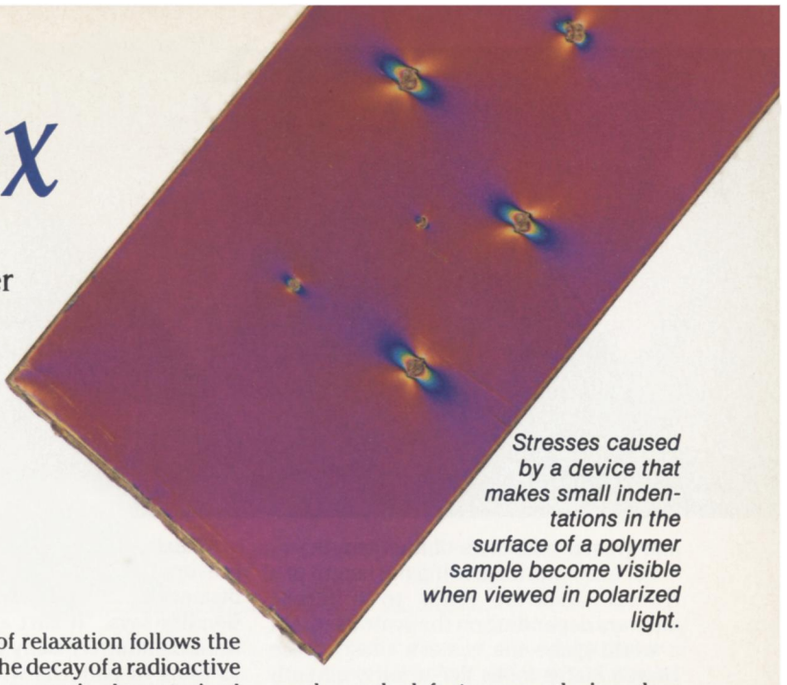
Time to Relax

The concept of fractal time ties together the stretchiness of silk and the brittleness of polymers



Stresses caused by a device that makes small indentations in the surface of a polymer sample become visible when viewed in polarized light.

By IVARS PETERSON

The rubber in a pair of boots, retrieved after a long sojourn in an attic, shows its age in an annoying way. No longer as flexible as it once was, the material — an elastomeric polymer — readily cracks and falls apart. Under the same conditions, many other plastics suffer a similar fate.

One cause is chemical. Sunlight or oxygen can initiate chemical reactions that alter the material's properties. But deterioration occurs even when a material is kept in the dark or away from oxygen. The material gradually becomes denser and more brittle, losing its toughness and impact resistance.

The explanation lies in the way "defects" within amorphous, or noncrystalline, materials reorganize themselves over long periods of time. When expressed in terms of a relatively new concept known as fractal time, the same mathematical model used to describe polymer aging also applies to the stretching of glass or silk fibers, the recovery of glassy materials after a stress has been removed and a wide range of other phenomena in amorphous materials.

"It's an issue of practical importance," says John T. Bendler of the General Electric Research and Development Center in Schenectady, N.Y. Slow aging processes, both environmental and physical, control the lifetimes of a great variety of manufactured products, from electronic devices to optical fibers and advanced composite materials. The new theory of how such processes occur suggests novel techniques for toughening ceramics and for designing polymers having particular characteristics.

Pull on a glass fiber, then let go. The glass first stretches, then shrinks. Apply a strong electric field to a polymer, then turn it off. Areas of positive and negative charge in the polymer line up with the field, then drift out of alignment. In each case, the material endures a stress, then recovers or "relaxes" when the stress is removed.

Relaxation in a crystalline material typically proceeds at an exponential pace. That type of relaxation follows the same pattern as the decay of a radioactive isotope. Such a process is characterized by a certain time, known in the case of radioactive decay as the half-life.

In contrast, physicists have discovered that an amorphous solid takes longer to relax than would be expected if the relaxation simply followed an exponential decay. No characteristic time can be defined for such an extended relaxation process.

"Normally, one finds that relaxation is clustered around a certain time," Bendler says. "It takes either a second, a day or a week. What we see in amorphous systems is that some parts relax very quickly, say, in seconds. But other pieces relax on a time scale of minutes, still others at days or weeks. If we wait long enough — even years — we still see things happening. There is no definable time scale."

This type of behavior goes by the name of "stretched exponential relaxation." It fits a wide range of relaxation processes in disordered systems, including the way many polymers, glasses and ceramics respond to stresses caused by changes in pressure and temperature, and the imposition of electric and magnetic fields.

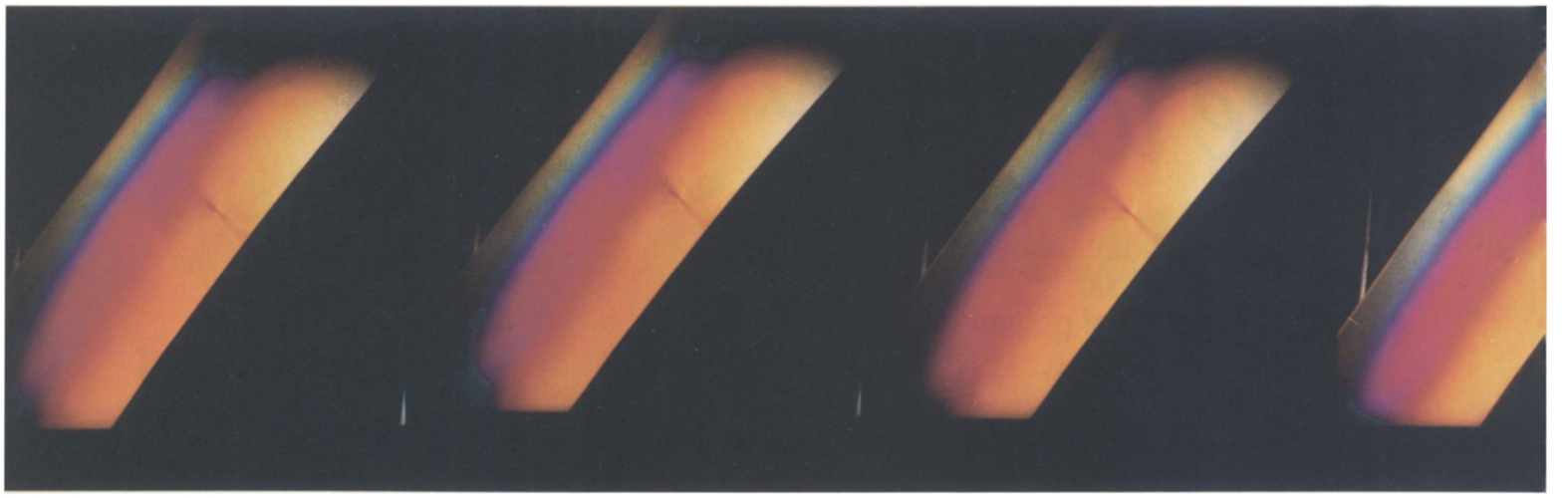
Because so many different systems behave in such a strikingly similar fashion, physicists, in their search for an explanation, have concentrated on what these systems share. They find what's important is not the details of a material's atomic and molecular structure but rather its state of disorder.

An amorphous material's constituent atoms or molecules lie in random positions rather than at well-defined sites, as happens in an orderly crystal lattice. Moreover, just as crystal structures are rarely perfect and contain dislocations and imperfections, amorphous materials also contain "defects," in which bonds between atoms or molecules may be strained, distorted or displaced. For example, such defects occur during glass formation because molecules find they have too little time during cooling to orient themselves into their proper positions to form a closely packed crystal structure. Inevitably, glasses end up containing "vacancies," or low-density regions.

In 1984, Michael F. Shlesinger of the Office of Naval Research in Arlington, Va., and Elliott W. Montroll of the University of Maryland in College Park proposed that migration, or diffusion, of mobile defects could account for stretched exponential relaxation in the case of an amorphous material relaxing after the application of an electric field. They suggested that defects, in order to move, must overcome different energy barriers scattered throughout the material. Whereas small barriers are easy to hurdle, larger ones significantly reduce mobility. Consequently, relaxation, which occurs through the movement of defects, stretches out over a long period of time.

"In the early stages of relaxation, those defects that are near low barriers don't have any trouble," Bendler says. "There's enough thermal energy, so they can jump and cause relaxation. Others, faced with moderate barriers, are not so well off. It takes them longer to get moving." Thus, a random distribution of energy barriers implies a wide range of relaxation times, leading to the stretched exponential relaxation observed for amorphous materials.

Mathematically, the situation relates closely to the problem of determining the length of a fractal, a geometric object in which the same pattern is repeated on ever smaller scales. Magnifying a fractal by any amount reveals a miniature version of the larger form. Finer and finer scales show more and more detail and lead to greater



and greater estimates of total length.

For example, measuring the length of a fractal coastline leads to different answers depending on the scale used. On a world globe the eastern coast of the United States looks like a fairly smooth line roughly 3,000 miles long. The same coast drawn on an atlas page showing only the United States looks much more ragged. Adding in the lengths of capes and bays extends the coast's length to 5,000 or so miles. Piecing together detailed navigational charts to create a giant coastal map reveals an incredibly complex curve perhaps 12,000 miles long. Each change in scale reveals a new array of features to include in the measurement.

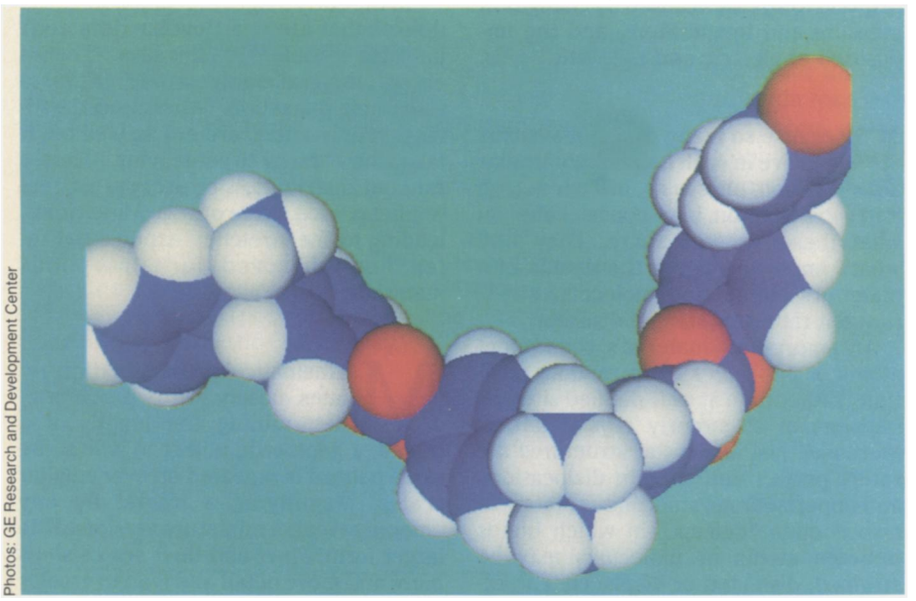
Similarly, relaxation processes in amorphous materials have no characteristic time scale. They occur on all time scales, an idea embodied in the concept of fractal time. Each shift in time scale — from seconds to minutes to days to years — adds new features to include in a relaxation measurement.

"What we have in amorphous materials is every time scale, just as we have every distance scale in the coastline problem," Bendler says. "It isn't as picturesque to think of infinitely many time scales as it is to think of patterns within patterns on different length scales, but the analogy is exact."

To support this theoretical picture, researchers have discovered that in polymer relaxation, some phenomena occur within picoseconds while other effects aren't apparent for years. "It's an astonishing array of time scales," Bendler says. "That makes it tricky experimentally because it's hard to measure things over so many orders of magnitude in time."

Shlesinger and Bendler have now applied the theory to key aspects of glass formation and to various types of relaxation phenomena in polymers. "One is now able to go from microscopic motions to macroscopic behavior," Shlesinger says. "And the theory can provide ideas on ways to modify in a useful manner the properties of industrially important polymeric materials."

This model of a polycarbonate molecule shows the key linkages (red) responsible for stress relaxation and creep. Fractal-time motion of the high-energy form of these "kinks" along the molecular chain results in stretched exponential relaxation.



Photos: GE Research and Development Center

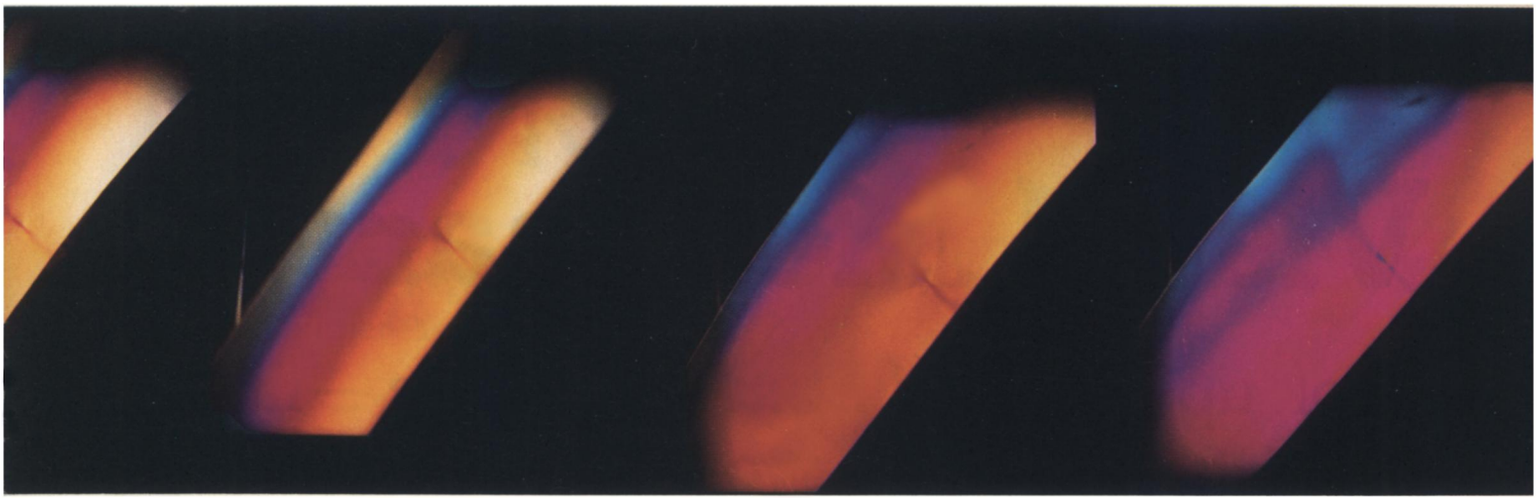
Bendler and his colleagues used the theory to explain the properties of Lexan, a tough polycarbonate resin used for making bulletproof windows for limousines. Defect diffusion turns out as a good model for how the material responds to stresses and how it ages.

A chunk of Lexan consists of an irregular, three-dimensional network of long polymer molecules, each a twisted chain thousands of atoms long, with a precisely defined, repeating pattern of atoms. Experiments indicate that cooling the polycarbonate freezes in a small population of high-energy "kinks" in the molecular chains. The kinks occur within segments where a ring of carbon and hydrogen atoms called a phenylene group meets a combination of carbon and oxygen atoms called a carbonate.

It's the movement of these kinks in a fractal-time process along the polycarbonate chains that leads to relaxation. They reorganize the molecular backbone and effectively absorb mechanical energy, such as the impact of a bullet or a sledgehammer. They are also responsible for aging. As energy-absorbing kinks reach chain ends, the material gradually becomes more brittle and weaker. With that insight, researchers now believe they might possibly slow aging by modifying chain ends.

The fractal-time, or defect-diffusion, model also helps explain the stretching of silk and glass threads. In 1835, German physicist Wilhelm E. Weber noticed that attaching a weight to a long thread causes it to stretch to a certain length immediately. But that instantaneous elongation is unexpectedly followed by a gradual further lengthening that depends on how long the weight is applied.

The reason for such behavior lies in the fractal-time movement of defects within the materials. Silk is a complicated natural polymer, occurring in a variety of



This sequence of photographs shows how the stress pattern in a sample of stretched polyvinylbutyrate changes as the material relaxes over a period of roughly 5 minutes.

different amorphous and crystalline forms. Under an applied load, the material tries to rearrange itself to redistribute and minimize stresses. Under those conditions, silk molecules relax by unwinding and changing the hydrogen bonding along their backbones. In a glass fiber, the mobile defects correspond to imperfections in the distorted, tetrahedral network of oxygen and silicon atoms.

"It's these mobile units of structure that cause something to happen under a load," Bendler says. "The material isn't just sitting there. There's a mechanical reorganization."

Although ceramicists, engineers and artisans have long recognized the peculiar behavior of glasses, polymers and ceramics and have taken these properties into account when working with the materials, until recently researchers made little progress in understanding relaxation phenomena because the mathematics used to describe such processes seemed so complicated and difficult, Bendler says. Now, the new concepts of mobile defects and fractal-time motion appear to provide a self-consistent picture of viscoelastic and thermodynamic behavior in supercooled liquids and glassy solids.

"One of the chief merits of the theory is that it's so simple mathematically," Bendler says. "We're able to use defect-diffusion mathematics – the mathematics of intermittent pausing – to model the kind of behavior displayed by almost all amorphous materials. It gives us a nice, satisfying picture." □

News of the week continued from p. 151

Earliest evidence for plate tectonics

Earth scientists are still trying to piece together the plate-tectonics puzzle. What exactly pushes the vast fragments of the Earth's outer shell around the surface, and when did the crustal plates first break up and start sliding around, warping, tearing and burying each other as they collide?

The Earth's surface provides solid evidence that the crustal plates have been moving for 600 million years. Less direct evidence supports plate tectonics back to 1.9 billion years ago. Now, four researchers say they have found the earliest geologic evidence yet for plate tectonics – in a formation in India where two plates apparently crashed together 2.5 billion years ago, when the Earth was less than half its present age.

These data challenge previous models in which some scientists envisioned the Earth's crust as lacking plate tectonics until fairly recent geological time. "Our findings show that plate tectonic processes in the very early Earth were much like those of the last 600 million years," says Eirik J. Krogstad of the State University of New York, Stony Brook.

Krogstad and co-worker Gilbert N. Hanson, along with S. Balakrishnan and V. Rajamani of Jawaharlal Nehru University and D. K. Mukhopadhyay of Roorkee University, both in India, describe the new findings in the March 10 SCIENCE. They gathered their evidence for early tectonics from a narrow, north-south-trending strip called the Kolar schist belt, where rocks of various ages and origins lie juxtaposed. Krogstad says two pieces of continental crust crunched together from the east and west, squeezing up a band of seafloor between them. This former seafloor, or oceanic crust, makes up the belt, and differs in composition and density from the surrounding two continental crusts.

The continental crust on the west side contains much older rocks than the east side. By measuring how much uranium has decayed to lead and comparing other radioactive-isotope ratios, the researchers estimate the oldest material on the west side at about 3.2 billion years old. Krogstad calls the estimated 2.5-billion-year-old rocks on the east side "juvenile." He thinks the age difference indicates these two continents formed in different places and times before colliding.

According to Krogstad, when the two plates moved together they consumed most of the seafloor separating them, leaving just the narrow belt. Lying side by side in the belt are slivers of fairly ordinary ocean crust and of ancient oceanic crust. Moreover, slivers on the east side of the belt of ocean crust contain more light rare-earth elements than those on the west. Because the levels of these elements are thought to vary from place to place within the mantle, the researchers reason that these oceanic crustal slivers with different ingredients had different sources in the mantle. They conclude that the oceanic crust here formed in different times and places, and crunched together as solid plates.

The researchers were able to estimate the time of the cataclysmic event because the collision introduced into the rock new radioactive material that started decaying at that time – approximately 2.5 billion years ago. In addition to radioactive elements, the tectonic crunch allowed gold to filter up, making the Kolar belt more than just a gold mine of knowledge. According to Krogstad, it's also the world's richest gold mine. His team plans to spend more time exploring the area, hoping to turn up more evidence of early tectonics. And perhaps, he says, they'll stumble across more gold. – *F. Flam*