

BIOMIMETIC MATERIALS

Marine inspiration

Sea cucumber skin is the architectural basis for polymer nanocomposites that can adapt their mechanical properties in response to biomedically relevant chemical stimuli, in a similar fashion to the animals' self-defence mechanism.

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Sea cucumbers have evolved an amazing and life-saving skin (Fig. 1). In the face of danger, they can rapidly and reversibly alter their dermal stiffness by several orders of magnitude. This kind of inherent response to stimuli, which in some biological systems is realized by a colour change, could mean the difference between life and death. In contrast, most engineered materials have no such adaptive mechanism — they are static and unable to respond to biologically relevant stimuli.

Drawing inspiration from the sea cucumber's self-defence strategy, the fabrication of a stimuli-responsive nanocomposite has been reported in *Science* by Jeffrey Capadona and colleagues¹. The inner dermis of the sea cucumber is composed of collagen nanofibres in a viscoelastic matrix of fibrillin microfibrils and, on the first sign of danger, the animal secretes certain chemicals that trigger the formation of transient interactions between the nanofibres. In a matter of seconds, the sea cucumber stiffens. This is mirrored in the architecture of the polymer nanocomposites designed by Capadona and colleagues, in which cellulose nanofibres are embedded in a matrix formed from either an ethylene oxide–epichlorohydrin (EO–EPI) copolymer or from poly(vinyl acetate) (PVAc). The degree of interaction between the nanofibres can be modulated by using a water-based solvent that disrupts the fibre–fibre interaction. In the absence of such a solvent, the cellulose fibres interact to form a percolating network, stress transfer is maximized between fibres and the tensile modulus is in the several GPa range — this rigid material is in the 'on' state (Fig. 2). The addition of a solvent that



Figure 1 A sea cucumber (yellow) nesting between coral.

forms hydrogen bonds with the nanofibres acts as a chemical trigger that disrupts these interactions, decreases the modulus, and thus switches the material to the 'off' state.

Biological strategies that arrive at such adaptive material properties may just be one of many solutions. Clearly, tailored properties can be designed without following a biomimetic approach — for example, airplanes don't flap their wings. Indeed, composites that are ultrastiff can be designed² and have applications in aerospace, automobiles and even sports equipment. Although these composites have an apparent bioinspired structure, containing a fibrous element dispersed in another matrix or 'solvent', their functional properties and mechanical behaviour are often not adaptive. What then, is the outcome of a truly biomimetic approach to materials design? As the report by Capadona *et al.* demonstrates, mimicking nature's lead can create a critical

distinguishing feature of biomimetic materials — the ability to respond to biomedically relevant stimuli.

Arguably, a common cause of implant failure *in vivo* is the inability of engineered materials to adapt to their biological environment — be it a change in size as a result of age or a change in the cellular response to the material over time. Therefore, the importance of 'tunability' or stimuli-responsiveness is critically important for implanted materials. Indeed, some triggered or tunable systems are already being developed for biomedical uses, for example, targeted drug delivery based on pH-sensitive swelling³, and heat-sensitive nanocarriers⁴ that deliver drugs to regions above a certain critical temperature.

The material developed by Capadona *et al.* is significant because of the demonstrated 'tunability' of its properties, which is achieved by the addition of biologically relevant solvents such as water or cerebrospinal fluid. Also, the combination of tunable nanofibre/solvent interactions with temperature-sensitive phase-transition effects, results in an initial material of desirable stiffness, which, on exposure to physiological conditions, can experience a host-triggered decrease in stiffness. This characteristic could be potentially useful in applications such as brain implants, where it is critical that materials are sufficiently stiff to facilitate insertion through the pial layer (outer lining) of the brain but, once inside, they soften to match the brain's stiffness and hence minimize injury.

The implication of this system for neural electrodes is not straightforward, however, given that the stiffness of the brain is in the KPa range⁵ and the 'softest' PVAc–cellulose composites are in the low MPa range. The addition of cellulose fibres increases the stiffness of PVAc so that it can be inserted through the pial layer, and equilibration with the cerebrospinal fluid makes the material soften to a certain extent, however, this softest state is still

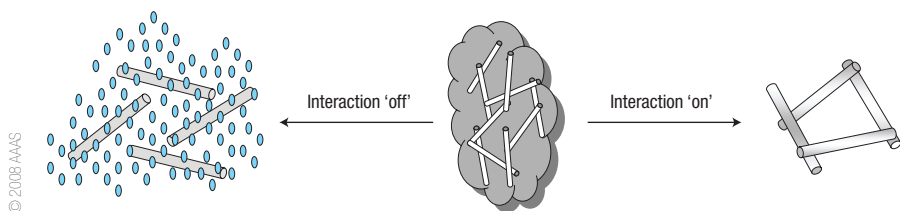


Figure 2 A schematic representation of the polymer nanocomposite. In the 'on' state, interactions are formed between the cellulose nanofibres, which maximize stress transfer between the fibres and, as a result, the tensile modulus increases. These fibre–fibre interactions are removed by the addition of a biomedically relevant chemical that competitively forms hydrogen bonds with the fibres, and the system is switched to the 'off' state. Reprinted with permission from ref. 1.

far from that desired for the brain. The second potential limitation is the swelling behaviour of the composite: An inward flow of cerebrospinal fluid is critical to modulating the cellulose fibre interactions and, in the current design, it seems as though swelling of at least 30% by volume is necessary to reach the softest state. In the confined space of the brain or spinal

cord, this large volume change could have damaging repercussions.

An interesting advantage of this material is the specificity of the stimulus (water) that causes the change in stiffness. Theoretically, as the 'modulating element' is determined by the chemistry of the fibre–fibre and fibre–solvent competition, it should be possible to carefully engineer

fibre side-chains and the solvent system so that the change in mechanical properties can be triggered by very specific stimuli such as ambient ions or protein or enzyme levels. For instance, one can imagine fibre–fibre interactions being engineered to occur via specific peptide or protein interactions that are then disrupted competitively by specific levels of proteinases.

This material is of particular importance because of its responsiveness to biocompatible, water-based triggers. So, for certain biological applications, the natural world may still offer exciting ways to create adaptive materials. Or, if you are a sea cucumber and know where to look, one potential recipe for true invincibility has just been uncovered.

References

1. Capadona, J. R. *et al. Science* **319**, 1370–1374 (2008).
2. Podsiadlo, P. *et al. Science* **318**, 80–83 (2007).
3. Peppas, N. A., Hilt, J. Z., Khademhosseini, A. & Langer, R. *Adv. Mater.* **18**, 1345–1360 (2006).
4. Needham, D. & Dewhirst, M. W. *Adv. Drug Deliv. Rev.* **53**, 285–305 (2001).
5. Ommaya, A. K. *J. Biomech.* **1**, 127–138 (1968).

MATERIAL MECHANICS

An angle on sticky films

The interplay of various mechanical forces leads to characteristic shapes of torn adhesive films. Analysis of these shapes provides potential for new approaches to material characterization.

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It is a phenomenon that all of us have encountered at some point in our lives: the annoying tendency of adhesive tape to not peel properly. Instead of the whole piece peeling nicely in rectangular fashion, a triangular section all too often narrows and detaches (Fig. 1). On page 386 of this issue, Eugenio Hamm *et al.* analyse this phenomenon, and show that the well-defined angle at the apex of the detached triangular piece is a function of the properties of the film¹. Moreover, this angle is shown to not only be exhibited by adhesive tape — it seems to be a general property of adhered films, which can also be seen in situations such as tearing wallpaper or peeling a tomato. The

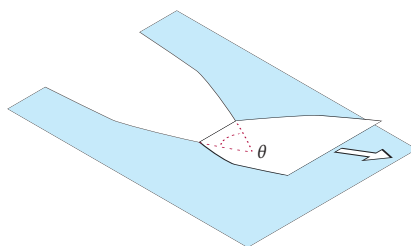


Figure 1 The geometry of a torn piece of film. The apex angle, θ , is related to the properties of the film.

derived relationships between material properties and the apex angle provide the potential for new methods of material properties characterization.

The work of Hamm *et al.* relates the angle at the apex of the torn piece of adhesive film to three parameters of the film on a substrate: the 'strength' of the glue, otherwise known as the work

of adhesion; the energy required to tear the film; and the stiffness of the film when bent. These three properties can be measured independently and thus the theoretically derived relation between them and the apex angle is experimentally checked. To relate the parameters, a straightforward analysis — based on the energetics of peeling and simple fracture — is presented.

The analysis results in a simple expression for the apex angle. The angle is found to increase with both the stiffness of the film and the work of adhesion, and it decreases with increasing force required to tear the film. The two former terms are both proportional to the width of the torn piece, whereas the tearing force is independent of the width. If all materials parameters remain the same except the film thickness, it is found that the resulting apex angle increases with increasing film thickness — a result that is very hard to guess without the analysis.