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Thermally Switching On/Off the Hardening of Soaked Nanocomposite Materials

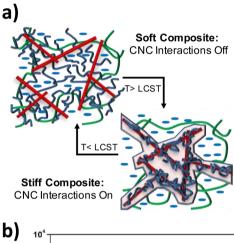Maria M. Pérez-Madrigal and Rachel K. O'Reilly

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Rowan and Maia use straightforward polymer science to mimic complex natural phenomena to create novel adaptive nanocomposite materials.

The area of smart materials is a hot topic as it allows access to adaptive/responsive materials with self-healing, shape memory, or actuation behavior. Indeed, scientists can make all manner of materials on-scale with controllable and remarkable properties, but designing materials with mechanical adaptability is much more challenging. Although the sea cucumber might seem like an unlikely source of scientific creativity, Rowan, Maia, and co-workers have taken inspiration from this remarkable creature in their recent *ACS Central Science* paper.[1] Building on their 2008 *Science* paper,[2] with Weder on the fabrication of artificial polymer nanocomposites that displayed mechanical morphing characteristics, they have made an impressive leap forward through the design and demonstration of a biomimetic reversible heat-stiffening polymer nanocomposite.

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Stimulus-responsive materials have benefited from significant advances in polymer science in recent years.[3] Many of the interesting properties of responsive materials arise from a transition in solubility or conformation of the polymer in the presence of an external stimulus. In this manner, transitions at the molecular level can be amplified to result in a change in nanoscale structure and/or material properties. Perhaps the most commonly utilized stimulus is that of temperature, with poly(*N*-isopropylacrylamide) being the most widely studied responsive polymer. Harnessing these transitions toward specific material applications is

Figure 1. (a) Schematic showing the concept of a reversible, thermally stiffening water swollen composite below the LCST and a stiff reinforced composite above the LCST. (b) Tensile storage modulus (E') of t-CNC-g-POEG$_3$A/PVAc composites dry as-processed (**1D$_{AP}$**, black squares), soaked in water (25 °C) below the LCST for 3 days (**1W$_{BL}$**, red circles), placed in water (60 °C) above the LCST for 1 h (**1W$_{AL}$**, blue triangles), and redried above 60 °C (**1RD$_{AL}$**, green triangles). Adapted with permission from ref 1. Copyright 2017 American Chemical Society.

challenging, but this is exactly what the Rowan and Maia groups have achieved in this work.

In their previous work, Rowan and Weder fabricated artificial polymer nanocomposites containing rigid cellulose nanofibers,[4] and then built on this to create artificial materials that displayed chemosoftening behavior when

exposed to water and body temperature.[2] This was achieved by embedding cellulose nanofibers in a rubbery polymer matrix. The surface of the cellulose fibers contains hydroxyl groups which can hydrogen bond where the fibers intersect to form a reinforced network. This network makes the material rigid. However, it can be disrupted by adding water, to break up the intersecting and hydrogen bonding nanofibers, and hence the composite material becomes flexible. While this was a radically new approach for synthetic material design, it was inspired by nature's approach to adaptive material design. For example, sea cucumbers can rapidly alter the stiffness of their skin in response to environmental cues. Indeed, their biological tissue is derived from a nanocomposite structure containing rigid collagen nanofibers embedded in a soft connective tissue. The stiffness of the animal is controlled by enzyme secretion (which switches "on" or "off" the interactions between the fibers) from the nervous system. When connected, the nanofibers form a reinforcing network that increases the overall stiffness of the sea cucumber considerably and provides an "armored" skin in response to a threat.

In this issue, Rowan, Maia and co-workers have designed a novel heat-stiffening polymer nanocomposite by grafting lower critical solution temperature (LCST) polymers to cellulose nanocrystals (CNCs) embedded in a poly(vinyl acetate) (PVAc) matrix. The role of the LCST polymers is to mimic the enzymatically activated switch of the reinforcing network observed in the sea cucumber, using CNCs as reinforcing fillers, while PVAc acts as the soft connective tissue. When swollen in water, an increase in temperature triggers the fully reversible stiffening of the material (Figure 1a). In contrast to commonly applied LCST polymers such as poly(N-isopropylacrylamide) or poly(N,N-dimethylaminoethyl methacrylate), their strategy exploits poly(oligo-(ethylene glycol)monomethyl ether (meth)acrylates). Interestingly, this class of polymers allows for tailoring the LCST transition (switching temperature in the range between 26 and 90 °C), and also shows high biocompatibility.[5] Both of these factors undoubtedly contribute to the potential widespread application of these new adaptive materials.

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In a wet, warm, and salty biomimetic environment, the nanocomposites underwent an impressive increase in their tensile storage modulus, ca. 2 orders of magnitude, from ~10 to 300 MPa (Figure 1b), which leads to a significant stiffening of the materials. Moreover, by altering the filler content, one can easily modulate the stiffening time from 2 to 4 min. When considering the potential application of this technology, this offers plenty of time to adapt the soft wet film to a specific shape before becoming stiff upon exposure to the body's environment. The authors demonstrate this feature by preparing a mechanically stiff human nose from a water-soaked film of the nanocomposite material (Figure 2). Such unique platform is envisaged as a promising new reinforcing medical implant for bone regeneration, especially in the craniofacial region where current alternatives lack the ability to shape and conform to a bony defect and also fail to allow for fitting to complex 3D anatomic defects. Excitingly, these new materials appear to offer significant advances toward tackling these challenges although they have not yet been optimized as the perfect bone scaffold: they would need to display mechanical features closer to the target native tissue (human cortical bone has an elastic modulus between 3 and 20 GPa).[6] Alternatively, their stiffening response could also be applied for tissues with lower elastic modulus, like cartilage or tendon (on the order of 1−100 MPa).[7] Undoubtedly, a future goal is to ensure their biocompatibility, bioactivity, and mechanical endurance, as well as stiffness yet flexibility and lightness yet strength.[6] Furthermore, the scaffold microarchitecture should provide sufficient porosity, interconnectivity, and transport properties for vascularization and blood vessel invasion (pore size of 150 to 500 μm).[8,9]
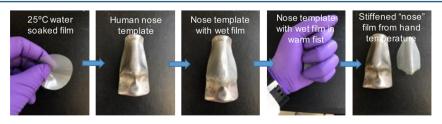

Figure 2. Images of a wet 30 wt % t-CNC-g-POEG2MA/PVAc composite stiffened enough to retain the shape of a human nose upon exposure to a warm hand. Reproduced with permission from ref 1 . Copyright 2017 American Chemical Society.

Nonetheless, as the authors point out, numerous opportunities exist to further develop this first generation of heat-stiffening polymer nanocomposites. The straightforward strategy presented in this issue opens the door to a new set of materials that could eventually meet all the requirements of a bone scaffold. It is clear that further interdisciplinary collaboration between chemists, biologists, material scientists, and orthopedic surgeons will help to realize the true potential of these new materials.

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