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Straining to expand entanglements

Porous solids comprising a self-entangled coiled polymer fibre or metal wire reversibly increase their volume when either stretched or compressed in an axial direction, possibly providing a new type of mechanical behaviour for tuning functional properties.

Ray H. Baughman and Alexandre F. Fonseca

Ordinary materials decrease in density when elastically stretched and increase in density when compressed, in any direction. A few rare types of crystal and some porous solids, called stretch-densified materials, have directions in which this behaviour is reversed — stretch increases density while compression decreases it[1,2]. Now, writing in *Nature Materials*, David Rodney *et al.* have demonstrated materials that increase their volume when either stretched or compressed, becoming less dense[3]. In so doing, they remove the asymmetry found for both ordinary materials and rare stretch-densified materials, wherein volume changes occur in opposite directions for stretch and compression.

The authors demonstrate this unusual behaviour for reversibly deformable structures that are easily made from a coiled nylon fibre or NiTi alloy wire. They self-entangled a coiled fibre to make a low-density, disordered fibre ball and then compressed this ball into a cylinder at a temperature sufficient to set the structure, without causing inter-fibre welding. Deformation of cylinder length reversibly increased cylinder volume by 29.7% for 32.3% cylinder stretch and by 25.9% for 20.1% cylinder compression for a self-entangled coiled structure (SECS) made from superelastic NiTi wire. To expand volume during stretch and during compression, an axially symmetric material must have an axial Poisson ratio of below and above 0.5, respectively, and the SECSs yield this by providing a Poisson ratio that goes from near zero or slightly negative[4] for large stretch to about 1.0 for large compression[3].

Useful insight into the reported behaviour can be obtained by considering a simple coil-based structural model that provides both stretch dilation and compression dilation. An increase in the force constant of the coiled fibres on going from tensile elongation to compression is needed for achieving these properties in the model, and the existence of such a force constant transition is supported by the observation[3] that the Young modulus for the SECSs dramatically increased as a tensile strain changed to a compressive strain. An abrupt 25-fold decrease in the fibre force constant has been observed with increasing mechanical load for high-strength nylon fibres that were tightly coiled by twist insertion without using a mandrel[5]. The explanation for this transition is that the coils in the non-stretched fibre are pulled out of contact by stretching, reducing the fibre force constant.

The present model has the lateral strut structure found in an ordinary wine rack, except that the rigid struts of the wine rack are replaced by coiled polymer fibres (or coiled metal wires), which provide high stiffness in compression and low stiffness in elongation. The only deformation modes allowed in the model are strut elongation during stretch and hinge deformation during compression. Figure 1 schematically depicts structural changes for compressive and tensile strains. The force constant for strut compression is much larger than for changing the wine rack angle, θ, that volume increases with increasing tensile compression by an increase of θ. The force constant for strut stretch dramatically decreases when coils are not contacting, which enables strut elongation to dominate over wine rack hinging, resulting in a volume increase during stretch. While this simple model cannot capture the complex deformations and structural features of the SECSs, it does illustrate how the switching of a force constant can result in a material that increases volume when either compressed or stretched. Note that pure

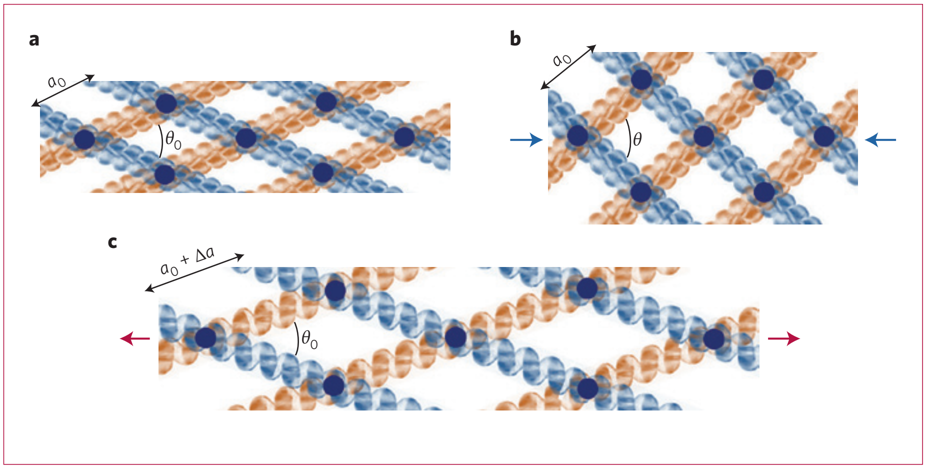

Figure 1 | Coil-based wine-rack model for describing how a transition in coil stiffness, caused by inter-coil contact, can produce a structure that increases its volume when either stretched (red arrows) or compressed (blue arrows). **a**, Illustration of the non-strained wine-rack structure, which uses coiled polymer fibres as struts. The blue circles indicate the hinges of the wine rack, a_0 is the coil length between hinges, and θ_0 is the initial inter-strut angle of the wine rack facing the direction of applied strain. **b**, Illustration of the volume increase caused by compression when the force constant for strut compression is much higher than for strut rotation. **c**, Illustration of the volume increase caused by stretch when the force constant for strut extension is much lower than for strut rotation, since coils are not contacting during stretch. Coil bending, which has the same effect at small strains as decreasing the force constant for hinging[6], is ignored in this simple model, as are changes in coil diameter during deformation. Figure adapted with permission from ref. 5, AAAS.

hinge deformation for a wine-rack structure with $\theta_0 = 90°$ could provide both stretch densification and compression densification for the same strain axis, which is a property that has apparently not yet been realized for any material.

It should be possible to make polymer-fibre-based SECSs in which volume expansion during compression either appears or disappears as a result of a temperature increase. To accomplish this, the mandrel-coiled fibres of Rodney *et al.*[3] could be replaced by polymer fibres that are highly twisted before coiling, and then thermally set by annealing to make powerful, giant stroke artificial muscles[5]. Depending on whether the chirality of fibre twist and fibre coiling are the same or different, these thermally powered muscles are known to reversibly contract or expand when heated[5]. Fibre contraction could bring coils into contact, and fibre expansion could then remove this contact, to generate or eliminate, respectively, the high force constant state needed for volume expansion during compression.

Of what potential use is the mechanical behaviour of the SECSs of Rodney and colleagues[3]? If you filled a uniaxially stretched SECS cylinder with a wetting liquid, it would extrude the liquid when the tensile stress is removed, and then suck it in when uniaxially compressed. By using a coiled fibre or wire that is a semiconductor, superconductor, insulating dielectric, thermal conductor, ferromagnet, or ferroelectric (and optionally include reversibly extrudable functional fluids in the SECSs), reversible properties enabled by the large per cent volume increase during stretch or compression might well enable interesting applications. Also, a targeted strain state having specific properties could be frozen by solidifying or crosslinking an imbibed fluid. There are therefore multiple ways in which these coiled structures could lead to interesting functionalities. ❐

Ray H. Baughman is at the Alan G. MacDiarmid NanoTech Institute at the University of Texas at Dallas, Texas 75083, USA. Alexandre F. Fonseca is in the Applied Physics Department at the State University of Campinas, Campinas SP, 13083-859, Brazil.
e-mail: ray.baughman@utdallas.edu

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