interfacial dielectric constant will probably be between that of Si and SiO\textsubscript{2}. The altered dielectric layers are not accounted for in our ellipsometric measurements, in which we assume that the oxide has only the dielectric constant of bulk SiO\textsubscript{2}. This is probably why ellipsometry has underestimated the width of the oxides in Fig. 3. The probe localization is obtained by constructing a wavepacket with a transverse momentum spread of more than a reciprocal lattice vector, and consequently all electronic momentum information is lost (as required by the uncertainty principle). Therefore these evanescent states responsible for tunnelling through the oxide and the states from the extended conduction band are treated on an equal footing, and cannot be separated in such a local measurement.

In the simplest model, the silicon wavefunctions decay exponentially into the oxide with a decay length for the evanescent states, $\lambda(E)$, determined by the energy difference between the interfacial state ($E$) and the conduction band edge of bulk SiO\text sub{2} ($E_c$), as $\lambda(E) = h/(E - E_c)$. The tunnelling current depends on the overlap of the evanescent states from either interface. A satisfactory tunnelling barrier is formed when the oxide thickness $t$ is $6\lambda$. This sets an absolute minimum thickness of $t_{\text{min}} = 0.7\text{ nm}$ for an ideal SiO\text sub{2} gate oxide. Interfacial roughness adds another $6\lambda$, to $t_{\text{min}}$. The main barrier to our thermally grown oxides was $6\lambda = 0.6\text{ nm}$ which puts a lower limit of 1.2 nm on the practical SiO\text sub{2} gate oxide thickness. The induced gap states also place severe constraints on the minimum allowed thickness for alternative dielectrics, many of which have large dielectric constants, but reduced bandgaps and hence longer decay lengths. Furthermore, there is the possibility of a reaction between the dielectric and the silicon substrate to form a silicon oxide interlayer. If the interlayer thickness exceeds 1.3 nm (and a typical native oxide is 2 nm thick), the gate capacitance is less than what could be obtained with a pure SiO\text sub{2} gate oxide.

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Correspondence and requests for materials should be addressed to D.A.M. (e-mail: davidm@bell-labs.com).

Molecular mechanistic origin of the toughness of natural adhesives, fibres and composites


* Department of Physics, † Department of Chemistry and Materials, and ‡ Department of Molecular, Cellular, and Developmental Biology, University of California at Santa Barbara, California 93106, USA
§ Department of Molecular Biology, Max-Planck-Institute for Biophysical Chemistry, 37070 Göttingen, Germany
 ¶ Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, USA

† These authors contributed equally to this work

Natural materials are renowned for their strength and toughness1–5. Spider dragline silk has a breakage energy per unit weight two orders of magnitude greater than high tensile steel6,7, and is representative of many other strong natural fibres8–11. The abalone shell, a composite of calcium carbonate plates sandwiched between organic material, is 3,000 times more fracture resistant than a single crystal of the pure mineral12. The organic component, comprising just a few per cent of the composite by weight, is thought to hold the key to nacre’s fracture toughness13,14. Ceramics laminated with organic material are more fracture resistant than non-laminated ceramics15,12, but synthetic materials made of interlocking ceramic tablets bound by a few weight per cent of ordinary adhesives do not have a toughness comparable to nacre15. We believe that the key to nacre’s fracture resistance resides in the polymer adhesive, and here we reveal the properties of this adhesive by using the atomic force microscope15 to stretch the organic molecules exposed on the surface of freshly cleaved nacre. The adhesive fibres elongate in a stepwise manner as folded domains or loops are pulled open. The elongation events occur for forces of a few hundred piconewtons, which are smaller than the forces of over a nanonewton required to break the polymer backbone in the threads. We suggest that this ‘modular’ elongation mechanism might prove to be quite general for conveying toughness to natural fibres and adhesives, and we predict that it might be found also in dragline silk.

We have looked for the mechanism behind the toughness of the organic adhesives and fibres, and, in particular from the nacre in abalone shells. Analysis of the insoluble organic matrix from the abalone shell revealed a fibrous core in the interlamellar sheets placed between successive nacre tablets, which probably serve as an adhesive holding the tablets together. The organic adhesive is readily apparent when the tablets are pulled apart (Fig. 1). At least one protein, lustrin A, has been isolated from this insoluble organic matrix. The complementary DNA and translated protein sequence reveal that the structure of this protein consists of about 10 alternating and highly conserved cysteine-rich and proline-rich domains, demonstrating that the structure is highly modular16. Immuno-histochemical analysis of the fibres (Fig. 1) revealed lustrin A to be a component of the adhesive between the nacre mineral tablets. Rief et al.17,18 demonstrated that the modular structure of a single molecule can be examined by attaching the molecule between a flat surface and a cantilever of an atomic force microscope (AFM). By pulling on the protein titin and plotting the force versus extension curves, these authors measured the force required to break open the individual subunit in its modular structure. As the titin

18,19 demonstrated that the modular structure of a single molecule can be examined by attaching the molecule between a flat surface and a cantilever of an atomic force microscope (AFM). By pulling on the protein titin and plotting the force versus extension curves, these authors measured the force required to break open the individual subunit in its modular structure. As the titin
molecule was stretched, the force-extension curve revealed a sawtooth pattern. Using titin constructs, Rief et al. demonstrated that every peak in the sawtooth pattern corresponded to a single domain unfolding. Apparently, it is the cumulative effect of the intermediate-strength hydrophobic bonds in the immunoglobulin-like domains of titin which contribute to the sawtooth force-distance curves found for this molecule. Stiffness studies using optical tweezers corroborated these results. The approach and retract curves show hysteresis, indicating that the rupture events dissipate energy.

We have used this technique to investigate the molecules that hold abalone shells together. Figure 2 shows force-extension curves for the organic material exposed on a freshly cleaved nacre surface. The hysteresis observed after a complete pulling cycle demonstrates that work has been done on the shell. This work is irreversibly dissipated as heat, and the area between the retracting and the approaching parts of the curve quantifies this heat. In this case, the dissipated heat is of the order of $10^{-17}$ J per cycle (Fig. 2). The sawtooth-like force-extension curves, and the observation that we could repeatedly unfold molecule(s) without touching the surface between pulls, suggest that bonds of some kind are breaking and reforming. As lustrin A is present on that surface, it is possible that we observed unfolding of this protein. However, and this is the key point, the mechanism behind the strength and toughness of the adhesive is revealed by the force-extension curves and does not depend on the identification of the specific molecules involved. This behaviour may reflect the successive opening of intra-chain loops or folded domains within a single molecule, or the successive release of sacrificial inter-chain bonds holding a crosslinked multichain matrix together.

To demonstrate the effect that a material with this type of force-extension curve can have on the properties of an adhesive made from modular fibres, we consider three different cases. Gluing materials together with conventional adhesives has traditionally involved either relatively stiff adhesives such as epoxies, or elastic adhesives such as silicon adhesives. When pulling on two surfaces glued together with a short molecule, the pulling force increases rapidly with only a little extension of the molecule (Fig. 3). First, a perfect stiff adhesive would be a short molecule bound to each surface by strong (that is, covalent or ionic) bonds and the molecules of the adhesive itself would be held together with strong bonds. Thus the break strength of each adhesive molecule would be the force required to break a strong bond: of the order of one nanonewton (estimated by dividing one electron volt by an extension of one ångström). For a material with many strongly bound molecules in parallel, the macroscopic tensile strength is expected to be of the order of several gigapascals. This is the order of magnitude for the breaking force of strong polymers such as Kevlar. The fracture toughness of such materials is rather small, however, even though the forces are large. This can be understood by considering the area under the force-extension curve (Fig. 3), which is the energy required to break the material. Because those stiff materials have a small elastic strain, the extension over which the force must be exerted until it breaks is small. Therefore the area under the curve, or the energy required to break the material, is small (Fig. 3).

Second, in contrast to this behaviour, the idealized curve for an elastic fibre made of long molecules shows that the force increases...
slowly as the elastic material is stretched to the point at which the elastic limit is reached (Fig. 3)²⁷,²⁸. Then the force increases rapidly for further extension until it breaks. This break will again occur at a force of the order of one nanonewton per molecular chain, assuming each chain is bound to each surface with a strong bond and is itself held together by strong bonds. Contrary to the case of short, inelastic molecules, the pulling force must be applied over much larger extensions. Therefore, the area under the force-extension curve would be larger (Fig. 3), and thus more energy would be needed to break the material. Unfortunately, the technology does not at present exist for making such an idealized elastic material. Real elastic materials such as rubbers have tensile strengths that correspond to breaking forces per molecule of the order of 0.1% of the theoretical maximum. But even if ideal elastic materials could be produced, there would still be a significant advantage to incorporating nature’s mechanism of tying up most of the molecule’s length with intermediate-strength sacrificial bonds.

Third, an adhesive or fibre that combines the best of both worlds would display a force-extension curve that rises to a large force quickly, but then maintains that force over large extensions. It would consist of long molecules with many domains that are either folded or looped, with intermediate-strength bonds (of the order of 0.1–0.7 nN) compacting the molecule. These intermediate-strength bonds are stronger than individual hydrogen bonds or van der Waals bonds, but weaker than covalent bonds. Alternatively, these may represent the cumulative effect of multiple weak bonds (either intra- or interchain) acting in concert. For such a molecule, the force rises quickly with extension (Fig. 3). But then, when the force rises to a significant fraction of the force required to break a strong bond and threatens to break the backbone of the molecule, a domain unfolds or a loop is opened, therefore avoiding the breaking of a strong bond in the backbone.

On further pulling, the force then again rises to a significant fraction of the force required to break a strong bond, but again, before a strong bond is broken, another domain unfolds. The process continues until all domains are unfolded (or loops are opened) and finally a strong bond breaks. The net result is to sustain

a large force over the pulling extension, making it ‘strong’, while producing a relatively large area under the force-extension curve, making it ‘tough’ as well.

An approximate analogy to this process is found in Greek mythology: Sisyphus was condemned by Zeus to push a heavy rock up a mountain only to have it slip out of his hands and roll back to the bottom just before he reached the summit. In such a fall, the rock would dissipate its potential energy into heat, and Sisyphus had to start all over again. The case of extending a modular fibre is analogous. One needs to pull hard, and do work, but before the breaking point (the ‘summit’) is reached, a domain unfolds or a loop opens, and the energy stored in the fibre is dissipated as heat. Then, the fibre has to be pulled on again, until the next domain breaks and so on, until no folded domains are left and the fibre at least breaks. (We note that if the force is relaxed before the fibre breaks, the domains or loops can reform as shown in Fig. 2.)

In natural materials, proteins provide the modular fibre: but this mechanism should work for other polymers, as long as it is possible to compact the length of the polymers using intermediate-strength bonds that break sacrificially with forces comparable to, but less than, the force of a nanonewton or so that breaks strong bonds in the polymer backbone.

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Correspondence and requests for materials should be addressed to B.L.S. (e-mail: bettye@physics.ucsb.edu).