MECHANICALLY ADAPTIVE POLYMER NANOCOMPOSITES

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Polymers which change their mechanical properties "on command", i.e. upon exposure to a pre-defined stimulus in a highly selective and reversible manner, are attractive for countless technologically relevant applications. Examples of technologically useful "smart" materials that exhibit such morphing mechanical behavior are, however, limited.[1]

We recently introduced a new family of stimuli-responsive nanocomposites that mimic the defense mechanism at play in the skin of sea cucumbers.[2] Like other echinoderms, these creatures have the fascinating ability to rapidly and reversibly alter the stiffness of their skin when threatened.[3] This dynamic mechanical behavior is achieved through a nanocomposite architecture, in which rigid, high-aspect-ratio collagen fibrils reinforce a viscoelastic matrix. The stiffness of the tissue is regulated by controlling the molecular interactions, and therewith the stress transfer, among adjacent collagen fibrils by locally secreted proteins.[3]

Intrigued by this capability and with the initial goal of creating new adaptive materials for biomedical applications, which change their mechanical properties upon exposure to physiological conditions, we recently began to investigate whether nanocomposites can be created that exhibit similar architecture and morphing mechanical properties. A first series of such adaptive nanocomposites was created from a rubbery ethylene oxide-epichlorohydrin copolymer (EO-EPI) into which a rigid network of high-stiffness, high-aspect ratio cellulose nanofibers was incorporated (Fig. 1).[2] The EO-EPI matrix displays a low modulus (~1 MPa) and can accommodate the uptake of several chemical stimuli. Cellulose nanofibers, isolated from the mantles of sessile sea creatures known as tunicates, were used as the reinforcing filler.[4] These "whiskers" exhibit high stiffness (tensile modulus ~130 GPa) and dimensions at the nanometer scale (26 nm x 2.2 μm). Similar nanofibers can be isolated from a range of renewable bio-sources, including wood and cotton.[4] On account of the high density of strongly interacting surface hydroxyl groups, cellulose whiskers have a strong tendency for aggregation.[5-6] As a result the fabrication of polymer/cellulose-whisker nanocomposites in which the nanofibers assemble into a percolating network can be intricate. Good dispersion during processing is achieved when whisker self-interactions are "switched off" by competitive binding with a hydrogen-bond-forming solvent.[5-7] Upon solvent evaporation the interactions among the whiskers are "switched on" and they assemble into a percolating network. This architecture and strong interactions among the whiskers maximize stress transfer and therewith the overall modulus of the material. Indeed, E' increased with increasing whisker content from ~4 MPa (neat polymer) to ~800 MPa (upon introduction of 19% v/v whiskers).[5] The non-covalent interactions between the percolating cellulose fibers in the nanocomposites can be mediated by chemical stimuli. Through modest aqueous swelling (20%), the reinforcing cellulose network can be disrupted, resulting in a dramatic modulus reduction from 800 to 20 MPa for a composite comprising 19% v/v whiskers (Fig. 2).[2] The original stiffness is restored when the composites are dried. Control experiments and analyses using mechanical models

(Fig. 2) support the conclusion that the stiffness change is due to the designed mechanism of altered whisker–whisker interactions, rather than alternative effects such as plasticization of the matrix.[2]

Developing a second generation of such adaptive materials based on poly(vinyl acetate) (PVAc) and cellulose whiskers we have shown that the combination of this effect with a chemically influenced thermal transition allows for amplification of the mechanical contrast. Mechanical switching over several orders of magnitude (5 GPa to 12 MPa) has now been achieved.[2,8]

These chemo-responsive mechanically-dynamic nanocomposites are potentially useful for a plethora of applications. For example, the chemo-responsive materials discussed here are currently being investigated for their potential to serve as 'smart' materials for biomedical applications. This presentation will highlight our recent efforts to develop adaptive substrates for intra-cortical microelectrodes.

References:

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Figures:

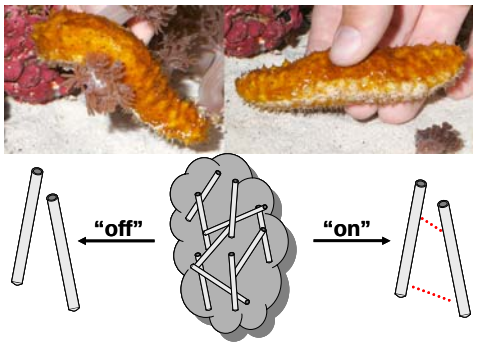

Fig. 1: Pictures of a sea cucumber in soft and stiff state and schematic of the switching mechanism in this biological model and the proposed biomimetic nanocomposites. The stress transfer among rigid, percolating nanofibers, and therewith the overall stiffness of the material, is controlled by a stimulus.

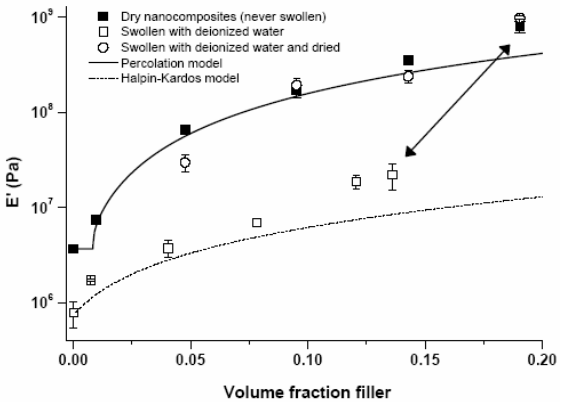

Fig. 2: Tensile storage moduli *E'* of EO-EPI/cellulose whisker nanocomposites. The materials were conditioned as indicated. Lines represent values predicted by the percolation and Halpin-Kardos models. The arrow indicates changes in modulus and volume fraction of whiskers resulting from aqueous swellling of one selected sample (19% v/v whiskers).