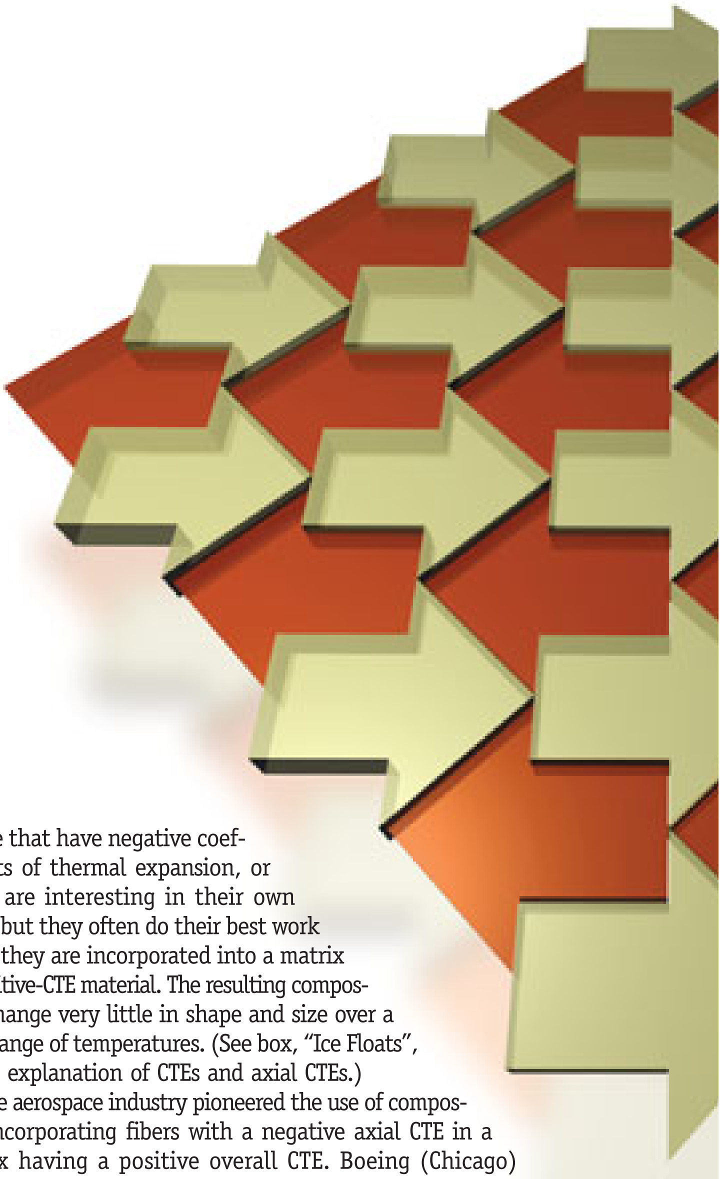
COMPOSITES



Negative-coefficient materials can point the way to positive value in the right matrixes.

Sometimes negativity is merely a disguise for nonconformity. Materials that follow the crowd expand when they get warmer, get thinner when they are stretched, and push back under pressure. If a material goes against the norm, it gets labeled a "negative-coefficient" material. That's not a value judgment, it's a mathematical convention. One way to describe a material is to list a set of mathematical coefficients that quantify how much a material "does this" when you "do that". The more a material responds to applied energy or force, the larger the corresponding coefficient. To keep the math simple, these coefficients are positive numbers for materials that behave like most other materials. However, in the field of materials design, thinking negatively can produce some very positive results.

Staying in Shape

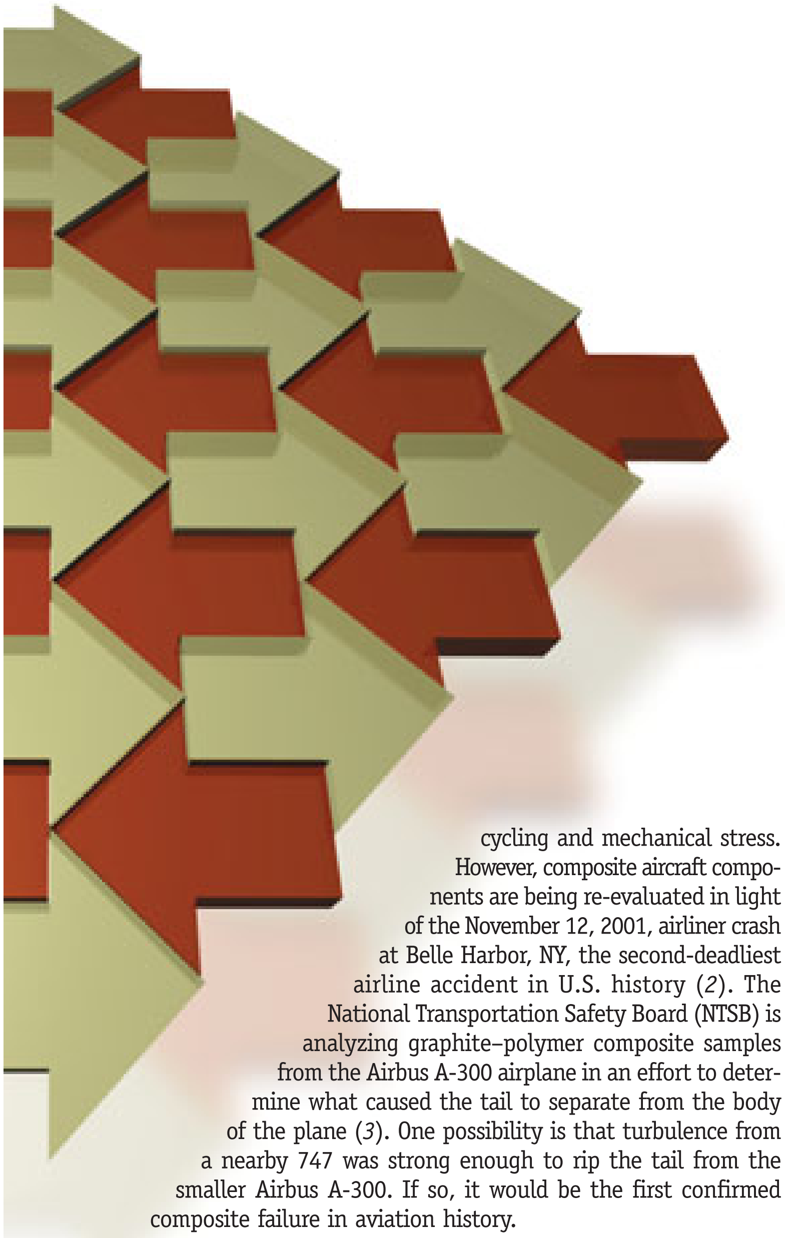
One area where negativity pays is in the quest for zero. Some applications demand materials that maintain their shape, size, and electrical properties in various environments. That is, the coefficients of expansion, conductivity, and so forth should be as close to zero as possible. Ideally, mixing fibers, particles, or layers of one material into a continuous phase, or matrix, of another material causes the properties to average out. Adding low-positive inclusions to a high-positive matrix is a step in the right direction, but it takes the counteractive effect of negative-coefficient materials to really hold things steady.

Materials that shrink when heated and expand when cooled (those that have negative coefficients of thermal expansion, or CTEs) are interesting in their own right, but they often do their best work when they are incorporated into a matrix of positive-CTE material. The resulting composites change very little in shape and size over a wide range of temperatures. (See box, "Ice Floats", for an explanation of CTEs and axial CTEs.)

The aerospace industry pioneered the use of composites incorporating fibers with a negative axial CTE in a matrix having a positive overall CTE. Boeing (Chicago) uses a lightweight carbon fiber–cyanate ester composite to make unibody casings for satellites (*1*). These composites form compact, lightweight casings that can maintain their shape and size from the red heat of the launch to the frigid vacuum of outer space, protecting the densely packed electronic circuitry inside. The molded unibody construction requires fewer fasteners and seams, reducing production costs and presenting fewer places to break apart. The fibers also interrupt vibrations and cracks as they travel through the matrix, providing a damping effect and strengthening the composite.

Over the past 20 years, composites containing carbon fibers, including the graphite–polymer composites, have become commonplace in airplane tail sections, vertical stabilizers, engine cowlings, and other external surfaces that must withstand thermal

# of OPPOSITES



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cycling and mechanical stress. However, composite aircraft components are being re-evaluated in light of the November 12, 2001, airliner crash at Belle Harbor, NY, the second-deadliest airline accident in U.S. history (*2*). The National Transportation Safety Board (NTSB) is analyzing graphite–polymer composite samples from the Airbus A-300 airplane in an effort to determine what caused the tail to separate from the body of the plane (*3*). One possibility is that turbulence from a nearby 747 was strong enough to rip the tail from the smaller Airbus A-300. If so, it would be the first confirmed composite failure in aviation history.

Composite casings for cell phones and laptop computers don't have to contend with passing jumbo jets, but they do face stress-producing situations—getting dropped on the ground or carried outside in all kinds of weather, for example. IBM Thinkpad laptop computers (Armonk, NY) came out with Ultracarbon composite casings in 1999, but Thinkpad has since switched to "titanium composite" (actually, a thin shell of titanium metal over a carbon-fiber–plastic casing) that IBM claims is three times stronger than ABS (acrylonitrile–butadiene–styrene) plastic (*www.pc.ibm.com/us/thinkpad/leadership.html*).

Fiber composites show up in the building industry as well (*1*). Existing structures in earthquake-prone areas can be retrofitted with column wraps and jacketing materials made of glass–aramid (aromatic polyamide) and carbon-fiber–epoxy composites. Sheets of carbon-fiber composites strengthen concrete walls, bridge decks, and exterior masonry. New buildings incorporate composites in suspension and stay cables, rebar material, prestressing tendons for bridges, and external reinforcements for structural beams. These lightweight composites exhibit high tensile strength and resist corrosion.

Perhaps the best-known composite incorporating negative-CTE aramid fibers is Kevlar (Dupont Advanced Fiber Systems, Newark, DE), but Twaron (Akzo Nobel Aramid Products, Inc., Conyers, GA) and Teknora (Teijin, Osaka, Japan) share the market as well (*1*). Aramid-fiber composites have high impact resistance as well as high tensile strength. This makes them useful for structures that must withstand elevated stress and vibration levels, such as helicopter rotor blades, compressed natural gas tanks, and of course, bulletproof vests.

Even polyethylene goes over to the negative side when it is formulated as a high-density, ultrahigh-molecular-weight (3–6 MDa) thermoplastic (*4*). Ultrahigh modulus or high-performance polyethylene (UHMPE or HPPE) fibers have a small negative CTE. Their tensile strength compares well with Kevlar, but they are not as strong as carbon fibers. UHMPE fibers in fabrics and composites outperform Kevlar in energy absorption, an important property for bulletproof vests. One HPPE fiber product, Dyneema (DSM High-Performance Fibers, Heerlen, The Netherlands, *www.dsm.com*), is the world's strongest material by weight. The fiber, which is used in personal armor and lightweight vehicle protection, earned DSM an ACS Heroes of Chemistry award earlier this year (*Chem. Eng. News*, Sept. 9, 2002, pp 50–52).

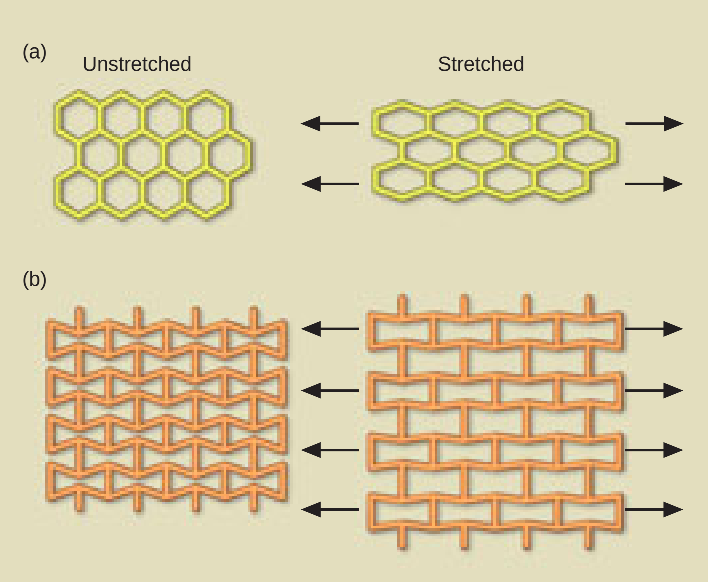


FIGURE 1: Stretching things a bit. Poisson's ratio is positive for materials that get longer and narrower when stretched (a), but negative for materials that expand in both directions (b). (Adapted from Ref. 7.)

Composites push the performance envelope for printed circuit boards as well. To achieve higher clock speeds, manufacturers are printing integrated circuits with more densely packed components, and bare chips are wire-bonded directly to substrates (*5*). These devices operate at high temperatures, and any mismatch in CTE between substrate and chip packaging manifests itself as a tug-of-war using the solder joints as the rope. Composites can be fine-tuned using mixtures of materials with negative and positive CTEs to produce a substrate that closely matches the corresponding electronic component, minimizing strain and embrittlement of the solder as the electronic device is powered on and off. Thermount, a nonwoven aramid reinforcement material (Dupont), can be combined with thermoset resins such as epoxy or polyimide for use in CTE-matched substrates.

A glass–ceramic material called Zerodur (Schott Glass Technologies, Yonkers, NY), used for high-performance optical systems, is actually a composite made of two phases of the same material. The starting glass is cycled thermally to produce 50-nm quartz-structured crystals dispersed throughout the vitreous matrix. The vitreous phase has a positive CTE, and the crystalline phase has a negative CTE, so the composite's dimensions change very little with temperature. At room temperature, the CTE is on the order of $\pm 1.5 \times 10^{-7}$/°C. This makes it especially useful for large telescope mirror substrates and for the laser gyroscopes used in aircraft navigational systems.

Fiber Bragg gratings, used in optoelectronic systems, are quite sensitive to thermal expansion and contraction. These short lengths of fiber have a periodic modulation of the index of refraction, and they reflect the desired wavelengths of light while transmitting the other wavelengths. Negative-CTE packaging and supports made of zirconium tungstate (ZrW_2O_8) contract uniformly in all directions when heated, counteracting the positive CTE of the fiber to keep it taut without distorting it (*6*). One silica-fiber device from Agere Systems (Breinigsville, PA) exhibits a 2.5-nm change in reflected wavelength between –40 and 80 °C without the ZrW_2O_8 packaging but reflects a constant wavelength with the packaging.

Pop Goes the Honeycomb

Auxetic materials have structural elements that produce an unusual response to applied force. When you stretch most materials, they lengthen in the direction of the stretch and contract at right angles to this direction. (The change in length divided by the change in width is called Poisson's ratio.) Auxetic materials, those having a negative Poisson's ratio, contain concave-celled honeycomb or foam-like structures that "pop out" when they are stretched (Figure 1).

Roderic S. Lakes (University of Wisconsin, Madison) and his research group have used heated, pressurized molds to make polymer foams with cells that protrude inward, producing "reentrant" structures that widen when they are stretched (*7*). Polyurethane works well for this purpose, but microcellular polyethylene foam doesn't—the cells retain their convex shape even when compressed. Lakes's group has developed an auxetic seat cushion that minimizes pressure points on the derriere of the person sitting on it. Cushions made of reentrant foam performed better (lower maximum seating pressure) than conventional foams of comparable densities.

During some future airplane flight, you may not only be sitting on an auxetic foam cushion, but listening to music using your auxetic earphones as well. Owen James claims that earphones cushioned with auxetic foam are comfortable to wear and provide better sound insulation than conventional earphone cushions. Thus, the wearer hears better sound quality (less distortion), and there is less sound leakage to annoy your seatmates (NCT Group, Inc., Westport, CT, U.S. Patent 6,412,593, July 2, 2002).

Polymers aren't the only materials that form auxetic foams—some metals do, too. Lakes and J. B. Choi demonstrated a copper auxetic-foam press-fit fastener that contracted under pressure for easy insertion into a steel socket. When the pressure was removed, the fastener expanded to fill the socket. Trying to remove the fastener by pulling on the attached polymer grip only made it expand and fit more tightly. The fastener finally broke, but it took 160 N of force, and the fastener fractured along its interior, away from the socket and embedded grip ends. Lakes and Choi suggest that stiff polymer foams could also be used as auxetic fasteners, depending on the strength required by the specific application. Although Lakes and Choi were mainly interested in these fasteners from an academic standpoint, they could eventually replace screws or bolts in applications where ease of installation overrides strength or stiffness considerations.

Floppy Reinforcements

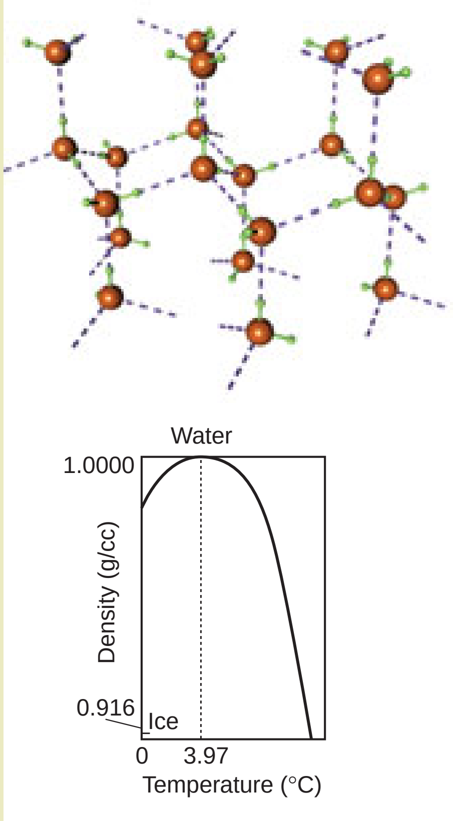
Negative stiffness is somewhat harder to visualize, but it has to do with materials that amplify rather than resist forces that act to deform them. Paradoxically, composites made from positive- and negative-stiffness components not only are stiffer than the positive component alone but also beat out positive–positive composites.

Ice Floats

Ice floating on water is a familiar sight, but it's definitely not the norm. Most materials adopt a dense, efficient atom-packing arrangement when they crystallize, but water's hydrogen-bonded network forces ice crystals to adopt an open architecture with a lot of empty space. Thus, the floating ice cube.

Water becomes more dense as it gets colder (just like most materials) until the temperature reaches about 4 °C (see figure). As the water freezes, the density actually decreases (the water expands). The slope of the density versus temperature line at any given point is water's coefficient of thermal expansion (CTE) for that temperature. Below 3.97 °C, this coefficient is less than zero. Water is unusual, but hardly unique, in this respect: Graphite, crystalline silica, some aramid polymers, metal alloys, and metal oxide compounds have negative CTEs over certain temperature ranges.

Water, with its highly symmetrical crystal structure, expands equally in all directions when it freezes. Other materials, especially those that form fibers or sheets, expand or contract to differing degrees along their wide and narrow dimensions. The term "axial CTE" refers to a fiber's tendency to expand or contract with temperature along its long dimension.



Water goes negative. Water contracts as it gets colder until it reaches 3.97 °C, then forms an open crystal structure (top) that causes it to expand as it starts to freeze. Below 3.97 °C, water's coefficient of thermal expansion (CTE) is negative (bottom).

Lakes is one of the few people looking into these ultra-floppy materials at present—his research group tested a composite consisting of a positive-stiffness tin matrix containing negative-stiffness vanadium dioxide inclusions (*8, 9*). Mixing in just 1% of the VO_2 particles increased the stiffness by about 8% compared with pure tin. How does it work? The VO_2 inclusions have a crystal structure that looks like stacked chevrons. These chevrons can switch their orientation when subjected to pressure or heat. By stabilizing these particles within the tin matrix, the resulting composite is stiffer than if high positive-stiffness inclusions (e.g., diamond) had been used. Lakes calculates that using the right concentration of inclusions having the right range of negative stiffness can increase a composite's overall stiffness by 40%, while the same concentration of "infinitely stiff" inclusions (another mathematical convention) increases overall stiffness by approximately 4%. These ultra-stiff composites may one day be used to dampen vibrations in aircraft wings or buildings (a useful feature in earthquake zones). The noise-reducing capabilities of these materials would make them a welcome addition to passenger compartments in airplanes or cars.

Achieving Balance

Engineers have known for centuries that if you want to hold something steady, you apply two opposing forces. What works for cathedrals and bridges also applies to computer cases and seat cushions. The challenge is in getting the positive and negative to work together without pulling each other apart. Fiber-reinforced polymer composites were originally developed with their high strength and light weight in mind, so mechanical and chemical compatibility was the main consideration. Subsequent generations of composites meet a host of additional requirements, from maximizing design and fabrication flexibility to minimizing vibrations, thermal expansion, and consumption of raw materials. It only goes to show that maybe negative behavior isn't so bad after all.

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