{1}{2\pi} \ln \left(\frac{1-\beta}{1+\beta} \right) \quad (\text{III-5})$$

$$r^{i\varepsilon} = \cos(\varepsilon \ln r) + i \sin(\varepsilon \ln r) \quad (\text{III-6})$$

The complex interface stress intensity factor K will in general depend on load, geometry, and the bimaterial parameters α and β . The nondimensional angular functions $\tilde{\sigma}'_{jk}(\theta, \varepsilon)$ and $\tilde{\sigma}''_{jk}(\theta, \varepsilon)$ are given by Rice et al. (1990). Note that the angular functions are normalized so that the interfacial tractions directly ahead of the crack tip are given by

$$(\sigma_{yy} + i\sigma_{xy})_{\theta=0} = \frac{Kr^{i\varepsilon}}{\sqrt{2\pi r}} \quad (\text{III-7})$$

Also note that the asymptotic result for the displacement jumps a distance r behind the crack tip $\delta_j = u_j(r, \theta = \pi) - u_j(r, \theta = -\pi)$ for $j = x, y$ is given by

$$\delta_y + i\delta_x = \frac{8Kr^{i\varepsilon}}{E^*(1 + 2i\varepsilon)\cosh(\pi\varepsilon)} \sqrt{\frac{r}{2\pi}} \quad (\text{III-8})$$

where

$$\frac{1}{E^*} = \frac{1}{2} \left(\frac{1}{E_1} + \frac{1}{E_2} \right) \quad (\text{III-9})$$

The singular stress field is fully defined once the complex stress intensity factor K is prescribed. Complex $K=K_1+iK_2$ can be expressed in a polar form defined by its magnitude and a phase angle. The energy release rate G for crack advance along the interface is related to the magnitude of the complex stress intensity factor $|K|^2 = K_1^2 + K_2^2$ by

$$G = \frac{(1 - \beta^2)}{E^*} |K|^2 \quad (\text{III-10})$$

Furthermore, Rice (1988) has suggested a generalized interpretation of mode measure, and this definition is now widely used. Mode mixity $\hat{\psi}$ is defined with respect to a reference $\hat{l}$.

$$\hat{\psi}_{r=\hat{l}} = \tan^{-1} \left[\frac{\text{Im}(K\hat{l}^{i\varepsilon})}{\text{Re}(K\hat{l}^{i\varepsilon})} \right] \quad (\text{III-11})$$

The choice of reference length $\hat{l}$ is arbitrary and is sometimes based on a characteristic inplane length of the body analyzed or on an intrinsic material length scale. In any case $\hat{\psi}$ defines the phase of the complex K and values corresponding to two different length scales $\hat{l}_1$ and $\hat{l}_2$ are related by

$$\hat{\psi}_{r=\hat{l}_2} = \hat{\psi}_{r=\hat{l}_1} + \varepsilon \ln(\hat{l}_2 / \hat{l}_1) \quad (\text{III-12})$$

Consequently, the singular asymptotic solution is fully specified by complex K or equivalently by G and $\hat{\psi}$.

The energy release rate G and mode mixity $\hat{\psi}$ has been determined for the sandwiched DCB specimen shown in Fig. III-1. G is determined by a J-integral evaluation, whereas mode mixity $\hat{\psi}$ is calculated using crack flank displacements (Eq. III-8, see Matos et. al., 1989). For the silicon epoxy interface $\alpha=0.95$ and $\beta=0.22$, and

$$G = 0.492 \left(\frac{P}{w} \right)^2 \quad \text{and} \quad \hat{\psi}_{r=0.01mm} = 8^\circ \quad (\text{III-13})$$

G has units of J/m² when the applied load P is given in Newtons and specimen width w is given in meters. If the mixity at $\hat{l} = 0.01 \mu\text{m}$ influences the crack trajectory, then a positive mixity would drive the crack into the epoxy layer.

Linear elastic, interfacial fracture mechanics can only be applied when there is small scale yielding. The length of the yield zone must be small compared to the size of the region

dominated by the stress singularity. Eq. III-7 indicates that within the region dominated by the stress singularity,

$$\left| (\sigma_{yy} + i\sigma_{xy})_{\theta=0} \right| = \frac{|K|}{\sqrt{2\pi r}} \quad (\text{III-14})$$

The finite element solution is within 10% of the asymptotic result when $r < 0.06$ mm (10 per cent of the 0.60 mm epoxy layer thickness).

III.b Modeling Epoxy Yielding

Epoxyes exhibit complex nonlinear behavior when tested below their glass transition temperature. (Fig. III-3). Yield is followed by softening, and subsequent hardening that becomes limiting at strains of order one. This behavior is rate, pressure, and temperature dependent. Furthermore post-yield softening introduces the complexity of localized deformation creating shear bands (Lai and Van der Giessen, 1997, Popelar and Liechti, 1997). Clearly modeling this complicated behavior is challenging, and such models are still evolving. Examples of such work include the viscoplastic model of Boyce, Parks, and Argon (1988) and the nonlinear viscoelastic model of O'Dowd and Knauss (1995). In the present study only very simple material models are used to model the epoxy. The primary calculations use a linear Drucker-Prager plasticity model as implemented in the ABAQUS (1998) finite element code. This plasticity model includes pressure dependent yield like that commonly observed in polymers. Since there is no known evidence that a large volume change occurs as the epoxy yields, the parameters defining the Drucker-Prager model were chosen so that there is nonassociated flow with no plastic volume dilatation. When pressure dependence is neglected, the Drucker-Prager epoxy model reduces to traditional J2-flow theory with a von Mises yield surface. Because of convergence difficulties with the pressure-dependent Drucker-Prager model when strains of order one occur, calculations investigating the effect of rapid work hardening at large strain used a standard J2-flow plasticity model. The postulated rapid hardening at large strains is consistent with the idea that 1) plastic deformation is associated with overcoming intra-molecular forces and 2) there is a finite amount of plastic deformation possible. In this epoxy model, plastic deformation initially occurs with little increase in stress (e.g., to 30 per cent strain). The stress for further plastic straining then rises rapidly until all the available plastic strain is

used up. Thereupon the material stiffens rapidly as intermolecular bonds are stretched and incremental strains are associated with an elastic response.

The calculations presented below are for an epoxy with an initial compressive yield strength of 50 MPa. To avoid potential computational complications, strain softening is neglected. Since the epoxy re-hardens at higher strains, the ultimate importance of strain softening is not obvious. The potential impact of strain softening clearly deserves consideration in future work. When pressure dependence is included, the tensile yield strength is taken to be 80% of the compressive yield strength. Epoxy hardening is defined by the true compressive stress-plastic strain relationship plotted in Fig. III-4. This set of material properties is based upon compressive test data for an EPON 828/T-403 epoxy at a 100:43 weight ratio and cured at 50°C for 24 hours followed by another 24 hours at 40°C. The stress-strain response beyond a strain level of 30 % is arbitrarily defined to represent rapid hardening at large strains. True stress-strain data to strains of order one are difficult to measure. For example, once softening commences a cylindrical compression specimens barrels, and indeed the plotted stress-strain data shown in Fig. III-3 does not correct for this localized specimen deformation. Although the epoxy models used in this study are relatively unsophisticated, they do include the important effects of yield and subsequent rapid hardening at large strains.

III.c. Sandwiched DCB with Epoxy Yielding

The sandwiched DCB specimen has been analyzed using an epoxy model that incorporates yielding to investigate the size of the yield zone and the extent of crack-tip blunting. This analysis utilizes the same finite element mesh as shown in Fig. III-1 except that the wedge-shaped elements at the crack tip are replaced by a 0.1 μm hole. The wedge-shaped elements used in the elastic analysis are unable to accommodate large-scale crack-tip blunting. They become so distorted that it becomes impossible to obtain a convergent solution. The analysis includes geometric nonlinearity and uses the pressure dependent Drucker-Prager epoxy model with hardening as defined by Fig. III-4. Convergent solutions were obtained for an energy release rate of up to 14 J/m²; 70% of the highest G level measured in the sandwich DCB test (Section IIc).

Figure III-5 shows the shape of the plastic yield zone and how it extends along the interface with increasing G. The plotted yield zone bounds those elements with a calculated equivalent plastic strain of 0.001 or more. The main part of the yield zone juts out at 72 degrees below the interface, however there is also a part that lies along the interface. The portion that extends along the interface, r_p^{int} , has a length that roughly equals that of the

portion that extends at 72 degrees, $r_p^{\max}$, when $G < 4 \text{ J/m}^2$. The ratio of these two yield zone length descriptors changes with G level. As the G level increases to 14 J/m^2 , the ratio of $r_p^{\max}$ to r_p^{int} increases to 1.6. This variation in the shape of the yield zone with G level is expected since the ratio of shear to normal stress – i.e. mixity – varies with distance from the crack tip (Rice, 1988). At $G=14 \text{ J/m}^2$, $r_p^{\text{int}}=9 \text{ }\mu\text{m}$; a distance of roughly 2 percent of the epoxy layer thickness. When $G=1 \text{ J/m}^2$, r_p^{int} is less than $2 \text{ }\mu\text{m}$. These results indicate that the size of the epoxy yield zone in the sandwich DCB tests is quite limited. Recall that when a full OTDS SAM layer is applied to the silicon substrate, the measured G_c is only a couple of J/m^2 or less (Section II.c). The plastic yield zone is expected to be about $2 \text{ }\mu\text{m}$ long at this G level.

The finite element analysis also shows that the crack-tip undergoes substantial blunting with increasing G (Fig. III-6). Recall that the elastic analysis indicates that the sandwiched DCB specimen has a mode mixity of 8 degrees at a characteristic length of 10 microns (Eq. III-13). This suggests that on the micron scale the crack will be subjected to largely an opening displacement. The finite element results for a yielding epoxy are consistent with this expectation. The normal blunting, δ_y , increases in a roughly linear manner with G , while tangential blunting, δ_x , show little dependence on G . At $G=14 \text{ J/m}^2$, $\delta_y=0.3 \text{ }\mu\text{m}$; or about 3 percent r_p^{int} . To fully capture the stress state in front of a blunted crack, the finite element mesh must be commensurate with the degree of blunting.

Figure III-7 plots the calculated interfacial normal stress for $G=14 \text{ J/m}^2$. The peak interfacial normal stress occurs right at the edge of the $0.1 \text{ }\mu\text{m}$ hole that was arbitrarily inserted at the crack-tip to avoid convergence problems. Immediately beyond the first two elements, at a position $> 1 \text{ }\mu\text{m}$ in front of the crack tip, the stress is 60 to 70 MPa over a distance of $5 \text{ }\mu\text{m}$. The insert in Fig. III-7 shows that the effective plastic strain is less than 10 percent in this region. An interfacial normal stress of 70 MPa is well below that thought necessary to break the bonds between epoxy and silicon (estimated to be on the order of 140-460 MPa, see Section V). This indicates that failure occurs on a length scale of less than a micron. At shorter length scales, one anticipates higher strain levels and the associated effect of rapid hardening at large strain.

III.d. Small-Scale Yielding Asymptotic Analysis

The small scale yielding asymptotic analysis considers a semi-infinite crack in an infinite media with the remote boundary loads specified by the elastic singularity solution (Eq. III-3, with $\hat{\psi}_{r=10\mu\text{m}} = 8^\circ$ for the sandwiched DCB). This asymptotic analysis is applicable when the yield zone is small relative to the region dominated by the elastic

singularity field. Here we will limit the maximum applied G to 1 J/m^2 . At this G level the calculated length of the yield zone is $2 \text{ }\mu\text{m}$ (Fig. III-5). In a finite element analysis of the small-scale yielding problem one typically considers a finite-sized circular region (Fig. III-8). The radius of the domain is chosen so that the plastic zone developed at maximum load is so small that its existence has no noticeable affect on the stresses near the outer boundary. In the present work a domain with a radius of 1 mm is used in the small-scale yielding analysis. This domain is 500 times the calculated plastic zone size for $G=1 \text{ J/m}^2$. A one nm radius void is inserted at the crack tip (Fig. III-8). This is done to avoid convergence problems, but can also be thought of as modeling the nano-voids detected in the molecular dynamics calculations (Section IV.b.8). Since a continuum representation of a glassy solid at the nano-scale is uncertain; a crack tip void seems as reasonable a choice as any other possibility. The mesh shown in Fig. III-8 spans six decades of length – nm to mm, with 10 logarithmically spaced rings of elements covering each decade.

Pressure dependent Drucker-Prager model ($G \leq 0.05 \text{ J/m}^2$). Attempts to obtain solutions that include geometric nonlinearity while using the pressure dependent Drucker-Prager epoxy model with hardening (Fig. III-4) met with only limited success. It was possible to attain a convergent solution for an energy release rate of up to 0.05 J/m^2 . This is the lowest G of any practical interest; it is of the order of the work of adhesion of an epoxy on a silicon substrate with a high coverage of ODTS (see Section II.b.2.a.2). Others have noted similar difficulties in using a pressure dependent Drucker-Prager epoxy model in conjunction with a highly refined mesh (Chiang and Chai, 1994). Calculations that neglect pressure dependence in the epoxy model could be carried out to $G=1 \text{ J/m}^2$.

Figure III-9 shows that the calculated yield zone in an epoxy with pressure dependent yielding has one lobe extending 90° from the interface and another extending along the interface. The portion along the interface is longer, with a length of $0.1 \text{ }\mu\text{m}$. The crack tip undergoes roughly equal tangential (1.0 nm) and opening (1.3 nm) displacement. The importance of including pressure dependence is assessed by repeating the calculation with the same epoxy model but with the pressure dependence suppressed. Figure III-10 shows that neglecting the pressure dependence reduces the length of the yield zone by about 50 per cent and also decreases crack tip displacements. These results are consistent with expectations. In the pressure sensitive epoxy model, the effective stress required for yielding is reduced in the presence of hydrostatic tension –i.e. negative pressure. Since hydrostatic tension is generated in front of the crack tip, yielding is enhanced. The impact of a pressure dependent epoxy model on calculated interfacial shear and normal stress distributions is shown in Figs. III-11 and III-12, respectively. It is not clear how to

interpret the spike in stress at the crack tip. The stress spike is generated by strain levels associated with rapid hardening, but strains of this magnitude are localized to a region extending less than one nanometer along the interface. Once beyond the first couple of highly strained crack tip elements, both shear and normal stress are fairly constant over a distance comparable to the length of the yield zone. In this constant stress region, the interfacial normal stress is about 60 MPa when pressure dependence is included in the epoxy model, and about 80 MPa when pressure dependence is neglected. These relatively low levels of interfacial stress are comparable to the 50 MPa uniaxial compressive yield strength for strains of < 0.3 (Fig. III-4). Although this compressive yield strength value was chosen somewhat arbitrarily in view of the observed softening (see insert in Fig. III-3), it seems unlikely that the value used in the calculations is in error by more than a factor of two. This suggests that an interfacial normal stress of on the order of 100 MPa may be capable of separating a silicon/OTDS/epoxy surface. Finally note that while the inclusion of pressure dependence in the epoxy model does affect the magnitude of the calculated interfacial stress, the stress state does not appear to differ in any fundamental way.

Pressure dependence suppressed ($G \leq 1 \text{ J/m}^2$). To investigate the effect of rapid hardening at large strains, solutions for $G \gg 0.05 \text{ J/m}^2$ are needed, consequently pressure dependence is suppressed in the results presented next. When pressure dependence is suppressed, a convergent solution for a G of up to 1 J/m^2 could be realized. At $G=1 \text{ J/m}^2$ the crack undergoes substantial blunting. The calculated displacements are greater than the size of the one nm radius void at the crack tip ($\delta_x=7 \text{ nm}$, $\delta_y=17.5 \text{ nm}$). Extensive blunting generates large crack tip strains (Figure III-13), and as a result rapid hardening at large strain leads to high crack-tip stress. Figure III-14 plots interfacial normal stress distributions for $G=0.05, 0.50$, and 1.00 J/m^2 . As the G -level increases to 1 J/m^2 , the zone of highly strained epoxy (strains > 0.3) extends to a length of 5 nm along the interface. Figures III-15, 16, and 17 plot interfacial normal stress, shear stress, and equivalent plastic strain as a function of G -level at both 1 and 9 nm from the crack tip. The 1 nm location is engulfed in the zone of rapid strain hardening with an equivalent plastic strain exceeding 0.45 at $G=1 \text{ J/m}^2$. As a consequence the peak interfacial normal stress exceeds 350 MPa whereas the magnitude of the peak interfacial shear stress exceeds 50 MPa. At 9 nm from the crack tip, the strain level is below 0.30, and the interfacial normal and shear stresses are only 120 and 30 MPa, respectively. Although large strains are localized to a small zone in front of a blunted crack tip, rapid hardening at high strains does provide a means for generating high interfacial stress. If a relatively high interfacial stress is required to break

strong interfacial bonds, this seems to be one way of accounting for such elevated stress levels. Without rapid hardening at large strain, interfacial stress would seem to be restricted to a magnitude comparable to the epoxy's initial yield strength.

All results presented to this point have been for a mixity $\hat{\psi}_{r=10\mu m} = 8^\circ$; the value applicable to the sandwiched aluminum/silicon/epoxy/aluminum DCB test specimen. To investigate the affect of mode mixity, calculations were also carried out for mixities of -22° and 48° . A comparison of Figures III-18, III-13 and III-19 shows that the applied mode mixity has a profound effect on the size and shape of the crack tip yield zone as well as the nature of crack-tip blunting. As the mixity increases, the length of the portion of the yield zone along the interface increases dramatically. The amount of tangential displacement at the crack-tip also increases rapidly. Figures III-20 and III-21 show interfacial normal stress versus G for the three different mode mixities at 1 nm and 9 nm from the crack tip, respectively. Interestingly, at 1 nm, for $G > 0.1 \text{ J/m}^2$ the interfacial normal stress is highest for a mixity of 48° , whereas at 9 nm from the crack tip the interfacial normal stress is highest for a mixity of -22° .

III.e. Summary

Using a two-step continuum calculation, the stress field and material deformation near the crack tip has been calculated for the DCB specimen down to the nanometer length scale. The relationship between fracture toughness and interfacial normal stress at a few nanometers from the crack tip in Figure III-15 is the input from these calculations to the overall fracture model. This relationship will be combined with a relationship from MD simulations between fracture stress and the interfacial interaction potential $\Psi(x,y,z)$, specifically the fraction of sites which chemically bond, in section VI to form the complete fracture model.

IV. Molecular simulations of fracture

In this section, the focus is on treating the interface between a polymer network and a solid at the molecular level. Molecular dynamics (MD) simulations are performed to determine the relationship between the local stress on a ~ 100 Å scale and the interfacial interaction potential $\Psi(x,y,z)$, or more specifically the fraction of sites which chemically bond. In Section VI this relationship will be combined with the relationship between G and stress at 90° from the crack tip from the previous section to form the complete fracture model. In addition, the MD simulations examine the role of connectivity in epoxies. It is well known that the connectivity of a polymer system controls much of polymer dynamics (Doi, 1986). Below we show that the connectivity of the network controls a number of important features of the system's fracture. We first discuss the methodology and then the results.

IV.a. Method

IV.a.1. Force Fields

Following a large body of work on polymeric systems (Binder, 1995), MD simulations are performed on a coarse-grained (i.e. bead-spring) polymer model. For focusing on the relationship between the network connectivity and the failure modes of the adhesive, the bead-spring model is ideal. Coarse-grained models have been very successful in describing polymer structure and dynamics (Binder, 1995). Because of the long relaxation times typical of polymer dynamics, atomistic simulations are not viable. By coarse-graining, a sufficient increase in computational speed is achieved to treat the relaxation times while still treating the fundamental aspects of polymers. The coarse-grained models are closer to the continuum models with which we ultimately want to connect.

A modification of the successful Kremer-Grest bead-spring model is used [Kremer, 1995]. In this model, polymer chains are composed of beads which interact via a Lennard-Jones (LJ) interaction with a cutoff at 2.5.

$$u_{LJ}(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right) \quad (\text{IV.1})$$

where here ϵ is the LJ energy unit and σ is the length unit and particle diameter. Unfortunately, the same symbols (ϵ, σ) are traditionally used for stress and strain. In order not to confuse the reader, all quantities in section IV will be in LJ units so that σ and ϵ represent the stress and the strain.

In the Kremer-Grest work beads are bonded together with a potential composed of two parts. The first part is just the purely repulsive version of the above LJ potential. This version is obtained by a cutoff at $2^{1/6}$ (LJ length units). The second part of the bond potential is the finite-extensible nonlinear elastic (FENE) bond potential

$$u_{FENE}(r) = -kR_0^2 \ln\left(1 - \frac{r^2}{R_0^2}\right) \quad \text{for } r < R_0 \quad (\text{IV.2})$$

This bond potential does not allow chains to cross; thus, it preserves the topology of the polymer system which is critical in the dynamics. In order to break bonds and preserve the continuity of the bond force, a breakable bond potential was initially created to approximate the FENE potential at the potential minimum. A quartic potential is used to create a potential with two minima.

$$u_4(r) = k_r(r - r_1)(r - r_2)r^2 + U_0 \quad \text{for } r < r_2 \quad (\text{IV.3})$$

The value of r_1 is set to match the FENE bond force minimum. The second minimum at r_2 is the cutoff point. Two parameter sets have been used. The parameter set 1 is: $k_4 = 1200$, $r_1 = 0.75$, $r_2 = 1.55$ and $U_0 = 34.69$. The maximum force to break the bond is 100 (LJ force units). Parameter set 2 is: $k_4 = 1434.3$, $r_1 = 0.7411$, $r_2 = 0.0$ and $U_0 = 67.2234$. The bond breaking force is 156.7. As in the FENE bond, the total bond potential includes the purely repulsive LJ interaction with a cutoff at $2^{1/6}$.

For the LJ pair interaction, the breaking force is 2.4. The scission force is then about 65 times the maximum LJ force for parameter set 2. For atomic force-fields derived from quantum mechanics, the force ratio between the bond and the van der Waals forces is about 1000. However, in the present coarse grained model a single bead represents several atoms, and so the LJ pair interaction represents multiple van der Waals pair interactions. Exact and unique calculations of mapping the real van der Waals interaction to the LJ bead interaction is not possible. We can only give an approximate mapping. With even just 3 atoms per bead, there are 9 pair interactions. Thus, one bead can easily correspond to about 10 van der Waals interactions. This implies that a force ratio of order 100 in the coarse-grained model is representative of the atomic system. The ratio 70 for parameter set 2 in the

present simulations is within a factor of 2 of the actual value. The main difference between parameter set 1 and 2 is the failure stresses at full coverage are larger than the yield stress for parameter set 2 and lower for parameter set 1.

IV.a.2. Geometry of molecular systems

The complete system consists of a polymer network between two walls [Thompson, 1990a]. The (111) direction (z-direction) is perpendicular to the walls. Each wall is composed of particles in two layers of an fcc lattice with nearest neighbor distance 1.204. The wall particles are bound to the fcc lattice sites by a harmonic spring with spring constant 100. The wall dimensions give the simulation cell lateral lengths, L_x and L_y . The separation distance between the innermost wall layers is L_z . The wall particles interact with the beads via the LJ potential, and some wall particles are bonded to the polymer network by Eq. (IV.3).

The dynamics of the system is performed at constant temperature using the Langevin thermostat (Schneider, 1985). The integration time step is 0.005, and the damping constants are 1 for the monomers and 5 for the walls.

IV.a.3. Networks

The general goal is to study networks as a function of the strand length. Here, the focus is on adhesives such as epoxies which have short strands. As outlined in the Section II, epoxies are chemically cured networks formed from a liquid mixture of a resin (here diglycidyl ether of bisphenol A) and a crosslinker (here T403). They form highly crosslinked molecular networks with each strand consists of only a few monomers. Each bead corresponds typically to 2 or 3 monomers (Kremer, 1995). A bead-spring model with two beads per strand was found to be the best match to epoxy material property data.

To create a random network similar to epoxy networks, a liquid mixture is crosslinked dynamically. The mixture consists of two bead and three bead molecules. The three bead molecule has a sixfold functional crosslinker bead already bonded to a two bead strand. The strand beads and crosslinker beads have identical potential parameters. Bonds are formed when the separation between a crosslinker and a strand end or wall particle is less than 1.3 (Kremer, 1995). After equilibrating the liquid mixture, crosslinkers are first bonded to the walls. Next, during a MD run typically of 150,000 time steps, the crosslinkers are bonded to strands until at least 95% of all possible bonds are made. Zero load is maintained on the walls during the crosslinking. Afterward, the temperature is

reduced below the glass transition temperature (0.5) to 0.3. This takes from 50,000 to 150,000 time steps with more steps required for the larger systems.

The tensile pull is performed by moving the top and bottom walls apart at constant velocity. Repeating boundary conditions are used at all sides. The tensile or normal stress is calculated from the total force on the wall divided by the wall area. The shear stress is determined by the force on the wall in the shear direction. The force on the wall is calculated by summing up the LJ interactions and the bond forces between a wall atom and a network monomer. As in experiments, simulations show that the yield stress and strain increase slightly with increasing strain rate. The wall velocities are in the range 0.001–0.1 which is slow enough not to perturb molecular scale relaxations, but much higher than in experimental systems. The failure strain does not depend on the strain rate in this velocity range.

IV.a.4. Checkerboard pattern of debond areas

To study the fracture behavior as a function of the number of bonds across the interface, a checkerboard pattern is used to restrict bonds to occur only in a designated area. Figure IV-1 shows an example of a 3x6 pattern. In the solid black regions bonds are not allowed to the surface. By varying the size of these regions, the bonding to the walls can be varied from 0% to 100%.

IV.a.5. System parameters

One set of different system sizes is given in Table 1. The smallest system has walls with a 32x16 lattice. The other systems have walls with a 64x24 lattice, or with area three times larger. As more particles are included in the system, the wall separation increases as is given in the table. Some data for each of the systems are given in Tables 2-5.

Table IV-1. Sizes of systems studied

System	no. particles	area	height
1	14000	$A_1=643$	15.1
2	51500	$1928=3A_1$	19.9
3	91000	1928	39.2
4	170000	1928	77.

Table IV-2. Data for system 1.

% bond area	no. bonds	tensile		shear	
		σ_f	ϵ_f	σ_f	ϵ_f
100	66	6.9	1.17	5.8	1.50
50	46	4.9	0.97	5.2	1.40
25	26	3.0	0.82	3.0	1.14
10	22	2.7	0.66	2.9	1.20
0	0	2.9	0.52	0.7	0.18

Table IV-3. Data for system 2.

% bond area	no. bonds	tensile		shear	
		σ_f	ϵ_f	σ_f	ϵ_f
100	230	6.2	1.05	5.8	1.86
50	119	4.5	0.94	3.9	1.64
25	63	2.8	0.60	2.6	1.44
10	25	3.0	0.5	1.4	1.06
0	0	3.0	0.54	0.6	0.16

Table IV-4. Data for system 3.

% bond area	no. bonds	tensile		shear	
		σ_f	ϵ_f	σ_f	ϵ_f
100	200	6.3	1.05	5.9	1.38
75	167	5.5	0.97	5.2	1.32
50	118	4.2	0.84	4.1	1.18
25	68	2.8	0.41	2.7	1.00
10	39	2.8	0.26	2.0	.90
0	0	2.9	0.21	0.6	0.09

Table IV-5. Data for system 4.

% bond area	no. bonds	tensile		shear	
		σ_f	ϵ_f	σ_f	ϵ_f
100	207				
75	163	5.6	0.94	4.9	1.25
50	128	4.7	0.86	4.7	1.21
25	71	2.8	0.46	2.9	1.03
0	0	2.8	0.22	0.5	0.11

IV.b. Results

IV.b.1. Stress-strain curves and network deformation

A typical stress-strain curve is shown in Fig. IV-2. The curve for full bonding has a typical shape that results from a set of corresponding deformations of the molecular structure. The peak at low strain is the yield stress due to separating the particles hydrostatically in a tensile pull. This involves just the van der Waals (or Lennard-Jones) interactions. This value of the peak stress is strain-rate dependent. Our simulation data agrees with experimental data showing an increasing yield stress with increasing strain-rate. Experimentally, the increase is logarithmic and this is consistent with simulation data, although the simulation data only spans 1 decade. At larger strains, the strands in the molecular network are stretched toward the taut conformation. Examination of bond separations shows that the bonds are not stretched in this regime. The only interaction is the van der Waals interaction. Once the strands have been pulled taut, then the bonds begin to stretch and the stress rises significantly. Upon sufficient stretching the bonds break, the interface fails and the stress drops to zero.

A key aspect of the fracture is that the bonds break in a succession of events, not simultaneously. This is seen in Fig. IV-2 which shows the strains at which bonds break in the set of points at $\sigma = 5$. The main consequence of the sequential bond breaking is that the fracture stress is less than the ideal stress to break all the interfacial bonds. At a given strain, only a fraction of the bonds break. This causes the actual fracture stress to be reduced relative to the ideal fracture stress. The value of the ideal stress will be determined shortly in upcoming subsections.

A similar picture occurs for shear simulations. The main difference is the much smaller yield stress. In shear, the particles 'roll' around each other so that the full van der Waals force is not necessary to separate particles as it is for hydrostatic deformations. Consequently, the shear yield stress is much smaller.

IV.b.2. Failure strain

The maximum failure strain particularly for small systems (tensile or shear) is related to the minimal paths within the network from a bond on the top wall to the network to a bond on the bottom wall to the network (see Fig. IV-3). These minimal paths have been calculated for many of the systems simulated using Dijkstra's method (Hu, 1982). The

minimal path is determined for all bonds to the top wall. We denote the length of a minimal path as P . For each wall atom, there is a value of P . Typically, we consider the minimal value of all P and the average value. We find the failure strain is closely correlated to the average P . The average minimal path is about twice the wall separation distance. There is a variation about this value of typically a few particle diameters. The strain at which the minimal path would be taut is

$$\varepsilon_p = \frac{P - L_z}{L_z} \quad (\text{IV.4})$$

where L_z is distance between the plates. The maximum possible strain at which the minimal strand would break is

$$\varepsilon_{\max} = \frac{r_b}{r_0} \varepsilon_p \quad (\text{IV.5})$$

where r_b is the bond breaking separation and r_0 is the equilibrium bond separation. However, our simulations show that $\varepsilon_{\max}$ is closer to P . This is a consequence of the fact that primarily just the interfacial bonds are stretched; bonds in the bulk are not stretched. This is consistent with the fact that the number of bonds at the interface is smaller than in the bulk. Consequently, on a per bond basis these bonds must support more stress causing them to stretch more and fail first. This will be further discussed below. Since P is a sum of bond vectors, stretching just one bond to break the path results in a path just slightly larger than P .

IV.b.3. Stress of self-assembled monolayer systems

Before further discussing the simulation results for the epoxy networks, we present calculations performed on the most simple systems, monolayers of small molecules aimed to represent self-assembling monolayers (SAMs). Experimentally, the use of SAMs provides a means to determine the ideal values of failure stresses. Simple geometries such as planes and spheres can be coated with SAMs. Two such SAM-coated surfaces can be brought together and the stress to separate the surfaces determined by atomic force microscopes. The terminal endgroup of the SAM molecule can be varied from a methyl group to an amine so that the interactions between SAMs varies from pure van der Waals to acid-base. In this manner, the fundamental interfacial strength for different interactions is obtained at the atomic level. Here, we are mainly interested in the two cases: pure van der Waals interactions and bonded (acid-base) surfaces. This has been measured experimentally (Thomas et al, 1995, Yoshizawa, et al, 1993, Yamada, et al, 1998) and here we present calculations.

For direct comparison with the bead-spring epoxy simulations, a bead-spring SAM is modeled. A bead-spring SAM is created by bonding a single layer of beads to a wall. The density of the SAMs is chosen to initially be that of the epoxy liquid and like the network formation, the load on the walls is set to zero and the temperature is set to 0.3. The SAM systems are then pulled or sheared apart just as the networks and the stress is calculated in the same manner.

The ideal interfacial (bond) stress required to fracture the interface is

$$\sigma_{id} = N_{int} F_b / A \quad (IV.6)$$

where N_{int} is the number of bonds across the interface, F_b is the force to break a single bond and A is the area of the plates. The total interfacial stress is the sum of the van der Waals interactions and the bond stress,

$$\sigma_{tot} = \sigma_{vdW} + \sigma_{bond} \quad (IV.7)$$

The van der Waals or LJ interaction for any particle involves many other particles. As such the calculation of the van der Waals contribution to the force depends on factors such as the density and the configuration of particles. To determine the ideal van der Waals contribution which involves statistical distributions, we use explicit MD calculations.

In Fig IV-4, the tensile stress-strain results of bead-spring SAM MD calculations are presented. For pure van der Waal interactions, a clear maximum of 5.6 in the tensile stress is observed. The stress-strain curve rises to this maximum stress and then decreases to zero as the LJ forces go to zero at large separations. When the two SAMs are bonded together with parameter set 2, the stress-strain curve initially follows the curve for nonbonded SAMs, but once the bonds begin to stretch the stress rises significantly. The maximum tensile stress reached is 111 which is very close to the ideal value of 124. For SAMs the difference between fracturing a bonded and a nonbonded surface is large—the ratio is 20.

In Fig IV-5, the shear stress-strain results of bead-spring SAM MD calculations are presented. The curves in Fig. IV-5 are similar to those for tensile loading in Figure IV-4, although some important differences are observed. For pure LJ interactions, no clear maximum is observed in the curves for shear loading, but rather strong oscillations appear which reach a maximum value of 4. These oscillations are due to the stick-slip motion of two commensurate surfaces. In real systems, typically two surfaces will be randomly

oriented with respect to each other and stick-slip does not happen. In that case, the stress will be much lower. Due to this complicating factor, the difference between the maximum stress for pure LJ interactions in tensile and shear is difficult to quantify from the simulations. However, the difference appears to be greater than a factor of 6. The stress does not become zero at larger strain for the shear geometry, since the monolayers never lose contact. For the bonded case, the fracture stress is 84, which is significantly smaller than for the tensile simulations. Including the substantial normal component of the stress (34), the total stress on the bonds is 91, which is still smaller than the tensile fracture stress. This may indicate that the distribution of bond scission events in time and in strain may be different in shear and tensile loading. Also, the failure strain is much larger. This is just a consequence of the geometry. Tensile pull directly pulls the bonds apart along the bond direction. Shearing the SAMs tilts the bonds and pulls them apart at an angle. The shear strain must be larger to achieve the same bond separation.

It is important to realize that for this model system the interface is completely bonded, i.e. *all* the beads representing SAM chains on one surface are bonded to beads on the second surface. Comparing SAMs with an epoxy, for the same surface area the SAM has 512 bonds across the interface, whereas the network has only 66 bonds (a factor of 7.8 smaller). The ideal failure stress for the epoxy network is then 8 times smaller than the SAM ($124/7.8=16$). This much reduced value for the networks is only a small factor (2.9 times) larger than the ideal van der Waals stress. Furthermore, the actual stress is further reduced from this ideal value due to the sequential breaking of the bonds, which is a stronger effect for the bonds than for van der Waals interactions. This is discussed further in Section V.

IV.b.4. Dependence of failure stress on number of bonds to surface

As we have seen the number of bonds across the interface is an important quantity affecting interfacial fracture, and is the main variable in the experimental system. The ideal stress (Eq.IV.6) to fracture the system is directly proportional to the number of interfacial bonds, N_b . Even though the actual value of the fracture stress will not be equal to the ideal value, the failure stress may still scale with N_b .

In this and the following sections, we distinguish between the “ideal” and “intrinsic” interface strength. By ideal, we mean simply the sum of all the interaction forces per unit area across the interface, where the interaction force is the maximum value in the molecular force-distance relationship. By “intrinsic”, we mean the actual maximum local

stress that the interface can support. As shown below the two terms differ due to the fact that all interfacial interactions are not broken simultaneously.

The dependence on N_b can be examined in a controlled manner by forbidding bonds to occur in a subset of the wall surface. Experimentally, this is done by coating the surface with SAMs which prevent chemical bonding. In the simulations, we simply forbid occurrence of the bonding reaction in a chosen region on the wall (Fig. IV.1). The fraction of the bondable area of the wall surface is denoted C (see Table IV-2 – Table IV-5). Note that the bondable area fraction C has the opposite effect as the fractional coverage of ODTS in the experimental work.

The variation of N_b can also be viewed as varying the intrinsic defect size at the interface. From this viewpoint, the nearest neighbor distance between bonds at the interface is related to the defect size. The nearest neighbor interfacial bond separation distance a_b is roughly

$$a_b = 1 / \sqrt{d_s} = \sqrt{A / N_b} \quad (\text{IV.14})$$

where d_s is the interfacial bond density. The maximum interfacial bond density puts a lower limit on the initial crack size. Any crack length less than a_b is meaningless. For system 3 at $C=1$, $a_b = 3.1$. For the epoxies we calculated d_s to be between $1/523 \text{ \AA}^2$ and $1/273 \text{ \AA}^2$ which gives a_b between 2.3 nm and 1.6 nm.

We examined the issue of initial flaw size in the MD simulations by imposing a nonbonding region between the polymer network and the substrate. By varying the size of the nonbonding region, we determine the critical stress as a function of the defect size. Two geometries were used for nonbonding regions. At first, a single rectangle in the middle commensurate with the wall sizes was designated as a nonbonding zone. We varied the area from 0% to 100%. To better match the experimental studies, a set of rectangles on a grid (Fig. IV.1) were used as the nonbonding region. This corresponds to the experiments which have a grid lithographically built to prevent bonding. However in comparison with the experiments, the simulation nonbonding regions are much smaller, at most 10 nm on a side.

Figures IV-6 and IV-7 shows data for systems 1-3 at the various C , under tensile pull and shear. We will specifically discuss the data for system 3. Even though the failure stress for full coverage is not equal to the ideal fracture stress, it is possible that the failure stress scales like the ideal fracture stress. Specifically, let N_1 and N_c be the number of interfacial bonds at full coverage ($C=1$) and partial coverage, C , respectively. Then, if scaling holds, the stress at C is related to the stress at $C=1$ by

$$\sigma_c \sim \frac{N_c}{N_1} \sigma_1 \quad (\text{IV.15})$$

We expect in the limit of large systems that $N_c = CN_1$. Then,

$$\sigma_c \sim C \sigma_1 \quad (\text{IV.16})$$

The data for the failure stresses for system 3 (Fig. IV-8) exhibits a linear dependence for the shear data over the complete range of C . The linear fit to the shear data is

$$\sigma_c = 5.4C + 0.7 \equiv (\sigma_1 - \sigma_0)C + \sigma_0 \quad (\text{IV.17})$$

where σ_0 is the shear stress at $C = 0$. The value of σ_0 is not zero, since sliding the network over the bottom wall even for no interfacial bonds requires some stress, i.e. there is friction. This is also seen for the bead-spring SAM simulations, and is generally well known.

The tensile data has a similar fit equation,

$$\sigma_c = 5.7C + 0.7 \equiv (\sigma_1 - \sigma_{s0})C + \sigma_{s0} \quad (\text{IV.18})$$

where σ_{s0} is the zero coverage *shear* stress. Not only is the y-intercept for the tensile data not the zero value of the tensile stress, but also the $C = 0$ data does not fall on the fit line. The second point is easy to understand. In the tensile stress-strain curve, for all C there is a yield stress, $\sigma_y = 4.0$ and a plateau stress, $\sigma_p = 3.0$. These stresses are due to the van der Waals interactions. For the case of $C = 0$, the failure stress becomes the plateau stress. In fact, there is a range of C for which $\sigma_c = \sigma_p$. This implies that the bond fracture stress is small at these C values. The value of C at which the van der Waals and bond contributions to the (ideal) stress are equal ($=C^*$) is easily calculated from Eq. IV.1 to be $C^* = 0.34$. In terms of ideal stresses, the total stress at C^* would be $2\sigma_p$, but the data has $\sigma_{\text{tot}} = \sigma_p$. Sequential bond breaking reduces the stress, as the stress to fracture all the bonds at C is spread over a range of strains. Thus, the instantaneous bond stress is much lower than the sum for all bonds. We can write the stress to break the bonds as

$$\sigma_{\text{bond}} = \frac{1}{A} \sum_i F_i \quad (\text{IV.19})$$

where F_i is the force to break the i th interfacial bond. At some instant or strain, only some of the bonds are strained. In this case, the bond stress can be written the same as Eq. (IV.19), but with F_i now denoting the bond stretch force on the i th bond and the sum is only over stretched bonds, i.e. unstretched or broken bonds are not included. If the number of stretched bonds is small compared to the total number of interfacial bonds, then the instantaneous value of σ_{bond} will be small compared to the ideal value, and for $C < C^*$ the value of σ_{bond} will be small compared to σ_p . Thus, σ_{tot} will be equal to σ_p .

The failure strain also depends on the C . A full understanding of this dependence requires treatment of the nonlinearity of the bond potential, but the basic trend can be understood in terms of a linear potential. If we take the bond force to be harmonic (i.e. linear), then the ideal bond stress can be written as

$$\sigma_{\text{bond}} = \frac{N_b k \varepsilon_b}{A} \quad (\text{IV.20})$$

where k is the bond spring constant and ε_b is the bond strain which is typically different from the system strain. As will be discussed in the next section, the strain has two parts, a bulk and an interfacial part. The total strain can be written as the sum,

$$\varepsilon = \varepsilon_{\text{bulk}} + \varepsilon_{\text{int}} \quad (\text{IV.21})$$

For the tensile mode, the bulk strain represents the deformation of the network strands without stretching the bonds. The interfacial strain is zero until the bonds stretch, which occurs at large strains, or when a nonbonding region detaches from the wall. Furthermore, it is predominantly the interfacial bonds that stretch such that bond stretching in the bulk can be ignored. At a total strain less than the failure strain, the stresses for two different coverages are equal (*cf.* Fig. IV-7). Since the bulk stresses are the same, the interfacial stress must also be equal. Using Eq. (IV.20) above, we obtain

$$\varepsilon_c = \frac{N_c}{N_i} \varepsilon_b = C \varepsilon_i \quad (\text{IV.22})$$

where here only interfacial strains are involved and the “int” subscript is dropped. We thus expect a linear relation of the type

$$\varepsilon_C = (\varepsilon_1 - \varepsilon_0)C + \varepsilon_0 \quad (\text{IV.23})$$

for the interfacial failure strain as a function of C . Since the total strain is just the sum of the bulk strain which is independent of C and the interfacial strain, an equivalent equation will hold for the total strain.

Figure IV.9 shows the failure strains as a function of coverage for system 3 for both tensile and shear modes. The linear behavior is obeyed for the shear data except at $C = 0$ for which no bonds are broken. Thus, the y-intercept ε_0 for $C > 0$ is not the $C = 0$ failure strain. As C goes to zero, the failure strain must tend toward ε_0 , but we have insufficient data to study this. We are constrained by the fact that at small C the number of interfacial bonds is small potentially yielding poor statistics. The source of the low C failure strain behavior remains to be understood.

For the tensile data the linear relation holds (albeit for three data points) at $C > C^*$. For $C < C^*$, the failure is dominated by van der Waals interactions which yields a different behavior. In tensile, the van der Waals interactions are relatively strong in comparison with the bond interactions. This suggests that the deviation from the failure strain which is based on bonded interactions should occur at a much larger C for tensile than for shear simulations.

IV.b.5. Strain localization at the interface

The structure and dynamics of the network at the interface are expected to be different from those in the bulk, and these differences are expected to be important contributors to the failure mechanisms of the adhesive. As has been discussed above, the number of bonds at the interface determines the strength of the interface. The number of bonds at the interface is typically much less than in the bulk (see Sec. IV.b.3, Stevens, 1999). This happens primarily due to geometric constraints. At a flat surface a molecule is limited in the number of bonds to the surface it can make while simultaneously still bonding to the network. The consequence of this is that the strain localizes at the interface. Since there are fewer bonds at the interface, maintaining uniform stress requires that the interfacial bonds stretch to produce a larger restoring force. This in itself results in an increased strain at the interface albeit on a molecular scale. The noticeable strain localization is the consequence of the fact that these stretched interfacial bonds are the first to break. This allows the neighboring part of the network to separate from the walls. Figure IV-10

shows the displacement field for the shear of system 1 at $C = 1$. The displacement of a single particle is calculated between its initial position at zero strain and its position at some nonzero strain. In Figure IV-10, the second strain is the failure strain. The figure shows the average value of the particle displacements binned by planes parallel to the walls. The dotted line in the figure shows the ideal, uniform displacement field. The data points at both ends correspond to the wall displacements which are constrained to move at constant velocity. The data shows a large deviation from this ideal field particularly at the bottom wall. Otherwise, the data shows a linear displacement field implying at least on average the deformation is uniform. Figure IV-11 shows displacement fields as a function of strain for the same system. Initially, such as for $\varepsilon = 0.33$ the strain field is linear over the complete range of positions between the walls. For all strains the displacement field is linear away from the bottom wall. Note that all curves except the highest strain curve cross at the midpoint. Thus, about the middle of the system, the strain is homogeneous. But, near failure a discontinuity occurs and grows at the bottom wall. Beyond failure, this discontinuity is large, because the system now slips at interface. Also, the displacement field for the rest of the system has changed since the boundary condition at the bottom wall has changed. The displacement fields in Figure IV-10 and Figure IV-11 show that the separation of the strain into two parts, bulk and interfacial is substantiated by the data.

For tensile pull simulations, the situation is similar. Figure IV-12 shows only bonds stretched approximately 5% for different C . Independent of C , the most likely place to find stretched bonds is at the interface. The lower the C , the more likely bonds at the interface are stretched and the less likely bulk bonds are stretched. Bonds stretched by 10% are much rarer and even more likely to occur at the interface. Bond breaking almost exclusively occurs at the interface.

IV.b.6. Size dependence

The size dependence of the stress-strain curves is given in Figure IV-6 and IV-7. Concentrating first on just the $C = 1$ case, the failure stress is independent of system size. For tensile pull, the value is 6.2; for shear it is slightly smaller at 5.9. On the other hand, the failure strain is clearly dependent upon the system size. This is more noticeable at small C than at large C . For example, the failure strain at $C = 0$ in system 1 is 0.52, but is 0.21 in system 3. At $C = 1$, $\varepsilon_f = 1.01$ for system 1 and 1.17 for system 3.

Some of the difference at $C = 1$ is related to the minimal path length. For system 1, the strain of the minimal path length is $\varepsilon_p = 0.83$ and the strain of the average path length is 1.05. For system 3, the strain of the minimal path length is 0.74 and the strain of the

average path length is 0.92. For the two systems sizes, the difference in the strain of the minimal path length strain is 0.09, and the difference in the strain of the average path length is 0.13. The failure strain differs by 0.16. Thus, the strain of the average path length is a better indicator of the dependence of fracture strain on system size.

IV.b.7. Importance of temperature during crosslinking

The network simulations discussed thus far have been for systems crosslinked at temperature $T_x = 1.1$, which is well above the glass transition temperature $T_g = 0.4$ of the liquid mixture. Far from T_g the diffusion is fast and the crosslinking is consequently fast. As the T_x goes toward T_g the crosslink process slows down. As the crosslinking process continues at any T_x , the diffusion decreases since some molecules are now bonded together and must move as a unit. Once the network structure has percolated, further crosslinking requires free chains to diffuse through the system and to find crosslinkers with open bonds. Thus, as the crosslink reaction occurs, T_g increases. This is shown in Figure IV-14 which shows the calculated density of the liquid mixture and two networks with functionality $f = 4$ and 6. The T_g of the networks is 0.5. The density of the liquid at $T = 1.1$ is 0.8 while the $f = 6$ network at $T = 0.3$ has a density of 1.08. Thus, crosslinking the network at $T = 1.1$ and then reducing the temperature to 0.3 will result in a rather large density change of 26%. Given that this density change occurs just through the temperature change, which does not break bonds, then under tensile pull the system is likely to be able to expand until the density reaches 0.8 without breaking bonds. In other words, a strain of 26% would not break bonds. This is typically true in our simulations. However, if the crosslinking were performed at lower temperatures closer to T_g , then the density difference would be smaller and potentially the failure strains would be different. We thus investigated this possibility.

Figure IV-13 shows the stress-strain curves at different crosslink temperatures for $C = 0$ and 1. The bond potential is parameter set 1. For $C = 1$, the failure strain decreases with decreasing T_x . The *strain* corresponding to the minimal path length also decreases with decreasing T_x . We do not have a satisfactory explanation for this. A possibility is that the higher density at the lower T_x enables a less zig-zag minimal path. This would require only that a few bonds in the path be more oriented perpendicular to the walls. In any case, as expected with a decreasing minimal strain for the minimal paths, the failure strain decreases. Unfortunately, the time to crosslink the system at $T_x = 0.6$ is about a factor of 10 more than at $T_x = 1.1$ to obtain about the same number of crosslinks.

A very satisfying result of crosslinking at lower T is the $C = 0$ data. At $T_x = 0.6$ the failure strain reduces to 0.2. Figure IV-13 shows that in this case the system basically fails once the yield stress has been reached. Another presumed effect of the lower T_x is that the network is stiffer with a larger elastic constant. At $T_x = 0.6$ the density is 1.04; the difference between T_x and T_g is just 4% strain. Thus, strains relatively small compared to the $T_x = 1.1$ data will have a larger impact on the network. Consequently for $C = 0$ at $T_x = 0.6$ the network will yield and then move as a whole separating from the bottom wall.

We note that the experimental systems are crosslinked at a temperature close to, but slightly below, the final T_g whereas the MD systems discussed in the previous sections are crosslinked at T_x much greater than T_g . We have demonstrated that crosslinking at temperatures close to T_g yields much smaller failure strains. This effect and the relatively small system size cause the failure strains in the MD simulations to be much larger than in experiment.

II.b.8 Void Formation

An important consequence of crosslinking the network is void formation. These voids are rather small, ‘nanovoids’, corresponding to a diameter of 1-10 nm (see Figure IV.14). They are local defects of the network. While such tiny voids have not been observed experimentally (a nontrivial issue), such defects have been expected. This expectation follows in part from the occurrence of shrinkage of the plate separation distance after curing due to a ‘cure’ stress. The curing stress and shrinkage occur because the chemical bond length is shorter than the van der Waals diameter. Thus, two atoms that are close, but not bonded are at the van der Waals separation ($\sim 3 \text{ \AA}$). Once bonded they are separated by only the bond length ($\sim 1.5 \text{ \AA}$). The system contracts locally as bonds form resulting in voids. In our coarse-grained simulations the LJ minimum is at 1.12σ and the average bond length is 0.97σ . This is sufficient to produce the cure stress; when we allow the plates to move under no load, they contract.

The voids occur where the minimal cycle length is large. A cycle is the path starting at a crosslinker going out from one bond and returning via a distinct bond. The minimal cycle is the cycle with the shortest path length. The minimal cycle defines the maximum void that can occur without breaking bonds. This maximum void size occurs for the minimal cycle being fully taut. For the highly crosslinked networks studied here, the typical minimal cycle is very short. Crosslinkers which have not filled all their bonds tend to have larger minimal cycles. There will be fewer paths where the crosslinkers have open bonds, and the cycle length will on average be longer with fewer possibilities. Any clustering of

open crosslinkers caused by the absence of resin molecules will likely result in relatively large minimal cycles and thus result in relatively large nanovoids.

These voids have some important consequences. The presence of voids impacts the value of the strain at failure. In simulations where the load is relaxed to zero along with lowering the temperature below T_g , the system will be able to expand under tensile pull to the original plate separation without breaking bonds. A network formed without voids would have to have regions that are rather tight. Most likely the tightness would be in the strands, not in the bonds. In any case, less strain, but more stress would be needed for a system without voids to reach the point of stretching and breaking bonds.

IV.c. Summary

We have developed a molecular dynamics capability to simulate polymer networks between solid surfaces. This includes:

- simulation of bond formation and breaking
- development of breakable bond potential without discontinuities
- use of grid of nonbonded areas on solid surface (i.e. patterned defects)

The main calculations are for tensile pull and shear simulations performed as a function of the areal density of chemical bonds for multiple system sizes. In order for these simulations to be possible and to understand their results, the following was also necessary:

- it was demonstrated that highly crosslinked networks can be formed with at least 95% of all possible crosslinks occurring.
- the glass transition temperature for the melt and network systems has been calculated.
- the ideal failure stresses (tensile and shear) for model self-assembled monolayers were calculated.

The relationship between fracture stress on the nanometer level and the interfacial interaction potential $\Psi(x,y,z)$ was determined. In Section VI, this will be combined with the relationship between G and stress at 90 Å from the crack tip obtained from the previous section to form the complete fracture model for the DCB specimen. Other major results of the simulation work are listed below.

1. Bond breaking occurs sequentially over a wide time or strain range resulting in the bond contribution to the failure stress to be significantly smaller than the ideal value.
2. Resolved the apparent stress paradox that the fracture stress for two SAMs is much greater than the fracture stress for the epoxy, even for SAMs that interact only through van der Waals forces. While the epoxy bonds to the surface (acid-base) are much stronger than van der Waals interactions, the number of chemical bonding sites per area for the epoxy is much smaller than the number of van der Waals interactions sites per area. Consequently, the sum of the specific interactions is on the order of (even less than) the integrated van der Waals contribution.
3. The failure stress (tensile and shear deformations) depends linearly on the number of interfacial bonds for the present method of restricting the bonding sites.
4. The minimal paths in the network between the two surfaces determine the failure strain.
5. The strain separates into distinct bulk and interfacial components. Furthermore, it is primarily the bonds at the interface that stretch.
6. The failure strain in shear simulations depends linearly on the number of interfacial bonds except in the limit of no bonds.
7. The failure strain in tensile simulations is linear in the number of interfacial bonds at high interfacial bond coverage, but at low coverage the van der Waals interactions dominate and the failure strain is constant.
8. Crosslinking needs to occur in the simulations as near to the network glass transition temperature as possible, as the minimal path lengths decrease as the crosslinking temperature decreases.
9. Void formation occurs due to defects in the network (i.e. incomplete curing). The nanovoids allow larger strains to occur without bond breaking.

V. Estimates of intrinsic fracture stresses in present experimental systems (NR and DCB)

Next we estimate the true molecular-scale fracture stress, or intrinsic interface strength, expected for the present experimental system in the NR and DCB geometries. (The intrinsic fracture stress differs from the ideal fracture stress due to the fact that all the interactions across the interface are not broken simultaneously.) To obtain these estimates we use experimental pull-off forces obtained with a noncompliant atomic force microscope called the Interfacial Force Microscope or IFM (Thomas et al 95) and experimental shear forces obtained with the surface forces apparatus (Yoshizawa 93, Yamada 98), along with important insights from the MD calculations. Many uncertainties exist as described below, so we attempt to determine upper and lower bounds rather than a unique estimate.

V.a. NR intrinsic fracture stress.

We begin with the experimental force to separate (in a tensile pull) two SAMs terminated with amine and carboxylic acid groups from IFM measurements. Two methods for determining a stress from these data will be used. The first is to use the measured force and estimated area of contact as shown below:

Pull-off force data for COOH and NH₂ terminated surfaces (acid-base interactions) (Thomas et al, 1995):

$$F/R = 4.3 \pm 0.4 \text{ N/m}$$

$$\text{For } R = 91 \text{ nm, } F = 391 \pm 36 \text{ nN}$$

Contact area by JKR theory (Israelachvili, 1997):

$$\text{At zero load: } A_o = \pi (6\pi WR^2/K)^{2/3} = \pi (12\pi\gamma R^2/K)^{2/3}$$

$$\text{At pull-off: } a_o = A_o/4^{2/3} = \pi (3\pi\gamma R^2/K)^{2/3}$$

$$\text{where } K = 4/3 ((1-\nu_1^2)/E_1 + (1-\nu_2^2)/E_2)^{-1} = 6.64 \times 10^{10} \text{ Pa}$$

$$\text{For COOH and NH}_2 \text{ terminated SAMs: } \gamma = 55 \text{ mN/m (Sinniah, et al 1996)}$$

$$\text{Thus } a_o = 1.27 \times 10^{-16} \text{ m}^2, \text{ or } 127 \text{ nm}^2 \text{ (for 91 nm probe tip radius)}$$

$$\text{Force per area: } 3,080 \pm 280 \text{ MPa}$$

A second method to approximate a force per area between two planes from the IFM data is to make use of the analytical expressions for the interaction energies ($W(D)$) to separate a) a sphere and a plane, and b) a plane of unit surface area and an infinite plane, where D is the minimum separation distance between the two bodies. These expressions can be obtained by integrating the interaction energies between molecules in both bodies using only the purely attractive part of the LJ potential: $w(r) = -C/r^6$. Here, C is an interaction constant related to the Hamaker constant. One obtains (Israelachvili, 1997)

$$W(D) = \frac{-\pi^2 C \rho^2 R}{6D} \quad (\text{sphere and plane}) \quad (\text{V.1})$$

$$W(D) = \frac{-\pi C \rho^2}{12D^2} \quad (\text{plane of unit surface area and infinite plane}) \quad (\text{V.2})$$

where ρ is the number density of molecules in the solid, and R is the radius of the sphere. By differentiation the forces can be obtained from these energies as:

$$\frac{F(D)}{R} = \frac{\pi^2 C \rho^2}{6D^2} \quad (\text{sphere and plane}) \quad (\text{V.3})$$

$$F(D) = \frac{\pi C \rho^2}{6D^3} \quad (\text{plane of unit surface area and infinite plane}) \quad (\text{V.4})$$

Thus the force per unit area between planes can be estimated from the measured F/R in the IFM experiment as:

$$F \text{ (per unit area)} = \text{local stress} = \frac{F}{R\pi D} \quad (\text{V.5})$$

Using the data of Thomas, *et al.*, and an estimate of the minimum separation distance at contact of 4 Å (twice the typical value of the hard-core repulsion in the full LJ potential) we obtain:

$$F \text{ (per unit area)} = \text{local stress} = \frac{4.3 \text{ N/m}}{\pi(4 \times 10^{-10} \text{ m})} = 3400 \pm 316 \text{ MPa}$$

This result is comparable to the value estimated directly from the measured force and the calculated area. We will use this latter estimate with the uncertainty in the calculation of upper and lower bounds given below.

The intrinsic fracture stress in the NR test is reduced from this value by a number of factors. First, the areal density of chemical bonds between the epoxy and substrate is far lower than the areal bond density for the SAMs, as was shown in the MD calculations. To calculate the areal bond density for the epoxy on silicon, we take the thickness of the surface atomic layer to be 4 Å. The density ρ is 1.13 g/cc. An assumption must then be made regarding the composition at the interface. We consider two cases: the interfacial composition is equal to the bulk composition, and strong segregation of the crosslinker to the interface such the concentration of T403 within the 4 Å layer is twice that of the bulk concentration. TOF-SIMS data supports segregation of T403, but the degree of segregation cannot be quantified to the extent needed for this calculation. The area per T403 molecule is $M/(N_A \rho t)$, where M is the molecular weight of one T403 molecule plus the molecular weight of x epoxide oligomers, where x is determined from the composition (takes the value 3 for 46 phr and 1.5 for the case of strong segregation). This leads to an area per T403 molecule of either 523 Å² or 273 Å², depending on whether the epoxy composition is uniform near the interface or whether the T403 strongly segregates. For SAMs, the area per molecule is in the range 20-25 Å². Taking the larger number to be conservative, the ratio of the areas per molecule for the epoxy and SAM cases is either 21 or 11. There is also uncertainty regarding the number of bonds between the crosslinker and the substrate surface. We consider the cases of either 1 or 2 bonds to the substrate per T403 molecule. This is an assumption that needs to be examined experimentally. With this assumption, the ratio of the number of bonds/area for the SAM and epoxy cases are 21 (uniform composition) or 11 (T403 segregates) for the case of 1 bond per T403 molecule, and 10.5 (uniform composition) or 6.5 (T403 segregates) for the case of 2 bonds per T403 molecule. We use the maximum and minimum values in the calculations below.

A further important factor is sequential bond breaking. Critical insight into this formidable problem has been gained by MD simulations. In the bead-spring epoxy simulations the fracture stress is reduced by 1/2.7 relative to the value that would occur if all bonds broke simultaneously. In the SAM simulations, the fracture stress is only reduced by 1/1.11 relative to the value that would occur if all bonds broke simultaneously. Thus we expect this to be important for the NR (epoxy) measurements, but not nearly as important in the AFM (SAM) measurements. We note that the factor is likely to be strain-rate dependent, which could be an important consideration since the simulations are at much higher strain rates than the experiments. Lower strain rates may enable more stress

localization and earlier bond breaking increasing this factor, or alternatively lower strain rates may allow greater stress relaxation, reducing bond breaking and decreasing the factor. This must be resolved in future work. Finally, the simulations showed that the shear stress at fracture is reduced by a factor of $84/124 = 0.68$ due to the substantial normal component of stress. That is, even in pure shear there is a substantial normal component to the bond stresses.

Thus we expect the following lower and upper bounds for the component of the fracture stress due to chemical bonding (acid-base) for epoxy bonding to bare silicon oxide in the NR experiment:

Lower Bound	Upper Bound
3084 MPa (IFM, lower limit)	3716 MPa (IFM upper limit)
$\div 21$ (# bonds/area, epoxy vs SAM)	$\div 6.5$ (# bonds/area, epoxy vs SAM)
$\div 2.7/1.11$ (sequential bond breaking)	$\div 2.7/1.11$ (sequential bond breaking)
<u>$\div 1.32$ (shear vs tensile)</u>	<u>$\div 1.32$ (shear vs tensile)</u>
47 MPa	178 MPa

The total fracture stress must also include a contribution from VDW interactions. However, we show below that this contribution is small in shear compared with the chemical bonding contribution.

For the case of epoxy in contact with the methylated tails of the fully dense ODTS SAM, two experimental measurements are relevant: shear forces between CH_3 -terminated SAMS have been directly measured using the surfaces forces apparatus (Yoshizawa, 1993, Yamada, 1998), and tensile pull-off forces have been measured between CH_3 -terminated SAMS using the IFM (Thomas et al, 1995). Both tensile and shear forces have been determined by simulation for SAMS, and in principle these results could be used to estimate a shear stress from the pull-off forces measured with the IFM. However, as discussed earlier, obtaining a quantitative estimate for shear stress values from tensile pull off values in the MD work is problematic. Therefore, we use only the directly measured (SFA) shear value of ~ 3 MPa in this discussion, which was obtained for shear rate of 200 s^{-1} . We note that this value is small compared to the values for chemical bonding given above.

Therefore, we conclude that the intrinsic interface strength for the present epoxy-silicon system in the NR loading geometry ranges from ~ 3 MPa for a fully coated ODTS substrate to $\sim 47 - 178$ MPa for the epoxy bonded to bare silicon. Importantly, it is clear

that the intrinsic interface strength, or the maximum local stress that the interface can support, is below σ_y (~ 46 MPa) for the case of full ODTS coverage and far above σ_y for the case of no ODTS coverage. The fact that the interface strength crosses σ_y over the range of ODTS coverage is consistent with the notion that the nonlinearity between fracture stress and interface strength comes from material deformation characteristics.

V.b. DCB intrinsic fracture stress. Next we calculate the intrinsic fracture stress in purely tensile loading, which approximates the loading in the DCB specimen (mixity = 8°). For the case of epoxy on bare silicon, the intrinsic fracture stress can be estimated from the IFM data as above, by simply omitting the final factor:

Lower Bound	Upper Bound
3084 MPa (IFM, lower limit)	3716 MPa (IFM, upper limit)
÷ 21 (# bonds/area, epoxy vs SAM)	÷ 6.5 (# bonds/area, epoxy vs SAM)
<u>÷ 2.7/1.11 (sequential bond breaking)</u>	<u>÷ 2.7/1.11 (sequential bond breaking)</u>
60 MPa	235 MPa

The total fracture stress must also include a component due to VDW interactions, which is calculated below. In the case of tensile loading, the VDW contribution is far greater than in shear, and cannot be neglected in the total fracture stress.

For the case of epoxy in contact with the methylated tails of the fully dense ODTS SAM, we use the tensile pull-off forces measured with the IFM (Thomas, et al. 1995):

Pull-off force data for CH₃ terminated surfaces (VDW interactions)
(Thomas et al, 1995):

$$F/R = 0.4 \pm 0.2 \text{ N/m}$$

$$\text{For } R = 230 \text{ nm, } F = 92 \pm 46 \text{ nN}$$

Contact area by JKR theory (Israelachvili, 1997):

$$\text{At zero load: } A_o = \pi (6\pi W R^2 / K)^{2/3} = \pi (12\pi \gamma R^2 / K)^{2/3}$$

$$\text{At pull-off: } a_o = A_o / 4^{2/3} = \pi (3\pi \gamma R^2 / K)^{2/3}$$

$$\text{where } K = 4/3 ((1-\nu_1^2)/E_1 + (1-\nu_2^2)/E_2)^{-1} = 6.64 \times 10^{10} \text{ Pa}$$

For CH₃-terminated SAMs: $\gamma = 20 \text{ mN/m}$ (Sinniah et al 1996)

Thus $a_0 = 8.9 \times 10^{-17} \text{ m}^2$, or 89 nm^2 (for 230 nm probe tip radius)

Force per area: $1034 \pm 517 \text{ MPa}$

Using the second method (Eq V.5), we obtain

$$F (\text{per unit area}) = \text{local stress} = \frac{0.4 \text{ N/m}}{\pi(4 \times 10^{-10} \text{ m})} = 318 \pm 159 \text{ MPa}$$

In this case there is a considerable difference in the values obtained by the two methods. We consider the lower value obtained from Eq (V.5) to be the better estimate, and use only this value with the uncertainty in the calculation of upper and lower bounds given below.

In MD simulations of CH₃-terminated SAMS, the fracture stress was reduced from the ideal value by a factor of 1.9 due to the fact that all interactions were not broken simultaneously. Thus we obtain for the lower and upper bounds:

Lower Bound	Upper Bound
159 MPa (IFM, lower limit)	477 MPa (IFM, upper limit)
$\div 1.9/1.0$ (sequential bond breaking)	$\div 1.9/1.0$ (sequential bond breaking)
84 MPa	251 MPa

Another estimate of the force to separate planes interacting only through dispersion interactions can be obtained from integrating the Lennard-Jones force. This is a simple, but weak approximation. The maximum stress derived by integrating the interactions is (Wu, 1982):

$$\sigma = \frac{4\pi}{45} \rho^2 \int_0^5 \epsilon_{vdW} \sigma_{vdW}^3 \quad (\text{V.6})$$

where ρ is the density, ϵ_{vdW} is the LJ interaction energy and σ_{vdW} is the LJ diameter. The area per SAM chain is $25 \text{ \AA}^2$ with the height being about $20 \text{ \AA}$ for hexadecane. This gives $\rho = 16/500 \text{ \AA}^3 = 0.032 \text{ \AA}^3$. The TRAPPE united atom force field has the following LJ parameters: $\epsilon_{CH_2} = 0.091 \text{ kcal/mol}$, $\sigma_{CH_2} = 3.95 \text{ \AA}$, and $\epsilon_{CH_3} = 0.194 \text{ kcal/mol}$, $\sigma_{CH_3} = 3.75 \text{ \AA}$.

This gives a stress of 88 MPa for CH_2 and 161 MPa for CH_3 . For separating two SAMs the number should be between these two, since the chains are methyl terminated with methylene backbones. Accounting for sequential bond breakage as observed in the simulations and taking the average of the two values, we obtain an intrinsic tensile stress of 65 MPa, which is just below the range determined from the IFM experiments. We note also that all these values are in reasonable agreement with the continuum calculations given earlier (Section III.d), which indicated that ~ 100 MPa was required to fracture ODTS coated surfaces in the DCB geometry based on a G value of $\sim 50 \text{ mJ/m}^2$ (thermodynamic work of adhesion) and reasonable material models.

Since the above values are comparable to the stress from chemical bonding for the case of epoxy on bare silicon, it is necessary to include the VDW contribution in the calculation of the total fracture stress in that case. The VDW contribution will depend on the fraction of the surface area which does not contain chemical bonds. For the case of uniform composition, we estimate from the area per chemical bond of $523 \text{ \AA}^2$ that 95 % of the surface area involves VDW interactions. So for a lower estimate of the total fracture stress we obtain $0.95 \times 84 \text{ MPa} + 60 \text{ MPa} = 140 \text{ MPa}$. For the case of strong segregation of crosslinker to the interface, we estimate from the area per chemical bond of $273 \text{ \AA}^2$ that 91 % of the surface area involves VDW interactions. So for an upper estimate of the total fracture stress we obtain $0.91 \times 251 \text{ MPa} + 235 \text{ MPa} = 463 \text{ MPa}$.

Therefore, we conclude that the intrinsic interface strength for the present epoxy-silicon system in the DCB loading geometry ranges from ~ 84 - 251 MPa for a fully coated ODTS substrate to ~ 140 to 463 MPa for the epoxy on bare silicon.

A key finding from the above is that VDW interactions contribute a large fraction of the interface strength in tensile loading, but constitute a negligible fraction of the interface strength in pure shear loading. We note that whereas such an effect was evident at low fraction of bonding sites in the MD simulations in Figure IV.8, it was not evident at high fraction of bonding sites. We would expect, based on the above calculations, roughly a factor of 2 difference for 100% sites bonding for shear and tensile loadings. However, the difference observed in the simulations is only $\sim 10\%$. This is due to the fact that in the MD tensile pull simulations of the epoxy, the density decreases dramatically prior to separation. The VDW contribution to the stress is proportional to the density; consequently, the decrease in density diminishes the contribution of the VDW interactions, such that they contribute a small fraction of the total stress for $C = 1$. This decreased density effect is not present in the MD simulations of the SAMs, nor is it present in the experimental SAM tensile data of Thomas, *et al.* Moreover, the magnitude of this effect in the epoxy system depends upon the elasticity of the epoxy, and thus on the temperature of crosslinking and

the rate of the fracture test. In the experimental epoxy system, the density drop is much smaller, since the failure strain is much smaller. Therefore, in the experimental failure stress there remains a substantial contribution of VDW interactions.

VI. Summary and significance

VI.a. New insights from the napkin-ring test

Over a large range, the interface strength has little effect on the fracture stress because failure apparently initiates cohesively. Only a low level of interface bonding is sufficient to achieve cohesive crack initiation. The transition from cohesive (high critical stress) to adhesive (low critical stress) crack initiation occurs over a narrow range of interface strength. Observations of the fracture surfaces suggests that the transition occurs when the interface strength is sufficient to support stresses high enough to cause deformation within the epoxy. The sharpness of the transition seems to imply that large-scale deformation is triggered over a narrow range of interface strength or local stress. At the transition, a large increase in applied stress is required to achieve a small increase in stress at the interface (rate or T dependent). This suggests the presence of stress gradients within the sample due to relaxation or dynamic processes on the time scale of the fracture test.

For further insight, we have compared the intrinsic fracture stress at the transition to the macroscopic yield stress. Using the estimated intrinsic interface stresses obtained from section V, and the fact that the transition occurs at a relative ODTS coverage of ~ 0.7 (Figure II.12), we estimate the intrinsic interface stress at the transition ($\sigma_{\text{intrinsic,T}}$) to be bounded by the following values: (lower bound) $0.3 \times 41 \text{ MPa} + 0.7 \times 3 \text{ MPa} = 14 \text{ MPa}$ and (upper bound) $0.3 \times 160 \text{ MPa} + 0.7 \times 3 \text{ MPa} = 50 \text{ MPa}$. The bulk yield stress in shear ($\sigma_{\text{y, shear}}$) is estimated to be $\sim 46 \text{ MPa}$. The close correspondence between the bulk yield stress and the intrinsic interface strength at the transition suggests the following simple criterion for the transition from interfacial to cohesive fracture:

$$\sigma_{\text{intrinsic,T}} = \sigma_{\text{y, shear}} \quad (\text{VI.1})$$

That is, the transition occurs when the local stress that the interface can support becomes on the order of the bulk yield stress. Note also that eq. VI.1 implies that material deformation characteristics determine the transition in fracture stress, even though local stress concentrations, such as occur at crack tips or near flaws, likely initiate the actual failure event.

The relationship in eq. VI.1 is supported by the observations of the fracture surfaces in Figures II-19 and II-20. It is also strongly supported by the data in Figure II-16, which shows that the coverage of ODTS at the transition decreases with decreasing

temperature. With decreasing temperature, the local and cooperative mobility decreases, the material becomes stiffer, and σ_y increases. Then by eq. IV.1, $\sigma_{\text{intrinsic},T}$ must increase as well, which corresponds to the observed decrease in ODTS coverage at the transition. Figures VI-1 – VI-3 show a quantitative comparison using the data of Figure II-16. Figure VI-1 shows the change in σ_y with temperature measured in compression (the scaling with T should be the same in shear). The arrows indicate the temperatures of the fracture experiments. Figures VI-2 and VI-3 show the expected shift in the 22 °C fracture stress data for 0 °C and –15 °C based on the fractional change in σ_y and assuming eq. VI.1 holds. The fracture data measured at the lower temperatures are also shown. The magnitude of the shift observed in the data is in excellent agreement with that expected based on eq. VI.1.

Eq. VI.1 also indicates that the transition is not determined by wetting of the epoxy, which has been a guideline suggested in the literature for achieving strong bonding (Pocius, 1997). Indeed, the data in Figure II-11 indicate that cohesive failure can occur even when the adhesive does not wet the substrate. We understand the transition from adhesive to cohesive failure as follows. As $\sigma_{\text{intrinsic},T}$ is attained, macro-scale yielding occurs in the bulk epoxy, and this leads to large-scale heterogeneity. Somewhere within this large-scale heterogeneity in the bulk epoxy, a crack forms which propagates to cause the fracture. Thus, we propose that yielding within the epoxy generates heterogeneities which grow until a flaw propagates as a crack. Flaw generation within the bulk of the epoxy is necessary to explain cohesive crack initiation, as the MD simulations show that the bond density of the epoxy to the substrate is always less than the bond density within the epoxy. Indeed, in the MD simulations where the length scales are too small (and time-scales too fast) to include the above process, strain localization and failure always occurs at the interface (section IV.b.5).

The criterion indicated by eq. VI.1 is certain to be over simplified. A full description must include the full stress-strain behavior of the material rather than just a yield stress value. Nevertheless, eq. VI.1 represents a first approximation which can be tested and modified in future work.

In the following section, a conversion factor of ~ 1 LJ stress unit/50 MPa will be derived from the comparison of model calculations with fracture toughness data for the DCB test. With this conversion factor, the MD results in Figure IV-8 can be converted to MPa. This allows another independent test of the relation in eq. VI.1. Using this conversion factor, Figure IV-8 indicates that $\sigma_{\text{intrinsic},T}$ will cross σ_y at a very low fraction of bonding sites, somewhere in the range of 0.10. This is in excellent agreement with the data in Figure II-23 for the mixed monolayers, where the transition in fracture stress occurs at a very low fraction of functionalized terminal groups.

While much evidence supports the criterion in eq. VI.1, an important unanswered question is the origin of stress concentration. The postulate for the transition in fracture stress in eq. VI.1 suggests that significant stress concentrations must occur, as the measured averaged stress levels (≤ 30 MPa) are always lower than the yield stress in shear (~ 46 MPa). Such stress concentrations could arise due to slight misalignment of the ring and substrate, or possibly due to flaws. A full stress analysis has not yet been attempted for this system. This issue must be resolved in future work.

The observed catastrophic relationship indicates that one cannot use joint strength as a measure of aging, since no change is observed until catastrophic failure occurs. The NR data also give insight into the importance of flaws or defects. The data imply that interfacial flaws greater than a certain size (not yet identified but less than $5\text{ }\mu\text{m}$) have a strong impact on the fracture behavior. This provides insight into the importance of various types of contamination or defects. Contamination will have a strong impact if it is distributed in domains greater than a critical size (not yet identified but less than $5\text{ }\mu\text{m}$). If uniformly distributed, contamination will be important only if enough surface sites are occupied that the number of bonding sites left available for the adhesive is insufficient to support local stresses comparable to σ_y .

VI.b. Comparison of fracture model with DCB data

As mentioned in section II.c.3, there are several indications that the fracture mechanisms for the DCB test samples are fundamentally different from the fracture mechanisms in the NR test, where the latter are summarized by eq VI.1 along with the transition from adhesive to cohesive crack initiation induced by bulk yielding. We reiterate those observations here. First, the rise in fracture toughness occurs at noticeably lower values of ODTS coverage (equilibrium water contact angle) in the DCB test than in the NR test. Second, the form of the fracture curve appears to be different in the two cases. Whereas in the NR test the onset of the plateau in fracture stress appears to occur very abruptly (Figure II-11 and Figure II-23), the fracture toughness data in the DCB test (Figure II-24) show a smoother or more gradual leveling off. Third, in the DCB test the failure remains interfacial for all values of interface strength, whereas a transition from interfacial-to-cohesive failure occurs in the NR test. Finally, the calculations in section V indicate that the intrinsic interface strength exceeds σ_y at all ODTS coverages in the DCB test, while the intrinsic interface strength ranges from far below σ_y to a value comparable to σ_y at the transition in the NR test. Thus, in the DCB test some degree of material yielding and plastic deformation must occur at all ODTS coverages. However, the yield zone is in

all cases small ($< 10 \mu\text{m}$) relative to the bond thickness, due to the mechanics of the loading geometry. As shown in Figure III-5, the size of the yield zone varies from $\sim 1 \mu\text{m}$ to $17 \mu\text{m}$, depending upon the ODTS coverage (or G values).

The approach for predicting interfacial fracture given the existence of a macroscopic crack is summarized below. This approach has been implemented for the DCB geometry in the present work, but the general approach should be applicable for other loading geometries as well. This is clearly an initial attempt and will certainly evolve with further knowledge. For simplicity, small scale yielding is assumed in the following – i.e. the yield zone at the crack tip is small when compared to all geometric length scales. This is true in many cases of practical interest, including the sandwiched aluminum/silicon/epoxy/aluminum DCB specimen tested in the present study. The steps are summarized below:

- Carry out a linear elastic fracture analysis of a bonded joint to determine the energy release rate G and mode mixity $\hat{\psi}$ for a characteristic interfacial crack. The G and $\hat{\psi}$ values fully define the elastic stress field in an annular region surrounding the highly deformed material at the crack tip.
- Perform a small-scale yielding analysis that considers the crack to be semi-infinite with the remote boundary loads specified by the elastic singularity solution. Here a highly refined finite element mesh is used to investigate the stress state on a nanometer scale. Geometric and material nonlinearities are included in the analysis. The analysis must accurately model crack tip blunting and the large strains generated by the blunting. Rapid hardening of the epoxy at large strains provides a means for accounting for high interfacial crack-tip stress. The result of this calculation is a relationship between G and the interfacial stress in close proximity ($\sim 100 \text{ \AA}$) to the crack tip.
- Determine the relationship between the maximum local stress the interface can support and the interfacial interaction potential $\Psi(\mathbf{x}, \mathbf{y}, \mathbf{z})$ by MD simulations. The MD calculation includes the effect of molecular packing at the interface and differences in bulk versus interfacial bonding.
- Combine the relationship between G_c and $\sigma_{100 \text{ \AA}}$ from continuum calculations with the relationship between the maximum local stress the interface can support

and the interfacial interaction potential $\Psi(x,y,z)$ from MD simulations. This yields a relationship between G_c and $\Psi(x,y,z)$ which can be compared to the experimental data.

This procedure has been implemented by combining the continuum calculations displayed in Figure III-15 with the failure stress results from MD calculations in Figure IV-8. The results are shown in Figure VI-4, expressed as fracture toughness versus the fractional coverage of bonding sites. We have used the interfacial stress at a distance of 9 nm from the surface from Figure III-15 to combine with the MD fracture stress data since that dimension is close to the separation distance of the plates in the MD simulation. A conversion factor is needed to relate the MD stress in Lennard-Jones units to MPa, and the curves in Figure VI-4 have been calculated for a range of such values. For comparison, the experimental data from the DCB test with varying ODTS coverage in Figure II-24 are replotted in Figure VI-5. The most favorable comparison occurs for a conversion factor of ~ 1 LJ stress unit/50 MPa. While the calculations are limited to $G \leq 1 \text{ J/m}^2$ due to numerical difficulties (convergence problems) and the experimental data cover $G \geq 2 \text{ J/m}^2$, the model qualitatively predicts a strong increase in G with interface bonding which is a key observation in the experiments.

While the strong increase in G with interface bonding is predicted qualitatively, the estimates of the intrinsic interface stress from section V are much larger than the stresses at 9 nm from the crack tip calculated in the continuum calculation. This seems to imply that much higher stresses occur immediately at the crack tip compared to a distance of 9 nm. Such an effect has been demonstrated in the continuum calculations with hardening shown in Figure III-14 and Figure III-15. If such an effect does indeed exist, we would expect to observe it in MD simulations. In fact, while the stress as a function of distance from the plates cannot yet be determined, the fact that high strain is localized at the interface suggests elevated levels of the force per bond there as well.

VI.c Final assessment

We have established and modeled the relationships between the nature of fundamental interfacial interactions and an engineering quantity related to fracture in both the NR and DCB test geometries. We have shown that the fracture mechanisms and criteria are much different in the two cases. A fundamental difference is the role that VDW interactions play in the two fracture tests. However, a few important aspects are common to both tests, as revealed by the MD simulations. First, there is a distribution of bond

breakage in time, even on a nm length scale. This effect has been quantified for the model MD system to estimate the decrease from the ideal stress value that results. However, the quantitative value may be rate sensitive, and this effect must be investigated in future work. Second, the local strain at break is due to the minimal path through the network. This will be a function of network structure and thus composition, crosslinker functionality, and crosslinking conditions. Third, high strain tends to be localized at the interfaces due to the lower areal bond density. Failure should thus always initiate at the interface unless flaws/stress concentrations are generated in the bulk.

The NR test is treated on a much simpler level than the DCB test. For molecularly smooth surfaces and a pure shear loading, VDW interactions play a negligible role. With increasing areal density of chemical bonds, the fracture stress rises rapidly and the failure changes from adhesive to cohesive when the interface strength approaches the bulk yield stress. The critical value of the areal bond density for this transition thus depends upon temperature and rate. This is a new criterion to describe fracture behavior, and should be further investigated for its applicability to other geometries. The detailed stress field has not yet been analyzed for this case.

The analysis of the DCB test is much more detailed, and involves an integration of continuum and molecular calculations. Since there is a substantial tensile component to the mode of loading, VDW interactions make a very large contribution to the intrinsic interface strength. Due to the large VDW contribution, the intrinsic interface strength is very high, and exceeds the bulk yield stress even in the absence of chemical bonding. Detailed continuum calculations have shown that strain hardening can account for the high degree of stress amplification at a crack tip required for interfacial separation. This effect remains to be confirmed by MD simulations, but appears to be consistent with the localization of strain at an interface. The experimental data show a strong increase in G_c over a narrow range of interface strength. The onset of nonlinearity apparently stems from the bulk deformation behavior, as shown in Figure III-15 and in Figure III-20, since no such nonlinearity appears in the MD simulations (Figure IV-8) on the nm scale. The model captures this effect qualitatively, although calculations have only been completed for $G_c \leq 1 \text{ J/m}^2$. An important aspect of the data which could not yet be addressed is the leveling off of the fracture toughness with interface strength at high values of the latter. Since the failure is known to remain interfacial even for a bare epoxy / silicon oxide interface, this leveling off is likely due to the number of bonding sites on the substrate exceeding the number of bonding sites within the first molecular layer of the epoxy. This must be confirmed in future work.

This first order model has spanned length scales from the continuum to the molecular, within the assumptions and simplifications cited above. To improve this model, further advances are required in a number of areas. A detailed list is given below and only a few general comments will be highlighted here. First, an improved epoxy constitutive relation is needed. Time-dependent epoxy yield, strain softening, pressure dependence, and rapid hardening at large strain must all be accurately modeled. Moreover, this model must apply to the sort of stress state found at a crack tip - high hydrostatic stress combined with large strains. Second, the failure criterion is based directly upon an estimate of the force required to pull the epoxy off of the interface. MD techniques for estimating these forces are in their infancy, and will surely improve in time. Third, an improved understanding is needed of the submicron flaws that may exist on the interface. Calculated stresses are highest in the region of the blunted crack tip, but this is where there is the greatest uncertainty in the geometry of the continuum. Fourth, the continuum analysis should include subcritical crack growth. When a crack extends it leaves behind a wake of yielded material. This wake of deformed material tends to close the crack, and provides initially increasing resistance to further crack extension until a steady state toughness is attained. Steady state toughness can be orders of magnitude greater than the toughness corresponding to crack initiation (Tvergaard and Hutchinson, 1992; and Hutchinson, 1997). The relationship between the initial and steady state toughness is known to be highly nonlinear, and reflects the way that yielding magnifies the initial work of separation. Note that the toughness values measured in the sandwiched DCB tests of the silicon/epoxy interface (Section II.c) correspond to steady state toughness.

VI.d Future work

The above report leads to a number of aspects that should be addressed in the immediate future.

- the continuum calculations must be performed for larger G values, up to 20 J/m^2 for the present epoxy silicon system. In general, one must be able to perform the calculations for any given G value. This may involve modification of the constitutive relations and inclusion of subcritical cracking.
- a critical factor in the estimate of intrinsic fracture stresses is the large effect resulting from the decreased number of epoxy bonds to the substrate relative to a fully bonding SAM. This can be determined experimentally using the IFM with a chemically functionalized tip and thin films of epoxy on silicon.

- the NR test should be performed at liquid nitrogen temperatures to complete the temperature study
- the DCB test should be performed with mixed SAMs and for varying temperatures.
- both smaller and larger lithographically patterned domain sizes should be examined in the NR test to identify the critical flaw size and further characterize this effect. Also, this effect needs to be addressed in the modeling.
- a better epoxy model is needed. Among other aspects, this may require experimental investigation of epoxy structure in high deformation fields, such as at loaded crack tips.
- the MD calculations should be extended to larger systems, lower crosslinking temperature, and lower strain rate. Also, better parameterization of the model potentials is needed.
- the continuum stress field should be directly incorporated into the MD simulation as a boundary condition.
- the fracture surfaces should be further examined by AFM to look for evidence of nanoscale dewetting or voids for the case of full ODTS coating.
- the effect of roughness should be examined in NR test. Roughness will likely add a tensile component to the local mode of loading, and so VDW interactions should become important.
- develop a fracture test which includes a pre-existing crack and is loaded in pure shear to test the relevance of the criterion in eq. VI-1 for another loading geometry.
- systematically vary the crosslink density near the interface. Compare experimental results with model predictions.

- add glass microbeads to the epoxy to vary yield behavior without changing interfacial chemistry. This will allow a further test of eq. VI-1.
- much insight could be gained by developing a method to measure strain in the NR test.
- perform dynamic experiments such as stress relaxation on the NR samples at loads that are lower than the fracture stress.

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Figure I-1. Illustration of the fundamental interaction potential acting across an interface. The graph on the right shows the force-distance law for a unit area from the derivative of the potential, which gives the energy and maximum stress for interfacial separation on the molecular scale. The ideal interface strength per unit area corresponds to the peak in this plot, whereas the energy per unit area corresponds to the area under the curve. Most interfaces involve a combination of fundamental interactions, and so the interaction potential varies in the plane of the interface. The goal of this work is to relate $\Psi(x,y,z)$ to engineering fracture quantities.

Figure I-2. Illustration of molecular-to-continuum fracture model

1) vary SAM coverage
via exposure time

2) vary SAM coverage
using lithography

3) mixed SAMs of
functionalized and
unfunctionalized

Figure II-1. Three methods of varying interface bonding using SAMs:

c:\spindata\04140013.hdf

Figure II-2. AFM image of ODTS incomplete monolayer deposited at room temperature ($\sim 24^\circ\text{C}$)

c:\epmdata\04260034.hdf

Figure II-3. AFM image of ODTS incomplete monolayer deposited at 10 °C

Figure II-4. Variation of ODTS coverage with soak time

Figure II-5. Advancing and receding water contact angles as a function of ODTS coverage for depositions at 24 °C.

Figure II-6. Advancing and receding water contact angles as a function of ODTS coverage for depositions at 10 °C.

Figure II-7. Advancing and receding epoxy contact angles as a function of ODTS coverage for depositions at 22 °C.

Figure II-8. X-ray reflectivity of ODTS monolayers at coverages corresponding to equilibrium water contact angles of 0.0° , 85° , 95.5° , 106° , 110° .

Figure II-9. Mass coverage of ODTS incomplete monolayers as a function of equilibrium water contact angle.

Figure II-10. Fracture stresses using rings of different diameters.

Figure II-11. Fracture stress as a function of equilibrium water contact angle for incomplete ODTS monolayers deposited at 22°C and 10 °C.

Figure II-12. Fracture stress as a function of fractional mass coverage for incomplete ODTS monolayers deposited at 22 °C.

Figure II-13. Fracture stress as a function of work of adhesion for incomplete ODTS monolayers deposited at 22 °C.

Figure II-14. Effect of epoxy composition on fracture stress for incomplete ODTS monolayers deposited at 22 °C.

Figure II-15. Effect of rate in the fracture test on fracture stress for incomplete ODTS monolayers deposited at 22 °C.

Figure II-16. Effect of temperature in the fracture test on fracture stress for incomplete ODTS monolayers deposited at 22 °C.

Figure II-17. Normalized TOF-SIMS D⁻ signal from fracture surface of silicon substrate as a function of ODTS coverage indicated by the work of adhesion (uncured epoxy).

equil. water contact angle = 113°

$\sigma_{\text{fracture}} < 2 \text{ MPa}$

Figure II-18. Optical micrograph of the surface of a ring after fracture. The ODTS monolayer was at full ODTS coverage.

equil. water contact angle = 99°
 $\sigma_{\text{fracture}} = 13 \text{ MPa}$

Figure II-19. Optical micrograph of the surface of a ring after fracture.

equil. water contact angle = 98°

$\sigma_{\text{fracture}} = 25 \text{ MPa}$

Figure II-20. Optical micrograph of the surface of a ring after fracture.

Figure II-21. Optical micrograph of the substrate with ODTS coating patterned lithographically.

Figure II-22. Fracture stress as a function of fractional mass coverage for ODTS deposited in square domains patterned with conventional lithographic techniques. Data for Method I are also shown for comparison.

Figure II-23. Fracture stress as a function of mixed monolayer composition.

Figure II-24. Fracture toughness in DCB loading as a function of ODS coverage (as indicated by the equilibrium water contact angle).

Figure III-1. Finite element mesh used to analyze a 120 mm long sandwiched DCB specimen with a 45 mm crack (9.1 mm aluminum / 0.6 mm silicon / 0.6 mm epoxy / 9.1 mm). Deformation corresponds to linear elastic analysis.

Figure III-2. Conventions used to define interfacial crack configuration.

Figure III-3. Compressive true stress-strain curve for EPON 828/T403 epoxy at a 100:43 weight ratio and cured at 50°C for 24 hours followed by another 24 hours at 40°C. Tested at room temperature and a strain rate of 0.0002/s. Solid line measured, dotted line assumed.

Figure III-4. True compressive stress-plastic strain curve used to define yield behavior in finite element calculations.

Figure III-5. The length of the yield zone vs. G in sandwiched al/si/epoxy/al specimen (yield zone defined by material with plastic strains exceeding 0.001).

Figure III-6. Crack-tip blunting vs. G in sandwiched Al/Si/epoxy/Al specimen.

Figure III-7. Interfacial normal stress in sandwiched Al/Si/epoxy/Al specimen when $G=14 \text{ J/m}^2$ (equivalent plastic strain shown in insert).

Figure III-8. Mesh used in small-scale yielding calculations (1mm region with 1 nm radius void in epoxy at crack tip)

Figure III-9. Yield zone and crack-tip blunting at $G=0.05 \text{ J/m}^2$ when epoxy model includes pressure dependence (yield zone defined by material with plastic strains exceeding 0.001).

Figure III-10. Yield zone and crack-tip blunting at $G=0.05 \text{ J/m}^2$ when epoxy model suppresses pressure dependence (yield zone defined by material with plastic strains exceeding 0.001).

Figure III-11. Comparison of interfacial shear stress distributions when pressure dependence is either included or suppressed in epoxy constitutive model ($G=0.05 \text{ J/m}^2$).

Figure III-12. Comparison of interfacial normal stress distributions when pressure dependence is either included or suppressed in epoxy constitutive model ($G=0.05 \text{ J/m}^2$).

Figure III-13. Yield zone and crack-tip blunting when epoxy model suppresses pressure dependence and for $G=1.0 \text{ J/m}^2$ (yield zone defined by material with plastic strains exceeding 0.001)..

Figure III-14. Interfacial normal stress distributions when pressure dependence is suppressed in epoxy constitutive model ($G=1.0 \text{ J/m}^2$).

Figure III-15. Interfacial normal stress versus G level at 1 and 9 nm from crack tip (epoxy model suppresses pressure dependence).

Figure III-16. Interfacial shear stress versus G level at 1 and 9 nm from crack tip (epoxy model suppresses pressure dependence).

Figure III-17. Equivalent plastic strain at interface versus G level at 1 and 9 nm from crack tip (epoxy model suppresses pressure dependence).

Figure III-18. Yield zone and crack-tip blunting when epoxy model suppresses pressure dependence when $G=0.83 \text{ J/m}^2$ and $\hat{\psi}_{r=0.01 \text{ mm}} = -22^\circ$ (yield zone defined by material with plastic strains exceeding 0.001).

Figure III-19. Yield zone and crack-tip blunting when epoxy model suppresses pressure dependence when $G=0.71 \text{ J/m}^2$ and $\hat{\psi}_{r=0.01\text{mm}} = 48^\circ$ (yield zone defined by material with plastic strains exceeding 0.001).

Figure III-20. Interfacial normal stress versus G at 1 nm from crack tip for three different mode mixity $\hat{\psi}_{r=0.01mm}$ (epoxy model suppresses pressure dependence).

Figure III-21. Interfacial normal stress versus G at 9 nm from crack tip for three different mode mixity $\hat{\psi}_{r=0.01mm}$ (epoxy model suppresses pressure dependence).

Figure IV-1. The checkerboard pattern used to create debond areas of varying size is schematically shown. The black squares represent the debond regions. The area fraction restricted from bonding depends upon the size of the squares.

Figure IV-2. The tensile stress vs. strain for system 2 at full bonding. The points represent the strains at which bonds break.

Figure IV-3. Schematic drawing depicting minimal path between bond on top and bond at bottom plates. Thick line represents a minimal path. Dotted lines represents a path with length larger than the minimal path.

Figure IV-4. The stress-strain curves for tensile pull of bead-spring SAMs with only LJ interactions (■) has a peak stress of 5.6. Bonding the two SAMs together with bond set 2 (O) results in a fracture stress of 111.

Figure IV-5. Same as previous Figure IV-4 except deformation is shear.

Figure IV-6. The tensile stress vs. strain for systems 1 (top), 2 (middle) and 3 (bottom). The points represent different bond fractions at the interface: 0% (▲), 10% (■), 25% (●), 50% (Δ), 75% (□) 100% (○).

Figure IV-7. The shear stress vs. strain for systems 1 (top), 2 (middle) and 3 (bottom). The points represent different bond fractions at the interface: 0% (▲), 10% (■), 25% (●), 50% (Δ), 75% (□) 100% (○).

Figure IV-8. Plot of failure stress versus coverage for system 3. The squares are for tensile simulations and the circles represent shear simulations. The solid line is a fit to the shear data; dotted line is for tensile data.

Figure IV-9. Plot of failure strain versus coverage for system 3. The squares are for tensile simulations and circles represent shear simulations. Solid line is a fit to the shear data, and dashed line is fit to high coverage tensile data.

Figure IV-10. The average displacement of particles in bins parallel to the walls for system 1 at full coverage. The dotted line is the ideal linear displacement field. The points show the calculated value for each bin. The displacement is between a configuration near the failure point and the initial configuration.

Figure IV-11. The displacements as a function of strain for system 1 at $C=1$. The strains are 0.33 (dotted), 0.66 (short dash), 0.99 (long dash), 1.33 (dot dash) and 1.53 (solid).

Figure IV-12. The distribution of stretched bonds for different fractional debond areas shows that bonds tend to be stretched near the debond areas and at the interface. The values of the fractional debond area are (a) 0%, (b) 25% and (c) 50%. The system size is $112\sigma \times 29\sigma \times 72\sigma$.

Figure IV-13. Stress-strain curves for systems crosslinked at different temperatures. Top figure shows data for networks fully bonded to both walls; crosslink temperatures are 1.1 (●), 0.8 (○) and 0.6 (□). Bottom figure shows the case of no bonding to bottom wall; crosslink temperatures are 1.1 (Δ) and 0.6 (□).

Figure IV-14. The density as a function of temperature for networks with functionality $f=4$ and 6, and for 'melt' of liquid components of model epoxy.

Figure IV-15. The above images are slices 10 LJ units thick. The left image shows a snapshot of an equilibrated liquid mixture. The green represent the strand monomers and red is the crosslinkers. The right image is a snapshot after crosslinking. Small 'nanovoids' are clearly visible. Here, the strand monomers bonded to a crosslinker are cyan. The crosslinkers with an unfilled bond are blue.

Figure VI-2. Comparison of the observed shift in the fracture stress curve with temperature in the NR test with that expected based on the variation in yield stress.

Figure VI-1. Variation in compressive yield stress with temperature.

Figure VI-3. Comparison of the observed shift in the fracture stress curve with temperature in the NR test with that expected based on the variation in yield stress.

Figure VI-4. Fracture toughness as a function of the fraction of surface sites available for bonding as calculated from the combined continuum-MD model.

Figure VI-5. Fracture toughness as a function of the ODTS coverage as determined from the DCB test specimens.

Manipulating polymer connectivity to control interfacial fracture

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Abstract

Coarse-grained molecular dynamics simulations are applied to fracture in highly crosslinked, polymer networks. Dynamically formed, random polymer networks between two solid surfaces under tensile strain are simulated. The molecular deformation sequence and the stress-strain behavior are determined. The failure strain is related to the minimal paths through the network connecting the solid surfaces. The fracture is interfacial due to the deficit of interfacial bonds. Ideal, ordered networks are constructed which enable easy manipulation of the network connectivity. By varying just the connectivity, the failure modes are changed. Failure stresses and strains can be made either larger or smaller than the dynamically formed networks.

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Progress in atomic aspects of fracture has recently occurred through simulations for bulk, crystals [1,2]. Less work exists for amorphous materials like polymers [3]. Since the typical adhesive material is a polymer network, the interfacial fracture of polymer adhesives bonded to a solid surface is a fundamental and practical problem [4]. Highly crosslinked polymer networks have been particularly neglected by simulations, yet they are an important class of adhesives. While linear elastic fracture mechanics works well for such polymers far from the crack tip, the method breaks down near the crack tip where large plastic deformation occurs and the molecular details become important [4]. Experimentally, it is known that as the crosslink density increases the failure mechanism changes from crazes to deformation zones [5]. This letter reports molecular dynamics simulations of highly crosslinked polymer networks bonded to a solid surface focussing on the role of connectivity.

In a random network, the stress on bonds is expected to vary, and the network bonds that are most stressed will break first [6]. Crack initiation should occur where a cluster of highly constrained bonds exists. There is no reason to expect the crack initiation site to occur at the interface, although we know experimentally that interfaces are often weak. The results to be presented show that the solid surface limits the interfacial bonding resulting in stressed interfacial bonds and interfacial fracture. Furthermore, the bonds in highly-crosslinked random networks do not become stressed as expected.

Molecular dynamics (MD) simulations can treat the complexities of interfacial polymer fracture. Simple coarse-grained bead-spring models have been successful in treating bulk polymer networks and melts to interfacial fracture [7,8]. This work extends these methods to fracture. Connectivity is an essential ingredient in polymer dynamics [9] and in simulations of fiber fracture [10]. The bead-spring models preserve the connectivity with more molecular detail than in simple lattice models [10].

Using coarse-grained MD, highly crosslinked networks are formed between and bonded to solid surfaces. The molecular deformation sequence is determined for an applied tensile strain. The failure strain is shown to be related to the minimal paths through the network between the two solid surfaces. The network connectivity is a critical determinant of many aspects

of the fracture. To demonstrate the effect of differing connectivities a very simple model is developed. This model system is more amenable to manipulation and theoretical treatment. Using this model, the number of bonds is shown to be critical in determining whether failure is adhesive or cohesive, and connectivity effects the scission rate and, consequently, the failure stress.

Polymer chains are composed of beads interacting via a Lennard-Jones (LJ) potential with a cutoff at 2.5 [8]. All quantities will be in LJ units; σ and ϵ represent the stress and the strain. Typically, beads are bonded together by a finite-extensible nonlinear elastic (FENE) bond potential preventing chain crossing. In order to break bonds and preserve the continuity of the bond force, a breakable quartic bond potential was created that approximates the FENE potential at the potential minimum.

$$U_4(r) = \begin{cases} k_4(r - r_1)(r - r_2)r^2 + U_0, & r < r_2 \\ U_0, & r \geq r_2 \end{cases} \quad (1)$$

The value of r_1 is set to match the FENE bond minimum. The second minimum at r_2 is the cutoff point. The potential parameters are: $k_4 = 1200$, $r_1 = 0.75$, $r_2 = 1.55$ and $U_0 = 34.69$. As in the FENE bond, the total bond potential includes the purely repulsive LJ interaction with a cutoff at $2^{1/6}$. With this bond potential, chains can cross only by breaking bonds.

The maximum bond force is 70, and the maximum LJ force is 2.4. For atomic force-fields, the force ratio between the bond and the van der Waals forces is about 1000 compared 30 for the simulation parameters. However, a single bead represents several atoms and the LJ pair interaction represents multiple van der Waals pair interactions. With even just 3 atoms per bead, there are 9 pair interactions. A force ratio of order 100 in the coarse-grained model is representative of the atomic system. The ratio 30 in the present simulations is small, but by a factor of less than 10. The effect of varying bond strength requires more space than available here.

The complete system consists of a polymer network between two solid walls. Each wall is two layers of particles in an fcc lattice with nearest neighbor distance 1.204. The (111) direction (z -direction) is perpendicular to the walls. The wall particles are bound to the

lattice sites by a harmonic spring with spring constant 100. The wall dimensions give the simulation cell lateral lengths, L_x and L_y , and periodic boundary conditions are applied in these directions. The separation distance between the innermost wall layers is L_z . The wall particles interact with the beads via the LJ potential [11], with some wall particles are bonded to the polymer network by Eq. 1. The dynamics is performed at constant temperature T using the Langevin thermostat [12]. The integration time step is 0.005, and the damping constants are 1 for the monomers and 5 for the walls.

To form the networks, we take a cue from an highly crosslinked adhesive, epoxies. Epoxies are chemically cured networks formed from a liquid mixture of a resin (Bisphenol A) and a crosslinker [13]. Each strand consists of only a few monomers. As a bead corresponds typically to 2 or 3 monomers [8], an epoxy model would have only a few beads per strand. The minimal case of two beads is used here. The emphasis is on understanding general features, not on optimally modeling epoxies.

The networks are dynamically formed in a manner similar to epoxy network formation. In epoxies, a liquid mixture of a crosslinker and a resin is crosslinked dynamically. In the simulations the mixture consists of two bead and three bead molecules. The three bead molecule has a sixfold functional crosslinker bead already bonded to a two bead strand. The strand beads and crosslinker beads have identical potential parameters. Bonds are formed when the separation between a crosslinker and a strand end or wall particle is less than 1.3. After equilibrating the liquid mixture, crosslinkers are first bonded to the walls. Next, during a MD run, the crosslinkers are bonded to strands until at least 95% of all possible bonds are made. Zero load is maintained on the walls during the crosslinking. Afterward, the temperature is reduced below the glass transition temperature ($T_g = 0.5$) to 0.3. Results will be presented primarily for system R: the random network with 9800 monomers and initial dimensions $L_x = 19.3$, $L_y = 33.1$ and $L_z = 15.1$.

The tensile pull is performed by moving the top and bottom walls apart at constant velocity. In Fig. 1 the stress-strain curve is shown for both walls pulled at a wall velocity of 0.01. The yield stress is about $\sigma_y = 4$ and the yield strain is 0.1. The stress drops suddenly

and complete failure occurs at $\epsilon_f = 1.0$ and $\sigma_f = 3.4$. The first bond breaks at $\epsilon = 0.62$. Between $\epsilon = 0.82$ and 1.0 all the bonds between the network and the bottom wall break resulting in failure.

Almost all broken bonds occur at the interface. Bonds in the bulk of the random network are not stressed. In fact, strains large compared to macroscopic measurements are required before any bonds are stressed and broken. To understand this, the molecular deformation sequence determined by examining configurations. At low strains, the near neighbor cage is plastically deformed producing the yield behavior. This deformation involves only LJ interactions and determines σ_y . Once the monomers have moved beyond their initial local position, further applied strains tighten the strands of the network. In the plateau region, bond lengths are rarely stretched. The bonds begin to stretch only after strands are pulled taut which requires large local strains. Most of the stretched bonds are interfacial bonds. Subsequently, these bonds break and the interfacial failure occurs. This sequence of molecular deformations corresponds to the deformation zones (DZ) seen experimentally [5]. The local strain at a DZ is much larger than the external applied strain. System R and even other simulated systems 10 times larger are still smaller than the typical DZ for epoxies let alone a complete system [14].

An upper limit to the strain at which scission must occur is given in the minimal path lengths P of the network. In fact, the simulations show that the average P is a good estimate of the failure strain. For a site on the bottom wall to which the network is bonded, there are many paths through the polymer network to the top wall. The shortest path defines P for that site. Conversion of P into a strain can be done via the relation, $\epsilon_P = (P - L_z)/L_z$. For $\epsilon > \epsilon_P$, some bond within the minimal path must break. Using Dijkstra's method [15], P has been calculated for all bonding sites on the bottom wall. The average P over all such bonding sites is typically about $2L_z$. In the absence of another constraint, this implies the system can be strained almost 100% before significant scission. For system R the path with the smallest P has $\epsilon_P = 0.84$, and by $\epsilon = 1.1$ all the paths' must break. These values are consistent with the major onset of scission and ϵ_f for R given above. Thus, scission is

determined by a global, not local constraint.

To provide a simpler model for theoretical treatment and to further test the connectivity constraints, an ordered network is constructed. The ordered network is designed to minimize the constraints of connectivity resulting in large minimal paths. As in R, the ordered network is sixfold coordinated with two monomers between each crosslinker. The network is constructed using the body centered cubic (bcc) lattice as a template (see Fig. 2(a)). Crosslinkers are the central particles in the bcc cells yielding a sixfold lattice. The z -direction is the (111) lattice direction. There are two (111) planes each with 3 sites in the bcc cell. These sites represent strands which form a zig-zag path between crosslinkers. This path is adjusted to achieve the correct density. The positions at the origin and at (1,1,1) in the bcc cell are vacant. Figure 2 shows the basic building block of the network and gives more details of the network geometry. The system is also created at $\rho = 0.8$ and then equilibrated to $T = 0.3$ and zero load.

When a tensile pull is applied to the ordered network, the strands can straighten out uniformly like an accordian. All strands are expected to become taut before any bond breaking occurs. Thus, this system should expand considerably more before failure than the random structures. In fact, even though the strands are very short, this system should behave like an elastomer.

The stress-strain curve is shown in Fig. 1 for the ordered system O1 with one bond per crosslinker to the wall as in R. The yield stress depending only on the LJ interactions is identical to the random network's. As expected, failure occurs at a much larger strain, $\epsilon_f = 2.5$. The fully taut configuration is a zig-zag path (see Fig. 3(b)). The strain for this taut configuration at which the bonds must begin to stretch is 2.3 calculated directly from the geometry. The stress begins to rise sharply at this strain because the bonds are being stretched. Figure 3 shows that the strands open up as expected. The network does not open up uniformly; instead, it progressively opens up around an initial nucleation site determined by the combination of local disorder ($T < T_g$) and thermal fluctuations. The initial region grows with increasing strain spanning the system in the x -direction. Then, layer by layer

the rest of the strands straighten out. The noticeable rises in the stress-strain curve before the final rise are due to the extra stress it takes to pull the two layers at the walls which are more strongly packed. More force is need to pull the layers apart. Only after all the strands are taut, do the bonds begin to stretch and then break at the interface.

The number of bonds to the solid surface are indentical in systems O1 and R, but O1 has a much larger failure stress. Because the O1 network completely opens before bond breaking occurs, more bonds break simultaneously and the failure stress is larger than in R. The ideal fracture stress is

$$\sigma_{id} = F_{br} * N_b / A \quad (2)$$

where F_{br} is the force to break a bond, N_b is the number of bonds to the wall, and A is the wall area. O1 and R have $N_b = 60$ and $\sigma_{id} = 6.5$. The fracture stress of O1, $\sigma_f = 4.9$ is much closer to the ideal value than R's value (3.4). For R, interfacial bond breaking occurs over a strain range of 0.18, but for O1 the range is just 0.005. Thus, at any given strain fewer bonds are broken in R, and the contribution to the stress by the bond forces is significantly smaller than for O1.

The reason for interfacial failure is especially clear for O1. The number of bonds at the interface is fewer than the number of bonds elsewhere in the network. In system R this occurs simply because only one bond per crosslinker occurs due to the to geometric constraints of the wall. The bond density $b(z)$ is calculated by counting the number of bonds that cross z -plane at z . Near failure, the average bulk $b(z)$ is 0.55 for R and 0.26 for O1. Since R is near failure at a much lower strain, the density and thus the bond density is larger than for O1. In both cases $b(z)$ is just 0.09 at the interface. Thus, the stress is applied to fewer bonds at the interface. These bonds must stretch more to individually apply a larger force; consequently, they break first and failure occurs at the interface.

Constructing an ordered network with three bonds per crosslinker to the wall (O3) can be done. By positioning interfacial crosslinkers above the the middle of the triangles of the wall fcc layer, the crosslinks can bond to each particle in the triangle. In this case, the same

number of bonds occurs for all crosslinkers. There should be no preference to failure at the interface. Given that the interface is a small fraction of the system, failure is likely to occur within the network—cohesively.

The bond distribution $b(z)$ for O3 is identical to O1 except at the interface where $b(z)$ matches the bulk value. Figure 3(c) shows that indeed cohesive failure occurs. The stress-strain curve for O3 (Fig. 1) is similar to the O1 case. The difference is mainly that the failure stress is larger ($\sigma_f = 8.7$), since there are more bonds to break. However, σ_f is larger by only a factor of about two, not three like the ideal value, $\sigma_{id} = 19.5$. All the bonds break at the interface in O1 in about 1000 time steps. For O3, 6000 time steps of bond breaking occur. As noted above, this results in a smaller σ_f .

Large strains occur in O1 and O3, because of the lack of constraints between strands connecting crosslinkers in neighboring planes. A network with some strands connecting next nearest neighbor planes of crosslinkers should have fundamentally different behavior. Such an ordered system (O2) was constructed (Fig. 2(c)). One of the three strands extending downward from every crosslinker is switched to connect to a next nearest crosslinker. This cannot be done for the crosslinkers two layers from the wall, resulting in some dangling ends. One could bond these ends to the walls, but here the wall bonding is kept the same as in O1. The random network R has about the same number of dangling ends. The stress-strain curve (Fig. 1) exhibits failure at a *lower* strain and stress than R. This lower strain agrees with the calculated strain $\epsilon = 0.6$ for the taut path of connected next nearest neighbor crosslinkers.

Thus, by manipulating only the network connectivity, the failure stress and strain can either be less than or greater than random network values. The fundamental point is that the network connectivity is a critical factor controlling the nature of interfacial fracture of highly crosslinked networks bonded to a solid. The connectivity defines the minimal paths which determine the failure strains. The connectivity effects the dynamical sequence of bond breaking and thus the failure stress. The tendency for adhesive fracture instead of cohesive fracture is because of the relative deficit of interfacial bonds, i.e. the interfacial connectivity.

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Structure within Thin Epoxy Films Revealed by Solvent Swelling: A Neutron Reflectivity Study

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ABSTRACT: Structure within thin epoxy films is investigated by neutron reflectivity (NR) as a function of resin/cross-linker composition and cure temperature. Variation in the cross-link density normal to the substrate surface is examined by swelling the films with the good solvent *d*-nitrobenzene (*d*-NB). The principal observation is a large excess of *d*-NB near the air surface. *This is not a wetting layer*, but rather indicates a lower cross-link density in the near-surface region. This effect is due to preferential segregation of the cross-linker to the air surface, driven by the lower surface tension of the cross-linker relative to the epoxide oligomers. The magnitude of the effect is a function of composition and cure temperature. Exclusion of *d*-NB from the region immediately adjacent to the substrate surface is also observed, possibly indicating a tightly bound layer of epoxy. Regarding swelling in the bulk of the films, the behavior is nonsymmetric with departure from the stoichiometric ratio. The films deficient in curing agent show greater equilibrium swelling and faster swelling kinetics than the films with an excess of curing agent.

Introduction

Due to a variety of factors, the structure and properties of polymer films can be different near interfaces compared to the bulk. At a substrate surface, polymer mobility is generally restricted due to adsorption of segments, restricted conformations, segment layering, alignment of chains, and decreased free volume.¹⁻⁵ Diffusion of small molecule probes appears to be less affected, with some studies showing a slightly reduced mobility within a polymer film near a substrate surface and others showing little or no reduction in mobility.⁶⁻⁸ At the air surface of glassy polymers, mobility is typically increased relative to the bulk.⁹⁻¹³ In multi-component systems, preferential segregation can occur at either interface due to both enthalpic and entropic effects.¹⁴⁻¹⁷ Similar considerations also drive segregation of chain ends to interfaces.¹⁸⁻²⁶ Kinetic effects have been shown to be important in the resulting structure of spin-cast films of glassy polymers.²⁷⁻²⁹

Structure near a substrate surface is important for stress transfer, mechanical properties, fracture mechanisms, and diffusion of penetrants, among others. Structure at the air surface can impact surface reconstruction, surface free energy, wettability, and reactivity. In addition, structural gradients at air interfaces can impact the interfacial strength that develops when contacted with a second polymer. This is particularly important in technological applications involving multiple thermosets such as multilayer paint films and manufacturing processes involving multiple adhesives and encapsulants that come into contact.

Our focus is the structure within highly cross-linked, two-component epoxy films. In such systems, preferential segregation of either component to an interface will strongly effect the structure by altering the local stoi-

chiometry and, therefore, the cross-link density. Variation in stoichiometry can affect not just the average cross-link density but also the distribution of cycles and dangling ends.³⁰ Several workers have reported evidence of gradients in cross-link density at substrate surfaces in such systems,³¹⁻³⁹ in some cases extending to ~1000 Å from the substrate surface.^{31-33,36} In addition to segregation at interfaces, unreacted monomer can segregate from high molecular weight gel fractions during cure, leading to heterogeneity within the bulk of the film.³⁹ In such systems, the rate of the cross-linking reaction(s) and the rate of segregation can be in competition. With a rapidly cured system, segregation will be minimized, whereas equilibrium interfacial concentration profiles and segregation within the bulk are expected for very slowly curing systems. Thus, cure rate is an important aspect explored in this work.

We examine variations in cross-link density within thin (600–1200 Å) epoxy films on silicon substrates by solvent swelling. The method is based on the fact that the equilibrium volume fraction of a swelling solvent is strongly dependent upon the local cross-link density. We examine the volume fraction profile of the good solvent nitrobenzene through the epoxy films by neutron reflection. Isotopic substitution is used to provide contrast between the epoxy matrix and the swelling solvent. Swelling is an important method that has been employed for many years to determine the average cross-link density in macroscopic bulk samples.⁴⁰ Variation in local swelling has been used to examine the degree of structural heterogeneity within the bulk of cross-linked samples, by neutron scattering.⁴¹⁻⁴⁵ Wu et al. examined the swelling of a bulk epoxy sample cross-linked with a linear diamine.⁴⁴ Their data are consistent with a heterogeneous distribution of cross-links. However, the absence of any peaks in the scattering data

Figure 1. Chemical structure of DGEBA epoxy resin and T403 polyethertriamine curing agent.

indicates the absence of a well-defined correlation length in the heterogeneous network structure. In particular, their data are not consistent with the presence of well-defined nodules as have been reported in some systems.³⁹

Following a description of the experimental details, the results are presented in two sections. The first deals with the equilibrium swelling as a function of stoichiometry and cure temperature. In the second section we examine the swelling as a function of time prior to attaining equilibrium.

Experimental Section

Materials. Research grade EPON 828 epoxy resin was obtained from Shell Chemical Co.⁴⁶ The resin was cured with an aliphatic polyethertriamine (T403, Huntsman Chemical). Both resin and cross-linker were used as received. The chemical structures of the amine and epoxide monomers are shown in Figure 1. If these monomers combine exclusively through epoxide-amine addition reactions, about 46 amine parts per 100 epoxide parts by weight (phr = parts per hundred resin) are required for complete cure. This is consistent with experimental measurements of the maximum glass transition temperature and the minimum swelling ratio.³⁰ To prepare uniform thin films by spin-coating onto silicon wafers, it was necessary to increase the molecular weight prior to spin-coating. This was accomplished by heating the resin and cross-linker mixtures at 60 °C for 70 min. The mixtures were then dissolved in toluene for spin-coating. Three solutions with different concentrations of T403 (36, 46, and 56 phr) were prepared. An aliquot of each solution was deposited onto a silicon wafer using a glass pipet and then spun off at 3000 rpm using a Headway photoresist spinner. The silicon wafers used as substrates in this study were polished 2 in. diameter single crystals (111) obtained from Semiconductor Processing Co. The wafers were cleaned using the "RCA" process: a sulfuric acid/hydrogen peroxide clean, followed by etching in an HF solution, and then the regrowth of silicon oxide with ammonium hydroxide/hydrogen peroxide solution. Two films were prepared for each mixture to examine the effect of curing temperature. One set of three samples (36, 46, and 56 phr) was cured at 50 °C for 48 h (cure A), while the second set of samples was cured at 80 °C for 1 h and then 120 °C for 2 h (cure B). Our goal was to achieve full cure with each condition. A previous study of this system indicates that full cure is achieved at 50 °C in roughly 24 h for the 36 phr composition.⁴⁷ However, no data are currently available for the 46 and 56 phr compositions, and we now suspect that the 46 phr films may not be fully cured with cure A. We will return to this point later in the Results and Discussion section. Following cure,

Table 1. Calculated Neutron Scattering Length Densities (b/V , 10^{-4} Å⁻²) of the Materials Used in This Study^a

	b/V		b/V
d-NB	0.0555	46 phr mixture	0.0113
EPON 828	0.0151	56 phr mixture	0.0107
T403	0.0029	silicon	0.0207
36 phr mixture	0.0119	silicon oxide	0.0300

^a The following densities were used in the calculations: $\rho_{\text{T403}} = 0.98$, $\rho_{\text{EPON 828}} = 1.17$.

the samples were desiccated until the reflectivity measurements were performed.

Methods. The surface tensions of the liquid epoxy resin, cross-linker, and resin/cross-linker mixtures were measured by the Wilhelmy plate technique using a sandblasted platinum plate and a Q11 force transducer from Hottinger Baldwin Measurements.

Neutron reflectivity (NR) measurements were performed on the NG7 reflectometer (NIST). A fixed wavelength of 4.74 Å was used. The intensity of reflected neutrons is measured as a function of momentum transfer ($q = 4\pi \sin \theta / \lambda$, where θ is the angle of incidence and λ is the wavelength). Such reflectivity curves are very sensitive to the 1-dimensional profile of the neutron scattering length density (SLD) normal to the substrate surface. The neutron SLD is a function of the density and atomic composition. The calculated SLD values of the materials used in this work are shown in Table 1. During the measurements, the samples were maintained at room temperature in a sealed aluminum chamber. The reflectivity of the as-prepared samples was first measured with desiccant in the chamber. The desiccant was then removed, and the chamber was saturated with *d*-nitrobenzene (*d*-NB), a good solvent for both the resin and the cross-linker. Since the surface tension of *d*-NB (~48 mN/m) is higher than that of the mixtures of epoxy resin and T403 (~34–37 mN/m), a wetting layer of *d*-NB does not form on the surface of the epoxy film. This was important since the neutron beam was directed onto the interface from the air side. Equilibrium saturation of *d*-NB within the films was confirmed by measuring the reflectivity with time until no further change was observed.

The SLD profiles cannot be obtained by direct inversion of the reflectivity data, but rather are obtained from a fitting procedure. This involves approximating the model profiles by a series of slabs of constant concentration and then calculating the reflectivity from the stack of layers using the optical matrix method.⁴⁸ The effects of roughness and finite interface width are included by dividing each interface into a number of small slabs to form a smooth gradient. Both the interface width and the functional form of the gradient can be varied. The resolution, $\Delta q/q$ where Δq is the standard deviation of a Gaussian function, was fixed at 0.02. Best-fit parameters were determined by the minimization of χ^2 using the Marquardt algorithm.

Results and Discussion

Equilibrated Films. Reflectivity from a 46 phr sample (cure A) as-prepared and after swelling to equilibrium with *d*-NB is shown in Figure 2a. With the low-temperature cure, we expect that equilibrium composition profiles at the interfaces are approached prior to cross-linking. The reflectivity for the as-prepared sample shows strong oscillations that persist to the highest values of q examined. This indicates that the epoxy film is quite smooth. The curve through the data for the as-prepared sample corresponds to the best fit using a single layer profile for the epoxy film shown by the solid line in Figure 2b. The SLD is consistent with that calculated from the atomic composition and the density given in Table 1. The roughness at the air surface corresponds to $\sigma = 4$ Å, where σ is defined as the root-mean-square (rms) value of the deviation of the

Figure 2. (a) Neutron reflectivity data from a 46 phr sample (cure A) as-prepared (O) and after swelling to equilibrium with d-NB (Δ). The curves through the data correspond to best fits using model scattering length density profiles. (b) Best-fit scattering length density profiles corresponding to the curves through the data in (a) for the sample as-prepared (—) and after swelling (---).

height relative to the average height of the surface. This simple model is entirely adequate to describe the data for the as-prepared sample. Similar profiles were also adequate for the as-prepared 36 and 56 phr samples. In each case, the reflectivity data could be described using a single-step profile with roughness at the air surface comparable to that for the 46 phr sample.

In Figure 2a, the 46 phr sample swollen with d-NB shows a large increase in reflectivity relative to the data for the as-prepared sample. The increase is due to adsorption of d-NB. The best-fit SLD profile for the d-NB swollen sample is also shown in Figure 2b. The thickness and SLD of the swelled film have both increased substantially relative to that of the as-prepared film. More importantly, in contrast with the results for the as-prepared sample, the reflectivity for the swelled sample is not consistent with a single layer profile, but rather increased SLD is required at the air surface. This indicates excess d-NB and thus a lower cross-link density in the region near the air surface. This effect is due to preferential segregation of the polyetheramine cross-linker to the air surface. Segregation of T403 to the air surface is expected on the basis of the surface tensions of the resin (47.8 mN/m) and the cross-linker (33.5 mN/m). The surface tensions for the 36, 46, and 56 phr mixtures were measured to be 36.7, 35.2, and 34.0 mN/m, respectively. The fact that the surface tensions of the mixtures are close to the value for pure T403 verifies that the surface is rich in T403. Segregation of low surface energy components to the air surface has been studied extensively in other multicomponent polymer films.¹⁴⁻¹⁷

Figure 3. (a) Neutron reflectivity data from 36 (O), 46 (Δ), and 56 phr ($\square$) samples (cure A) after swelling to equilibrium with d-NB. The data have been shifted on the y-axis for clarity. The curves through the data correspond to best fits using model scattering length density profiles. (b) Best-fit scattering length density profiles corresponding to the curves through the data in (a) for 36 (—), 46 (---), and 56 phr ($\cdots$) samples. The inset shows the depletion layer of d-NB at the substrate surface.

Figure 3a compares NR data from 36, 46, and 56 phr films with cure A after swelling to equilibrium with d-NB. The SLD profiles are shown in Figure 3b. Note that the form of the reflectivity curve is different for each film. These data reveal several important differences in the structure of the epoxy films. For the 36 phr film the reflectivity curve shows very high reflectivity at low q ($0.01 \text{ \AA}^{-1} < q < 0.04 \text{ \AA}^{-1}$). Without any detailed analysis, the enhanced reflectivity at low q for the 36 phr film is a clear indication of much greater absorption of d-NB near the air surface. The magnitude of this effect for the three compositions occurs in the following order: 36 phr $\gg$ 46 phr $>$ 56 phr. This trend can be understood by considering the composition perturbation near the air surface to consist of two layers as illustrated in Figure 4: an excess of T403 immediately at the surface followed by a layer that we will refer to as the "near-surface" layer which is depleted of T403. A 36 phr film would be deficient in T403 if resin and cross-linker were uniformly distributed. Strong segregation of T403 to the air surface leaves the near-surface region even further depleted of T403. This leads to a highly imperfect network and a high degree of swelling over a relatively large length scale. With the 46 phr sample, preferential segregation of T403 also leads to a depletion of T403 in the near-surface region; however, the composition will be much closer to the stoichiometric ratio, and thus the network is not nearly as imperfect as for the 36 phr sample. With the 56 phr sample, T403 would be in excess if resin and cross-linker were uniformly

Figure 4. Qualitative illustration of the composition perturbation near the air surface. Strong segregation of the cross-linker to the air surface likely leads to a depletion of cross-linker in the near-surface region.

distributed. Depending upon the degree of preferential segregation of T403, the composition in the near-surface layer may actually approach the stoichiometric ratio. Thus, the surface region swells the least in this case, due primarily to the excess T403 immediately at the surface.

As shown in Figure 3b, a thin region of low SLD is detected near the silicon oxide surface for the 36 and 56 phr films. The length scale of this region is roughly 10 Å, much smaller than that of the layer of excess d-NB at the air surface. This indicates exclusion of d-NB from the region immediately adjacent to the substrate surface, apparently due to strong binding between epoxy and the native silicon oxide. The effect on the NR data is weaker than that of the excess d-NB layer at the air surface but is still very significant for the 36 phr sample. The effect of the depletion layer on the reflectivity is more subtle for the 56 phr sample. The reflectivity for the 46 phr film is insensitive to the presence or absence of a depletion layer of this magnitude, so a determination cannot be made in that case.

Finally, we note that the amount of d-NB in the bulk of the film is much higher for the 36 phr sample than for the other two compositions, indicating a lower cross-link density for the 36 phr composition. We also note that the roughness of the air surface for the 56 phr sample after swelling is much greater than that of the other samples.⁴⁹ We will return to this point later in the discussion.

Figure 5a compares NR data from 36, 46, and 56 phr films with cure B after swelling to equilibrium with d-NB. The best-fit SLD profiles are shown in Figure 5b. With the elevated temperature cure, it is expected that cross-linking occurs before the equilibrium composition profiles at the interfaces are approached. Indeed, the reflectivity curves in Figure 5a show two distinct differences from those of the films cured at room temperature. First, the reflectivity over the q range $0.01 \text{ Å}^{-1} < q < 0.04 \text{ Å}^{-1}$ for the 36 phr sample is comparable to that for the other samples. The very high reflectivity observed over this q range for the 36 phr sample with cure A is not observed with cure B. Thus, preferential segregation of T403 occurs to a much lesser extent with cure B. This is likely due to a competition between the rates of reaction and segregation. The degree of excess d-NB in the near-surface region for the three compositions with cure B occurs in the following order: 36 phr $\geq$ 46 phr $>$ 56 phr. Second, for the 46 phr film the Kiessig fringes are much stronger with cure B than with cure A. The magnitude of the Kiessig fringes is determined by the SLD of the film relative to that of the substrate and air. Strong fringes result if the SLD is

Figure 5. (a) Neutron reflectivity data from 36 (○), 46 (Δ), and 56 phr (□) samples (cure B) after swelling to equilibrium with d-NB. The data have been shifted on the y-axis for clarity. The curves through the data correspond to best fits using model scattering length density profiles. (b) Best-fit scattering length density profiles corresponding to the curves through the data in (a) for 36 (—), 46 (---), and 56 phr (· · ·) samples. The inset shows the depletion layer of d-NB at the substrate surface.

intermediate between that of silicon and air or is substantially greater than that of silicon. In the case of the 46 phr film with cure B, strong fringes result because the SLD is intermediate between that of silicon and air, as shown in Figure 5b. The Kiessig fringes are weak for cure A because the SLD is comparable to that of silicon. Thus, cure B results in a much lower equilibrium concentration of d-NB within the 46 phr film than cure A, indicating that with cure B the network is more highly cross-linked or has fewer defects.

We note that again a significant depletion of d-NB is observed at the substrate surface for the 36 and 56 phr samples with cure B. The magnitude of this effect is substantially greater for cure B than for cure A. The reason for this is not clear. Such a layer is not required by the data for the 46 phr sample with cure B, as the data for this composition are again insensitive to this effect.

The degree of swelling within the bulk of the films is examined in Figure 6. This plot shows the volume fraction of d-NB as a function of T403 concentration for the equilibrated samples, where only the SLD of the central portion of the film was used in the calculation. Interestingly, there is a large variation in the degree of swelling with cure temperature for the 46 phr epoxy films, whereas only a very small variation with cure temperature is observed for the 36 and 56 phr films. The lower volume fraction d-NB for the 46 phr sample with cure B indicates a network that has achieved a higher cross-link density than is obtained with cure A.

Figure 6. Volume fraction of d-NB as a function of T403 concentration for cure A (●) and cure B (▲). Note that the volume fraction is determined only from the scattering length density of the central portion of the film and does not include the interfacial regions.

The most likely explanation is that the epoxide-amine reaction does not go to completion in 48 h at 50 °C for the 46 phr composition but does go to completion for the 36 and 56 phr samples. The available kinetic data indicate only that the reaction goes to completion in roughly 24 h at 50 °C for 36 phr.⁴⁷ Indeed, DMA measurements suggest that bulk samples of nearly stoichiometric composition are not fully cured following cure A.⁵⁰ The fact that the central portions of the 36 and 56 phr films are not strongly affected by cure temperature argues against an explanation based on the competition between the rates of reaction and segregation. Further experiments on the extent of cure are underway to resolve this.

As shown in Figure 6, the swelling ratios of the epoxy films with off-stoichiometric compositions are not symmetric, regardless of curing conditions. Rather, a higher swelling ratio results for the 36 phr film than for the 56 phr film for both curing conditions. This is consistent with the results of bulk swelling experiments for the same epoxy/cross-linker system reported by Morgan et al.³⁰ They concluded that a more rapid increase in the molecular weight between cross-links (M_c) with deviation from the stoichiometric composition occurs on the excess epoxide side than on the excess T403 side. A similar conclusion has been reported by others.^{51,52} This can be understood by considering the functionality of the resin and cross-linker and the network structures. As the fraction of T403 decreases below the stoichiometric ratio, unreacted epoxide groups are present and form dangling chain ends. The size and number of defects in the network become larger as the number of unreacted epoxide groups increases. As the amount of T403 decreases to 23.7 phr, M_c increases to infinity.³⁰ On the T403-rich side, all epoxide groups are reacted completely and unreacted amine groups are present. However, the effect of unreacted amine groups on the network structure is not as dramatic because each amine group has two reactive protons. If it is assumed that all primary amines react with epoxide groups prior to the onset of secondary amine-epoxide reactions, ring and branched network structures form even up to 94.7 phr.³⁰

Figure 7 shows film thicknesses for the as-prepared and d-NB-swelled samples as a function of T403 concentration. The thickness is determined from the spacing of the fringes in the reflectivity curves and is thus determined independently of the d-NB volume fraction.

Figure 7. Film thickness as a function of T403 concentration for samples as-prepared (○) and after swelling (●) with cure A and as-prepared (Δ) and after swelling (▲) with cure B.

Figure 8. Relative change in film thickness ($\Delta Z/Z_{dry}$) vs time (t) for 36 (○), 46 (Δ), and 56 phr (□) samples with cure A and for 36 (●), 46 (▲), and 56 phr (■) samples with cure B.

The trends are consistent with the volume fraction data shown in Figure 6. The 46 phr film with cure B shows a much smaller increase in film thickness upon swelling compared to that with cure A. The 36 and 56 phr film thicknesses show a large increase upon swelling for both cure conditions. The swelled thickness of the 56 phr films are nearly independent of cure temperature, whereas for the 36 phr films a greater increase in thickness with swelling occurs with cure A than with cure B. The difference for the 36 phr film is due to the much greater excess swelling in the near-surface region for cure A. Such a trend does not appear in Figure 6 because only the central portion of each film was used in the d-NB volume fraction calculations.

Kinetics of Swelling. Since the equilibration time (>24 h) was much greater than the measurement time (4 h), certain aspects of the kinetics could be examined by monitoring the reflectivity as a function of time. The phenomena governing these rather long time processes are not clear. Diffusion of d-NB through the films is not the controlling process, as diffusion of a good solvent through the ultrathin films takes place on a time scale that is short compared to the measurement time. Indeed, no gradients in d-NB through the bulk of the films were detected even at the shortest exposure times examined (~ 6 h). The reflectivity data would be quite sensitive to such an effect if it were present. Apparently, the time for solvent to equilibrate within the film is short compared to the time for plasticizing or softening of the network. Thus, this study probes the relaxation of the network when subjected to a swelling pressure, rather than the rate of adsorption and diffusion of d-NB.

Figure 8 shows the relative change in film thickness ($\Delta Z/Z_{dry}$) vs time (t) for each sample. Several general

Figure 9. Scattering length density profiles for (a) 36 phr sample as-prepared (thin —) and after exposure to d-NB for 12 h (---), 20 h (···), and 27 h (bold —); (b) 46 phr sample as-prepared (thin —) and after exposure to d-NB for 14.5 h (---), 29.5 h (···), 39.5 h (— · —), and 51 h (bold —); (c) 56 phr sample as-prepared (thin —) and after exposure to d-NB for 6 h (---), 21 h (···), 36 h (— · —), 46 h (— · — · —), and 67.5 h (bold —) with cure B. The insets for (a) and (b) show enlargements of the near-surface region.

trends are observed. First, the initial rates of swelling for 36 phr films are much greater than those for the 46 and 56 phr films. This can be understood in terms of the more imperfect network structures of T403-deficient compositions relative to resin-deficient compositions discussed earlier. Second, the initial rate of swelling is much greater for the 46 phr film cured at low temperature than for the 46 phr film cured at elevated temperature. (Low time data for 36 and 56 phr are insufficient to draw conclusions.) This can again be explained by a more rapid relaxation under swelling pressure for a more imperfect network structure.

Figure 9a–c shows SLD profiles as a function of time exposed to saturated d-NB for the 36, 46, and 56 phr films, respectively, with cure B. As shown in Figure 9a, the 36 phr film shows a large increase in film thickness

at relatively short exposure times (12 h) due to swelling of the bulk of the film. Data at sufficiently short times were not obtained to resolve the initial penetration of d-NB into the film. As time proceeds, only a small increase in film thickness occurs, mainly due to increased swelling near the air surface. The 46 and 56 phr films in Figures 9b and 9c show a distinctly different swelling behavior than the 36 phr film. For the 46 and 56 phr films, swelling is initially detected in the near-surface region, followed by gradual swelling of the center of the film. For the 46 phr film, the roughness of the air surface decreases from 3.5 to 1.7 Å upon initial swelling. The magnitude of the swelling at the air surface then continues to increase with time while the roughness at the air surface remains low. The 56 phr film shows a similar swelling behavior as for the 46 phr film during an initial period. However, between 36 and 46 h, the roughness at the air surface of the 56 phr film suddenly becomes greater, and the interface between the near-surface layer and the center of the film becomes sharper. We suggest that swelling stresses cause scission of some network strands at weak points for the 56 phr films, leading to roughening at the air surface. Nevertheless, an apparent steady state appears to be approached at long times (68 h). The very clear difference in swelling behavior between the 36 and 56 phr films revealed in Figure 9 is again attributed to the more imperfect network structures of T403-deficient compositions relative to resin-deficient compositions.

Conclusions

NR from epoxy films swelled with d-NB reveals variations in SLD at both the air surface and the silicon substrate surface. Excess swelling of d-NB at the air surface is observed for all the films. This indicates a lower cross-link density and is due to preferential segregation of the cross-linker to the air surface. The degree of excess swelling at the air surface depends on both the bulk epoxy composition and the cure temperature. To our knowledge, this effect has not been previously reported and may have important implications for multilayer paint films and other applications where thermosetting films are deposited and cured sequentially. A thin (~10–20 Å) layer depleted of d-NB at the substrate surface is also required to fit the NR data for the 36 and 56 phr films. For the 46 phr film, the sensitivity to this feature is very low, such that a clear determination about the presence of this layer cannot be made. The depletion of d-NB may be due to strong binding between the epoxy and the substrate. The effect is greater for films cured at elevated temperature than for films cured at room temperature. Large length-scale variations in cross-link density, such as have been reported at interfaces of epoxy with aluminum^{31–33} and germanium,³⁶ were not observed at the silicon oxide surface. Asymmetry in the network structure with departure from stoichiometric composition is observed from the equilibrium degree of swelling, as well as from the relative rates. This is consistent with previous reports for bulk samples.

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