

(A292S) usually decreases $\lambda_{\max}$ by 10 nm. That substitution was acquired by one of the conger eel opsins from its immediate ancestor. Making the reverse substitution (S292A) in the conger eel opsin increased $\lambda_{\max}$ by 10 nm, as you'd expect.

Here's the surprise. When A292S was applied to the immediate ancestor, it had no effect on $\lambda_{\max}$! Evidently, two other substitutions found by the Emory team were responsible for the decrease, not A292S. Other cases occurred in which quite different substitutions could shift $\lambda_{\max}$ by more or less the same amount.

Opsins are important not only for vision; they are also candidates for light-switched, high-density data storage. When physicists and chemists calculate $\lambda_{\max}$, they typically focus on amino acids that lie within 4.5 Å of retinal. However, the substitutions that blueshifted the conger opsin's $\lambda_{\max}$ occurred at sites 20 Å away from retinal. Moreover, as figure 2 shows, some sites that shifted $\lambda_{\max}$ don't even belong to opsin's functional core.

A bigger surprise occurred when Yokoyama ran the opsins' genetic sequences through programs designed to identify naturally selected mutations. Three DNA bases suffice to encode a particular amino acid, but the coding has redundancies. For example, GCT, GCC,

GCA, and GCG all encode alanine. Changing the third base in any of those four codons would still yield alanine.

Changing the first base from guanine (G) to cytosine (C) would yield a different amino acid, proline. Usually, such "nonsynonymous" substitutions impair a protein's ability to fold or function. They aren't passed on to the next generation.

But some nonsynonymous substitutions turn out to be beneficial. As DNA mutates randomly from generation to generation and from species to species, more synonymous substitutions than nonsynonymous substitutions accumulate. Any nonsynonymous substitutions that get passed on are likely to be evolutionarily significant.

Statistical algorithms implement those expectations. They digest a family tree of genetic sequences and, by comparing rates of synonymous and nonsynonymous mutations, identify putative mutations that constitute evolutionary adaptations.

Yokoyama had determined which mutations really do change $\lambda_{\max}$. Could the statistical methods find them too? The answer turned out to be no. Why that should be the case isn't clear. Ziheng Yang of University College London has developed some of the statistical methods used by evolutionary

biologists. Those methods, he points out, may lack the sensitivity to detect adaptive mutations that become fixed within a short period of time, as may be the case in vertebrate opsins.

Gavin Naylor of Florida State University in Tallahassee points out another possible limitation: Statistical methods don't take into account the many-body nature of proteins. "Shozo shows quite compellingly that just because you change one site doesn't mean you're going to get a functional change," he says. "It depends, rather, on the context of the other amino acids."

Showing conclusively how the survival of the fittest plays out on the molecular level would require reconstructing not only the protein but also the whole organism. And you'd have to observe the organism and its descendants in their original, long-lost habitats.

Still, the Emory researchers did find a piece of reassuring evidence: The opsin of the vertebrates' piscine ancestor tuned retinal to absorb at 501 nm. That $\lambda_{\max}$ is consistent with the shallow-water habitat of its fossilized remains.

Charles Day

Reference

1. S. Yokoyama, T. Tada, H. Zhang, L. Britt, *Proc. Natl. Acad. Sci. USA* **105**, 13480 (2008).

Experiment probes pattern formation during debonding of viscoelastic adhesives

In at least one respect, adhesives always behave as either viscous liquids or elastic solids, and the boundary between the two regimes is sharp.

Poke your finger into a jar of honey, and you feel a drag force that depends on how fast you're moving your finger. Remove it, and some honey clings to your finger and stretches into a long fibril that eventually breaks. Those properties are characteristic of a viscous liquid. When you push against a piece of soft rubber, on the other hand, the force you feel is proportional not to speed but to displacement, and when you pull away, the rubber remains in one piece; such are the properties of an elastic solid. Typical commercial adhesives have both viscous and elastic properties—that is, they are viscoelastic.

When a film of viscous, elastic, or viscoelastic material is sandwiched between two smooth, rigid surfaces that are then pulled apart, patterns form that include "fingers" of air penetrating the gap between the surfaces. Fingering patterns in the viscous and elastic cases have both been studied before. But pat-

tern formation in the viscoelastic regime, which is most relevant to adhesive failure and thus to adhesive performance, has remained unexplored. Now, Julia Nase, Anke Lindner, and Costantino Creton of the École Supérieure de Physique et de Chimie Industrielles in Paris have taken a first look at fingering patterns in adhesive materials with a range of properties, spanning the continuum between viscous liquid and elastic solid.¹

The researchers' first task was to find a good model material whose viscous and elastic properties they could tune reproducibly. They settled on a commercially available kit consisting of a polymer fluid and a curing agent that forms cross-links among the polymers. Typically, the fluid and curing agent are mixed in a 10:1 ratio to form a clear elastic solid that can be used for microfluidics devices. But the researchers found that smaller amounts of curing agent

produced materials with the desired range of viscoelastic properties. A mixture with 2–3% curing agent forms a softer solid, similar to the protective film that comes on a new computer monitor. A mixture with 1% curing agent forms a material at its gel point: the minimum density of cross-links needed to connect all the polymers in an infinite network. That material feels sticky to the touch and forms visible fibrils, like the adhesive on a piece of packing tape. (For more on polymers, viscoelasticity, and stickiness, see the PHYSICS TODAY articles by Tom McLeish, August 2008, page 40, and by Cyprien Gay and Ludwik Leibler, November 1999, page 48.)

To study the fingering patterns, the researchers coated a glass slide with a layer of the polymer adhesive between 50 μm and 500 μm thick. They brought a 6-mm-diameter steel probe in contact with the material from below and

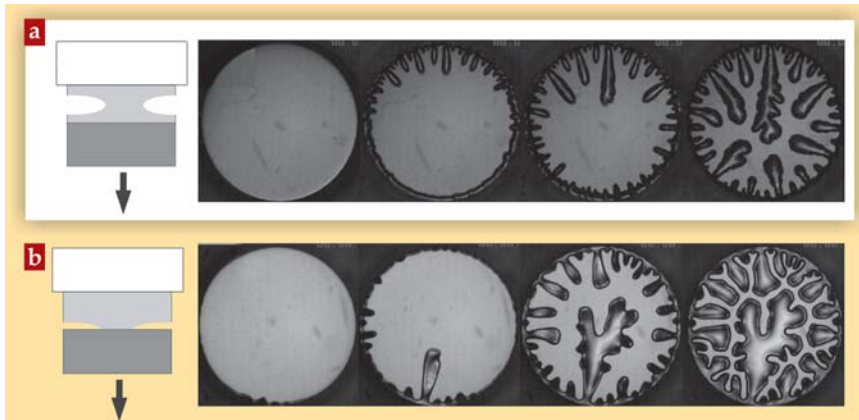


Figure 1. Two debonding mechanisms of viscoelastic adhesives. The panels on the left are schematic representations of the side view: White represents the glass slide; light gray, the adhesive layer; and dark gray, the steel probe that is brought in contact with the adhesive and pulled away. The panels on the right show top-view time-sequence shots of each mechanism. **(a)** An adhesive behaving as a viscous liquid stretches and deforms as air penetrates its bulk. **(b)** When the adhesive behaves as an elastic solid, air enters the cracks that form between the adhesive and the probe. (Adapted from ref. 1.)

pulled it away, while watching the air fingers using a camera mounted above the slide. In particular, they looked at the initial fingering wavelength, the distance from one finger to the next at the moment the fingers started to form.

In the case of a viscous liquid layer, the fingers penetrate the bulk of the material, as shown in figure 1a, and the wavelength is known to depend on the thickness of the layer, the speed of the probe, and the material properties of the liquid. That result is described by the so-called Saffman–Taylor instability, which occurs when a less viscous fluid (air, in this case) enters a more viscous fluid in a confined geometry. For

an elastic solid layer, the fingers enter at the interface between the layer and one of the surfaces, as shown in figure 1b, and the wavelength depends only on the layer’s thickness.

The researchers found that for every amount of curing agent, the initial wavelength they observed was described by either the viscous model or the elastic model. Example data are shown in figure 2. (As the debonding progressed, though, the sizes and shapes of the fingers deviated from either of the two models.) The sharp transition between viscous and elastic behavior occurred at around 1.5% curing agent—meaning that even some

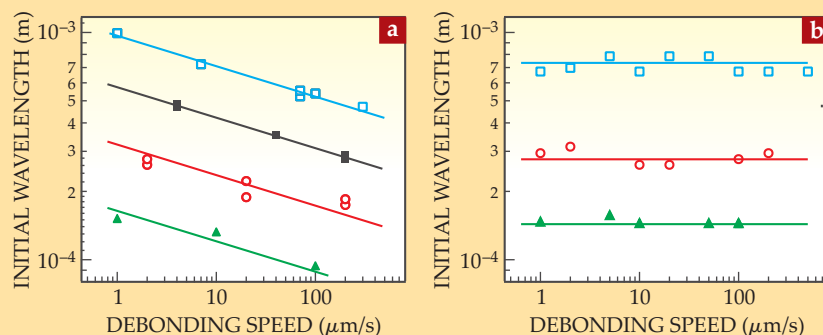


Figure 2. Initial fingering wavelength as a function of debonding speed for films of two viscoelastic materials. Each of the colors represents a different film thickness, increasing from bottom to top. **(a)** Material with 1.2% curing agent exhibits viscous-liquid behavior: The wavelength decreases with increasing debonding speed. **(b)** Material with 2.0% curing agent behaves as an elastic solid: The wavelength is independent of the debonding speed. (Adapted from ref. 1.)

materials with cross-link densities well above the gel point behaved like viscous liquids. That seemingly strange result occurs because the debonding behavior depends not only on the properties of the adhesive layer but also on how well the probe sticks to the adhesive. If the energy needed to deform the adhesive material is less than the energy needed to create a crack between the adhesive and the probe, then the debonding will follow the bulk-deformation mechanism of viscous liquids. Otherwise, it will follow the

interfacial mechanism of elastic solids.

To test that explanation, the researchers ran a new experiment on material with 2% curing agent. But instead of a steel probe, they used a glass probe that had been treated with plasma. The plasma opens up sites for chemical bonds that enhance the adhesion between the probe and the polymer material. Sure enough, the material that displayed the elastic mechanism when the steel probe was used followed the viscous mechanism in the new experiment with the treated glass probe.

There's a lot left to understand about pattern formation in the viscoelastic regime. In particular, the shapes of the fingers and their behavior in the later stages of debonding remain unexplained. Says Lindner, "We would be happy if our results stimulate theoretical investigations and help answer these questions."

Johanna Miller

Reference

1. J. Nase, A. Lindner, C. Creton, *Phys. Rev. Lett.* **101**, 074503 (2008).

physics update

These items, with supplementary material, first appeared at <http://www.physicstoday.org>

Frequency combs help untangle astrophysical spectra. By resolving light into its component frequencies, spectrographs can reveal, for example, the Doppler shift in light that travels to Earth from other solar systems with orbiting exoplanets or from the far reaches of the universe. But before it can be put to work, a spectrograph must be calibrated, and that process inevitably introduces measurement uncertainty. To reduce those uncertainties, Tilo Steinmetz and colleagues developed a calibration procedure that can dramatically improve spectroscopic precision, and they demonstrated their technique by obtaining the most accurate spectrum of the Sun's photosphere to date. The key ingredient is a laser frequency comb, a series of equally spaced, precisely known frequency spikes that, as the white stripes in the figure show, can serve as a template with which astrophysical spectra can be compared (see *PHYSICS TODAY*, June 2000, page 19, and December 2005, page 19). Because the comb is reproducible, the calibration can be replicated from run to run. Moreover, frequency combs may help isolate systematic spectrograph uncertainties that, one hopes, can be

understood and minimized. A plausible goal, according to Steinmetz and company, is to measure redshifts of objects whose speed along the line of sight is changing by 1 cm/s over a year's time. That would allow for a direct measurement of cosmic acceleration. Closer to home, higher-precision spectroscopy would enable astrophysicists to identify Earth-like exoplanets by measuring the characteristic Doppler shifts experienced by a star as it is gravitationally tugged by an orbiting planet. (T. Steinmetz et al., *Science* **321**, 1335, 2008.) —SKB

New limits on prehistoric oxygen levels. The evolution of life on Earth is closely intertwined with the evolution of Earth's physical environment, particularly the concentration of atmospheric O₂. The oxygen increase arising from the development of photosynthesis in the Precambrian is thought to have created an "oxygen catastrophe" that challenged the dominant anaerobic organisms but spawned increased biodiversity and set off the Cambrian explosion in the fossil record. And low oxygen availability has been associated with two large-scale extinctions in the past 550 million years. One record of atmospheric oxygen levels is evidence—such as charcoal or polycyclic aromatic hydrocarbons—for prehistoric wildfires in the geological record. Such wildfires would have required a minimum O₂ concentration for combustion, and new work by Claire Belcher and Jennifer McElwain at Ireland's University College Dublin has refined what that minimum concentration is. Unlike prior investigations of combustion limits, the researchers simulated realistic atmospheric conditions and used natural samples of pine and moss. The team found that the threshold O₂ concentration for combustion is 15%. Several models infer O₂ levels from paleogeochemical records for carbonates, sulfates, and other materials. But some of those models may now need to be reevaluated, since they predict prolonged periods with oxygen concentrations below the 15% threshold at times in the Mesozoic Era for which there is fossil evidence for wildfires. (C. M. Belcher, J. C. McElwain, *Science* **321**, 1197, 2008.) —RJF

Holography in quantitative biology. In recent years, scientists have learned to make light-sensitive molecular probes and incorporate them into biological tissue. When stimulated by the correct wavelength, the probes then make available for study targeted dynamic processes of living systems. In a typical experiment, static optical elements such as lenses are used to focus light on a region of tissue, where all photoactivity—wanted or unwanted—is then observed. A new, active element for optical imaging is the liquid-crystal spatial light modulator, used to tailor light's distribution in such applications as optical tweezers and adaptive optics. Valentina Emiliani of the University of Paris

