A robust nanoscale experimental quantification of fracture energy in a bilayer material system

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Accurate measurement of interfacial properties is critical any time two materials are bonded—in composites, tooth crowns, or when biomaterials are attached to the human body. Yet, in spite of this importance, reliable methods to measure interfacial properties between dissimilar materials remain elusive. Here we present an experimental approach to quantify the interfacial fracture energy $\Gamma_i$ that also provides unique mechanistic insight into the interfacial debonding mechanism at the nanoscale. This approach involves deposition of an additional chromium layer (superlayer) onto a bonded system, where interface debonding is initiated by the residual tensile stress in the superlayer, and where the interface can be separated in a controlled manner and captured in situ. Contrary to earlier methods, our approach allows the entire bonded system to remain in an elastic range during the debonding process, such that $\Gamma_i$ can be measured accurately. We validate the method by showing that moisture has a degrading effect on the bonding between epoxy and silica, a technologically important interface. Combining in situ through scanning electron microscope images with molecular simulation, we find that the interfacial debonding mechanism is hierarchical in nature, which is initiated by the detachment of polymer chains, and that the three-dimensional covalent network of the epoxy-based polymer may directly influence water accumulation, leading to the reduction of $\Gamma_i$ under presence of moisture. The results may enable us to design more durable concrete composites that could be used to innovate transportation systems, create more durable buildings and bridges, and build resilient infrastructure.

Significance

Accurate measurement of interfacial properties is critical any time two materials are bonded—in composites, tooth crowns, or when biomaterials are attached to the human body. Yet, in spite of this importance, reliable methods to measure interfacial properties between dissimilar materials remain elusive. Here we present an experimental method for robust characterization of organic–inorganic interfaces. Combining theory, experiment, and molecular simulation, we show that debonding between layers of materials can be controlled through residual stresses in a deposited metallic layer. We validate the method and show that moisture degrades the bonding between epoxy and silica, a technologically important interface. This may enable us to design more durable concrete composites that could be used to innovate our nation’s aging infrastructure.

Author contributions: D.L., M.J.B., and O.B. designed research; D.L., M.J.B., and O.B. performed research; D.L. and K.B. contributed in the experimental program; D.L., M.J.B., and O.B. analyzed data; and D.L., M.J.B., and O.B. wrote the paper.

The authors declare no conflict of interest.

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†To whom correspondence may be addressed. E-mail: mbuehler@mit.edu or obuyuk@mit.edu.

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components with interfacial fracture energy below 50 J/m² as encountered in such material systems.

Results and Discussion
To demonstrate the applicability of this experimental approach, epoxy-silica interface is used as an example, and its interfacial fracture energy (\( \Gamma_i \)) is characterized under both dry and wet conditions. The epoxy–silica interface is fabricated using a silicon wafer with a thermal oxide layer coated by a 20-μm-thick SU-8 film (a type of epoxy commonly used in microfabrication); the results of \( \Gamma_i \) under moisture effect are summarized in Fig. 1. For the dry specimens, the bilayer remained attached to the substrate when the Cr superlayer was 1 μm thick. Conversely, when the Cr layer was either 2 μm or 3 μm thick, debonding occurred, followed by curling of the film as shown in Fig. 2. Consequently, the critical thickness of superlayer, \( h_c \), was between 2 μm and 3 μm for the dry specimens. For the wet specimens, debonding occurred, followed by curling of the film, for all three tested Cr thickness (1 μm, 2 μm, and 3 μm), and hence \( h_c \) is less than 1 μm for the wet specimens. After determining these values, together with the measured residual stresses, bounds for the interfacial fracture energy can be calculated. The details are given in Methods. At the critical point when interfacial fracture is initiated, \( \Gamma_i \) is equal to the steady-state energy release rate (\( G_{ss} \)). Hence, by varying the thickness of the superlayer, various theoretical \( G_{ss} \) can be calculated, and by observing if debonding is initiated under the chosen thicknesses, bounds can be placed on the interfacial fracture energy.

For this purpose, the elastic modulus of the film is needed. Generally, polycrystalline thin films can have a lower modulus than the bulk material, because of porosity at the boundaries of the columnar grains. Although we determined the Young’s modulus of SU-8 (\( E_s \)) using the nanoindentation approach, literature values of polycrystalline Cr thin films (\( E_i = 93 \) GPa) are used here instead because the variation of \( E_i \) under the concerned experimental conditions is very small (18). With the chosen \( E_i \) and \( E_s \), the bounds on the interfacial fracture energy are 12.0 J/m² ≤ \( \Gamma_i \) ≤ 24.5 J/m² for the dry specimens as shown in Fig. 1A. For the wet specimens, only the upper bound can be obtained based on the chosen Cr thicknesses (1 μm, 2 μm, and 3 μm), and the results show that \( \Gamma_i \) ≤ 12.7 J/m² as shown in Fig. 1B.

With a higher-resolution SEM image, we observe that the interfacial crack does not separate SU-8 and silica in a clean manner; instead, some hair-like structures connect SU-8 and silica at the vicinity of the crack tip as shown in Fig. 3. These hair-like structures can be observed in both dry and wet specimens. Such observation can validate that the debonding between epoxy and silica is initiated by detachment of the epoxy polymer chain from the silica substrate. When debonding occurs, hair-like structures are formed at the vicinity of the crack tip. In wet conditions, water molecules can seep into the gaps generated by the hair-like structures and eventually weaken the adhesion at the interface as reported in a recent study of the interfacial integrity between a single polymer chain and a silica substrate, using molecular modeling (19, 20). An earlier study of concrete–epoxy interfaces indicated that \( \Gamma_i \) usually ranged between 10 J/m² and 20 J/m² for the dry case and between 5 J/m² and 10 J/m² for the wet case (21). Such consistency implies that using silica as a substitute for concrete is a reasonable approach in the modeling and simulation process.

To complement the experimental work, interfacial debonding is simulated using an atomistic model. Metadynamics (22, 23) is applied to study the adhesion between diglycidyl ether of bisphenol A (DGEBA) and silica. This algorithm can be used to reconstruct the free-energy landscape by accelerating the sampling of rare events in the system. In particular, it has been demonstrated that this technique can be used to measure the free-energy landscape as a function of the distance between the mass center of a polymer chain structure and silica surface as shown in Fig. 4 (20, 24). The converged free-energy landscape is observed when the simulation time is 100 ns for both dry and wet scenarios, and provides the physical energy landscape of the adhesion between DGEBA and silica as a function of the distance as shown in Fig. 4B.
The simulation results show that the depth of energy barrier in the wet scenario (10.2 kcal/mol) is only about one third of that in the dry scenario (31.8 kcal/mol). This result agrees very well with the experimental measurement using the superlayer approach. A possible scenario to explain these differences is that the space surrounding the hair-like structures allows for the accumulation of water molecules. Based on our prior work, it is noted that the adhesion between polymer and silica can be weakened when the polymer is surrounded by water molecules (19). By carefully observing the entire simulation, it is noted that water molecules seep into the gap between the polymer chain and the substrate. When focusing on the nanoscale, our model can mimic the debonding mechanism both in the dry and wet scenarios by capturing the formation of hair-like structures through the peeling and shearing of the polymer chain tail on the substrate surface. This implies that the debonding mechanism, which is initiated by the detachment of a finite amount of polymer chains, is hierarchical in nature, and the three-dimensional covalent network of the epoxy-based polymer may have influence on the water accumulation, leading to the reduction of interfacial fracture energy under the effect of moisture. It is noted that similar hair-like structures have also been reported in the dental research field, and this common observation further implies that the fracture process along the interface can drive material transformation from a continuum to a discrete nature via a series of hair structures. It is likely that this mechanism occurs within the fracture process zone (25).

This paper is believed to be the first attempt to explain the moisture degradation using both experimental and simulation techniques at a closer length scale, leading to the observation of the continuum-discrete transformation at the fracture initiation state. It should be emphasized that the superlayer approach reported here can be used in a range between 1 nm and 10 μm and has advantages over various conventional fracture tests. For instance, peeling approaches may create a significant plasticity in the thin film due to an enormous bending effect, and nanoindentation approaches may create a significant plastic deformation at the indenter tip. Such plasticity may hardly be separated from the fracture process and may lead to an inaccurate measurement of fracture energy. We also believe that the approach can be used with adequate accuracy for measuring the interfacial fracture energy of metal-related interfaces, in which the plastic zone cannot be avoided. Using this method, a better accuracy may be achieved compared to some existing fracture testing approaches such as microscraping tests, peel test, Blister tests, and mixed mode fracture tests; because, in this case, the plasticity may be confined to a limited plastic zone in the vicinity of the crack tip. The newly developed approach involves preparation of testing samples; a great number of small specimens can be coated by Cr simultaneously by sputtering, and hence a higher accuracy and a smaller standard deviation of the measured interfacial fracture energy can be achieved.

**Conclusion**

Here we developed a superlayer experimental approach for quantifying the interfacial fracture energy at the nanoscale. We have demonstrated the applicability of this experimental technique on organic–inorganic interface by using epoxy (SU-8) and silica as an example. It was found that one can accurately quantify the interfacial fracture energy, while the debonding process can be observed in situ through scanning electron microscope images, and that moisture has a significant effect on the interfacial fracture energy of the epoxy–silica bonded system. The proposed approach using the Cr superlayer enabled us to confine the range of the actual interfacial fracture energy with high fidelity. By considering upper and lower bounds of the
interfacial fracture energy for both the dry and wet specimens, we hypothesized that the interface fracture energy of the bonded system can decrease down to 50% of its original value in the presence of water. More importantly, we observe hair-like structures that connect SU-8 and silica at the vicinity of the crack tip, which are formed when the interfacial crack is initiated.

This experimental technique enables us to capture various debonding stages with the increase of the driving force through the increasing deposition depth of the superlayer, can be used from the nano to the micro level, and has advantages for overcoming the plasticity that is generally involved when debonding is initiated by an externally applied force. The developed approach can be widely used in various bilayer material systems, including those found in construction and composite materials as well as metallic and organic-based thin films, provided that a smooth thin film-free surface can be obtained for the deposition of the Cr superlayer. Furthermore, durable concrete material and resilient infrastructure designs can be achieved with the assistance of this robust measurement technique. The experimental quantification introduced could also be useful for nano-/micro-based manufacturing practices, in particular in medical and bioengineering applications, which require an accurate characterization of the interfacial integrity in a bonded material system under different surrounding conditions, such as moist environment.

Methods

Experimental Procedures. In the developed superlayer experimental approach, a silicon wafer with an oxide layer and an epoxy-based polymer (SU-8) were used. Silicon (Si) is a blue-gray, brittle, chemical element in the same group as carbon (C). At 27.8%, it is second only to oxygen (O) as the most common element on the surface of the earth. Silicon is the main ingredient of glass, quartz, soil, and sand. It contributes to hardness and structural strength in many metals such as aluminum–silicon alloy and bronze. The majority of semiconductors and microchips are built on silicon. Before a semiconductor can be built, silicon must be transformed into a wafer. This begins with the growth of a silicon ingot. A single silicon crystal is a solid composed of atoms arranged in a three-dimensional periodic pattern that extends throughout the material. Because silica is the interest of this study, silicon wafers with a 0.9-μm-thick thermal oxide were used. The thermal oxide layer is also crystalline in nature with [1 0 0] orientation. The diameter of the silicon wafer used here was 100 mm, with a thickness of 525 μm.

The experiment relies mainly on measuring the curvature of the thin film system using profilometer. Based on the curvature measurement, the stress in the film can be calculated with the associated standard deviation. With the calculated stress, the interfacial fracture energy can be quantified accordingly. Deposition and photolithography were conducted. Residual stresses were measured from beam deflections using the mechanical surface profilometer. Then, film severing above the precrack is conducted. The films were inspected to assess the critical thickness, hcr, using SEM. Finally, the interfacial fracture energy was determined by the measurement of this critical thickness.

The fabrication of the specimen to be used for the superlayer test involves two major steps: (i) gold (Au) patterning on silica for creating precrack regions and (ii) SU-8 patterning with the preexistence of Au. The choice of SU-8 is particularly attractive due to its emerging importance as an adhesive that is usually used in various engineering fields including microelectromechanical systems, optics, and bioengineering. Careful substrate cleaning is essential. For this purpose, the silica substrate (silicon wafer with thermal oxide) was solvent cleaned in trichloroethylene, acetone, and isopropyl alcohol in order to remove organic contaminants. Then, the wafer was water cleaned, followed by etch cleaning in buffered hydrofluoric acid, in order to remove all inorganic contaminants. Finally, the wafer was rinsed in deionized water and dried by putting it on the 105 °C hot plate for 10 min. In order to achieve the Au pattern, a negative photoresist (AZ5214) was first coated onto the silicon wafer with thermal oxide using a spin coater with a speed of 3,000 rpm for 30 s. After that, the wafer was soft-baked with a mini oven for 105 °C hot plate for 3 min. Then, the wafer was exposed under ultraviolet (UV) light for 20 s using a hard contact approach with the transparency mask shown in Fig. S8. It should be mentioned that the hard contact approach involves a clean glass plate and a transparency mask placed on top of the wafer. Postexposure baking was conducted on a 105 °C hot plate for another 3 min, followed by flood exposure under UV light for another 1 min without the transparency mask, which is regarded as soft contact. Finally, the negative photoresist was developed in AZ422 for 1 min, followed by rinsing using deionized water. Au layer (thickness ~30 Å) was then deposited onto the negative photoresist patterned wafer by electron beam evaporation. The Au pattern was achieved by removing the AZ5214. The stripper for the AZ5214 used to “lift off” the Au was an n-methyl-2-pyrrolidone-based solution. The obtained Au pattern acts as the precrack region for the epoxy–silica bonded system.

After achieving the Au pattern, SU-8 was coated on Au strips using spin coater. SU-8 2015 was spin-coated onto the Au patterned wafer using a speed 3,000 rpm for 30 s. After that, the wafer was soft-baked on a 95 °C hot plate for 5 min. Then, the wafer was exposed under UV light for 45 s using a hard contact approach with the transparency mask shown in Fig. S8. It should be mentioned that the solid and hollow square symbols shown in Fig. 5 are for aligning purpose during the patterning process. Postexposure bake was conducted on a 95 °C hot plate for another 5 min. Finally, SU-8 was

Fig. 6. (A) Au pattern on Si wafer with a layer of thermal oxide (0.9 nm). (B) SU-8 was spin-coated on the wafer with a thickness of 20 μm. (C) Cr was deposited onto the SU-8 surface by the sputterer. The residual tensile stress in Cr leads to the crack initiation at the SU-8–SiO2 interface when the critical Cr thickness is achieved. This technique was originated by Bagchi et al. (17), and here we have successfully extended its applicability toward construction-related material systems.

Fig. 7. A plot of the total film stress with the normalized Cr layer thickness.
Residual stress measurements were performed on a batch of three samples with the same nominal SU-8 thickness (20 μm) and with three Cr thicknesses: 1 μm, 2 μm, and 3 μm. On each sample, five profilometer scans were made before and after depositing the film onto the substrate. A least square regression fitting to the data gave the measured radius of curvatures and their respective standard deviations. The film thickness was also obtained from the scans by making small scratches on the coated surface. The level difference measured by the profilometer indicated the film thickness accordingly. The stresses obtained in this manner are plotted in Fig. 7. A linear fit is obtained, consistent with stresses in each separate layer being independent of thin film thickness as shown in Eq. 2. This fit indicates that the residual stresses in the SU-8 and Cr layers are 17 MPa and 1,248 MPa, respectively, with standard deviations ~5%, and these values are within the range measured by others (17, 28). It is noted that similarities can be seen between Figs. 1, 7, and 8 and comparable figures in ref. 28. However, the approach reported therein is limited to interface systems containing a metal component (such as electronic applications) while the current approach is applicable to various applications of construction and composite materials.

The steady-state energy release rate, \( G_{ss} \), controls the interfacial debonding motivated by residual stresses in the deposited thin film layers when the interfacial flaw size, \( a_0 \), exceeds the film thickness. Moreover, since the film stress diminishes upon occurrence of the interfacial debonding, the energy release behavior is entirely elastic. For the thin film system as shown in Fig. 8, \( G_{ss} \) can be calculated by considering the strain energy far ahead and far behind the growing interfacial crack. It should be mentioned that the interfacial crack in the thin film-substrate system is propagating under the plain strain condition. If \( U_a \) and \( U_b \) denote the strain energies in the two volume elements having the width \( \Delta a \) as shown in Fig. 8, then

\[
G_{ss} = \frac{U_a - U_b}{\Delta a}
\]

For a bilayer, the strain energy far ahead of the crack tip is the sum of the elastic strain energy associated with each layer (SU-8 and Cr) and can be written as:

\[
U_a = \sum U_i^a = \left( \frac{\sigma_1^2 h_1}{E_1} + \frac{\sigma_2^2 h_2}{E_2} \right) \Delta a.
\]

At this stage, it is required to link up \( P_i \), \( P_b \), \( M_1 \), \( M_2 \), and \( \kappa \) to the residual tensile stresses \( \sigma_1 \) and \( \sigma_2 \) and the film thickness \( h_1 \) and \( h_2 \), which are the known parameters. This procedure involves five linear equations with five unknown parameters. The solution to these equations is not straightforward and requires numerical methods, such as the Newton-Raphson method. However, for simplicity, it is assumed that the solution is found through an iterative process, where the stresses are updated until convergence is achieved. The final solution gives the stress distribution as a function of crack length, which can be used to predict the crack propagation behavior.

\[
G_{ss} = \frac{U_a - U_b}{\Delta a} = \frac{1}{E \kappa \mu} \left( P - \frac{M_1}{h_1} - \frac{M_2}{h_2} \right) \Delta a.
\]
unknowns (i.e., \( P_i, P_j, M_i, M_j, \) and \( x \)). Two equations are obtained from the consideration of force and moment equilibrium. Another two equations are obtained from the consideration of geometry between the moments and the curvature. Finally, by considering the strain compatibility at the interface between \( \alpha \) (subscript \( i = 1 \)) and SU-8 (subscript \( i = 2 \)), one more equation can be obtained. Hence, an analytical solution for \( P_i, P_j, M_i, M_j, \) and \( x \) can be evaluated, and, eventually, the steady-state energy release rate can be solved accordingly.

**Molecular Modeling.** To complement the experimental work, interfacial debonding is simulated using an atomistic model. DGEBA is one of the major epoxy types and the main component found in SU-8. The adhesion between DGEBA and silica is the focus of this model. We use a consistent valence forcefield (CVFF) to describe the interactions of atoms, where the total potential energy of the system is composed of bonding, angular, dihedral, improper, and pair potential including a 12-6 Lennard-Jones potential and Coulombic interactions. We extended the CVFF parameter files (29) to describe the interactions of atoms within DGEBA and between DGEBA and silica, together with the CVFF water potential, a three-site model with internal geometry corresponding to the gas-phase experimental structure (30). Flexibility of water molecules is modeled through the use of harmonic bond stretching and angle bending potentials. Our simulation box includes a silica slab with its top surface corresponding to \( \gamma \)-quartz (001) surface in contact with DGEBA molecules as shown in Fig. 10, fully surrounded by water molecules in the wet scenario. Periodic boundary conditions are applied in all directions, and dimensions of the simulation box are large enough beyond the simulation cutoff to ensure that the interactions between mirror solutes are minimal. The system is equilibrated for 1 ns in an NPT (number/pressure/temperature) ensemble, i.e., constant number of particles, constant pressure (1 atm), and constant temperature (300 K), and energy and root-mean-square deviation calculations are performed to ensure that an equilibrium state is reached. The metadynamics simulations are then performed by LAMMPS and the PLUMED packages (31, 32). The external energy in a Gaussian distribution with a height 0.005 kcal/mol and width 0.35 Å is deposited into the system every 100 fs.

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