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Designing Sensory and Adaptive Composite Materials

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14. ABSTRACT

We developed new computational approaches to design composites that exhibit remarkable abilities to both sense external cues and adapt to these cues in controllable, 'programmable' ways. We focused on two particular classes of materials; both include hard particles and soft, cross-linked polymers. The first class of materials involves polymer-grafted nanoparticles (PGNs) that are cross-linked into extensive networks. Our aim was to devise PGN networks that become stronger and tougher in response to an applied force. In effect, these composites would mimic a salient feature of bone remodeling, which leads to the improvement of mechanical properties after deformation. The second class of materials that we considered is stimuliresponsive, fiber-reinforced gels. Here, the gels provide the composite with considerable mutability in response to environmental cues, such as variations in light and heat. Our models also allow us to predict and optimize the performance and mechanical integrity of these systems in response to changes in the surrounding environment.

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DESIGNING SENSORY AND ADAPTIVE COMPOSITE MATERIALS

RESULTS FROM PRIOR AFOSR FUNDING: JUNE 2015-JUNE 2018.

We developed new computational approaches to design composites that exhibit remarkable abilities to both sense external cues and adapt to these cues in controllable, "programmable" ways. We focused on two particular classes of materials; both include hard particles and soft, cross-linked polymers. The first class of materials involves polymer-grafted nanoparticles (PGNs) that are cross-linked into extensive networks. Our aim was to devise PGN networks that become stronger and tougher in response to an applied force. In effect, these composites would mimic a salient feature of bone remodeling, which leads to the improvement of mechanical properties after deformation.

The second class of materials that we considered is stimuli-responsive, fiber-reinforced gels. Here, the gels provide the composite with considerable mutability in response to environmental cues, such as variations in light and heat. The fibers improve the mechanical robustness of the system and can also be stimuli-responsive, allowing the composite to respond to a broader range of external signals. Notably, this system also captures features of the skeletal system, with the fibers effectively providing a skeletal framework for the gel "muscle". We specifically focused on gels containing spirobenzopyran (SP) chromophores, which allow the material to be manipulated with light. By exposing the sample to blue light, we can remotely and non-invasively drive the structure to change conformation and hence, functionality. This system represents a novel form of photo-chemo-mechanical transduction where light drives a chemical change within the gel, which drives the mechanical actuation of the composite.

The studies described below can offer fundamental guidelines for designing new hybrid materials of importance to the Air Force. Our models also allow us to predict and optimize the performance and mechanical integrity of these systems in response to changes in the surrounding environment. (Papers acknowledging funding from the prior AFOSR grant are indicated with the prefix "P".)

Harnessing Biomimetic Catch Bonds to Create Mechanically Robust Nanoparticle Networks [P1]

Biological systems have developed structural motifs that allow these systems to resist mechanical deformation. On the molecular scale, biological catch bonds play a vital role in this functionality since these bonds effectively become stronger under deformation. Inserted into hybrid materials, biomimetic catch bonds could lead to composites that exhibit improved mechanical properties in response to an applied force. Using computer simulations, we investigated the mechanical properties of a network of polymer-grafted nanoparticles (PGNs) that are interlinked by labile "catch" bonds. In contrast to conventional "slip" bonds, the life time of catch bonds can potentially increase with the application of force (i.e., the rate of rupture can decrease). Subjecting the PGN networks to a tensile deformation (see **Fig. 1**), we found that the networks encompassing catch bonds exhibit greater ductility and toughness than the networks interconnected by slip bonds. Moreover, when the applied tensile force is released, the catch bond networks exhibit lower hysteresis and faster relaxation of residual strain than the slip bond networks. The effects of the catch bonds on the mechanical behavior are attributed to transitions between two conformational states, which differ in their sensitivity to force. The findings provide guidelines for creating nanocomposite networks that are highly resistant to mechanical deformation and show rapid strain recovery.

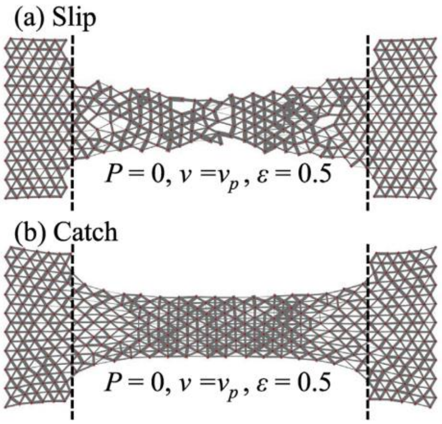


Fig. 1 Snapshots of the dog-bone shaped samples at strain of ε = 0.5. (a) Slip bond network. (b) Catch bond network. In the slip bond network (a), we observe the onset of failure through the formation of voids. In contrast, the catch bond network (b) appears to be intact and relatively homogeneous at this strain.

Tuning the Mechanical Properties of Polymer-grafted Nanoparticle Networks through the Use of Biomimetic Catch Bonds [P2]

While the calculations for the above model were formulated for a 3D system, [P1] the simulations were carried out in 2D, presenting a slice through the sample. We extended the approach by developing the full 3D simulations and introducing a method for systematically varying the fraction of catch bonds in the network (see **Fig. 2**). [P2] The ability to precisely tune the mechanical properties of polymeric composites is vital for harnessing these materials in range of diverse applications. Polymer grafted nanoparticles (PGNs) that are cross-linked into a network offer distinct opportunities for tailoring the strength and toughness of the material. Within these materials, the free ends of the grafted chains form bonds with the neighboring chains, and tailoring the nature of these bonds could provide a route to tailoring the macroscopic behavior of the composite. Using computational modeling, we simulated the behavior of three-dimensional PGN networks that encompass both high-strength "permanent" bonds and weaker, more reactive labile bonds. The labile connections are formed from slip bonds and biomimetic catch bonds. Unlike conventional slip bonds, the lifetime of the catch bonds can increase with an applied force, and hence, these bonds become stronger under deformation. With our 3D model, we examined the mechanical response of the composites to a tensile deformation, focusing on samples that encompass different numbers of permanent bonds, different bond energies between the labile bonds, and varying numbers of catch bonds. We found that at the higher energy of the labile bonds ($U^l = 39\,k_B T$), the mechanical properties of the material could be tailored by varying both the number of permanent bonds and catch bonds. Notably, as much as a two-fold increase in toughness could be achieved by increasing the number of permanent bonds or catch bonds in the sample (while the keeping other parameters fixed). In contrast, at the lower energy of the labile bonds considered here ($U^l = 33k_b T$), the permanent bonds played the dominant role in regulating the mechanical behavior of the PGN network. The findings from the simulations provide valuable guidelines for optimizing the macroscopic behavior of the PGN networks and highlight the utility of introducing catch bonds to tune the mechanical properties of system.

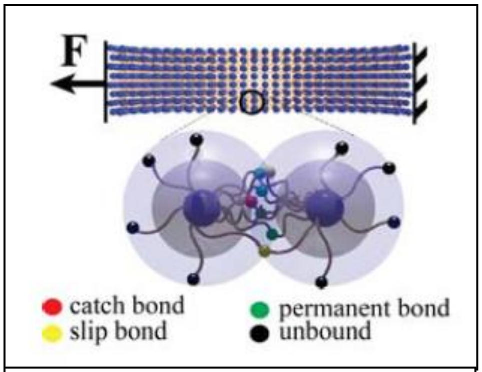


Fig. 2. Schematic representation of 3D PGN network with the various types of bonding interactions.

Tailoring the Properties of Biomimetic Catch Bonds in Nanoparticle Networks to Improve the Mechanical Behavior of the Composite [P3]

By deriving a master equation for the interaction of two polymer-grafted nanoparticles (PGNs) that are interconnected by biomimetic catch bonds, we determined the parameter space where these bonds display optimal properties in resisting tensile deformation. We then utilized this set of parameters in three-dimensional (3D) computer simulations of larger PGN networks that are interconnected by both catch bonds and slip bonds (whose lifetimes decrease with force). We demonstrated that the strain at break, ε_b, and toughness, W, of the networks can be significantly enhanced by "tuning" the attributes of the catch bonds. In particular, networks with catch bonds can exhibit up to a fourfold increase in ε_b and W relative to

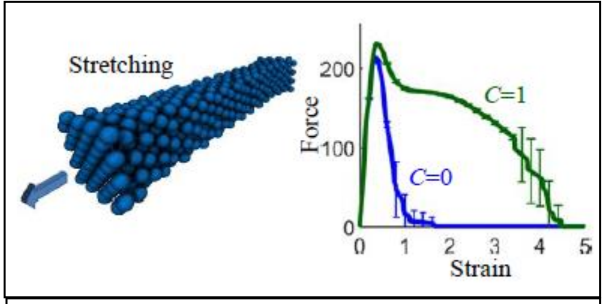


Fig. 3. Comparing the force versus strain for a network with no catch bonds (C=0) and 100% catch bonds (C=1). The mechanical properties for the C=1 case are significantly improved relative to the C=0 case.

networks interconnected solely by slip bonds (see **Fig. 3**). Hence, the studies indicate a new route for tailoring macroscopic mechanical properties by controlling molecular-scale interactions in the composite.

Using Torsion for Controllable Reconfiguration of Binary Nanoparticle Networks [P4]

As indicated by the above studies, mechanical deformation can potentially provide an effective means of controlling the nanoscale morphology and macroscopic properties of hybrid materials. The challenge, however, is establishing optimal couplings of the deformation and mechano-responsive components in the material to achieve nanoscopic structural reorganization without causing catastrophic damage. The introduction of catch bonds provides one possible means of addressing this challenge. Through computational modeling, we investigated another possible route. Namely, we examined how torsion can be utilized to induce controllable structural changes in networks formed from binary mixtures (A and B) of polymer-grafted nanoparticles (PGNs) (**Fig. 4a-c**). The nanoparticles' rigid cores are decorated with a corona of grafted polymers, which contain reactive functional groups at the chain ends. With the overlap of the neighboring coronas, these reactive groups form labile slip bonds, which can reform after breakage. The labile bond energy between similar PGNs (U_{AA}, U_{BB}) is different than the energy between dissimilar species (U_{AB}). By tailoring the relative values of these bond energies and the boundary conditions acting on the system, the application of a torsional deformation can result in a controllable reconfiguration of the network, leading to intertwining helical structures, or homogeneously mixed nanocomposites. **Figure 4c** shows the force *vs.* strain curves obtained from the tensile deformation of samples with three different structures. The figure shows that the strain at break, tensile strength, and toughness of the helical samples (**Fig. 4b**) are approximately 1.4, 2.4, and 4.3 times greater, respectively, than those for the random samples (**Fig. 4a**). In effect, our mechano-mutable system resembles a "Rubik's cube" material, whose nanostructure, and hence global properties, can be tailored by mechanically twisting the sample.

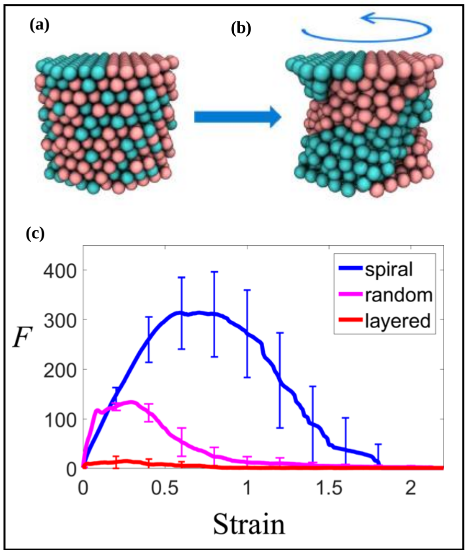


Fig. 4 (a) Random structure. (b) Helical (spiral) structure. (c) Force versus strain curves.

Modeling Heterogeneous Polymer-grafted Nanoparticle Networks Having Biomimetic Layered Structures [P5]

We also used 3D computational modeling to study the behavior of heterogeneous polymer-grafted nanoparticle (PGN) networks under tensile deformation (**Fig. 5**). In particular, we considered binary PGN

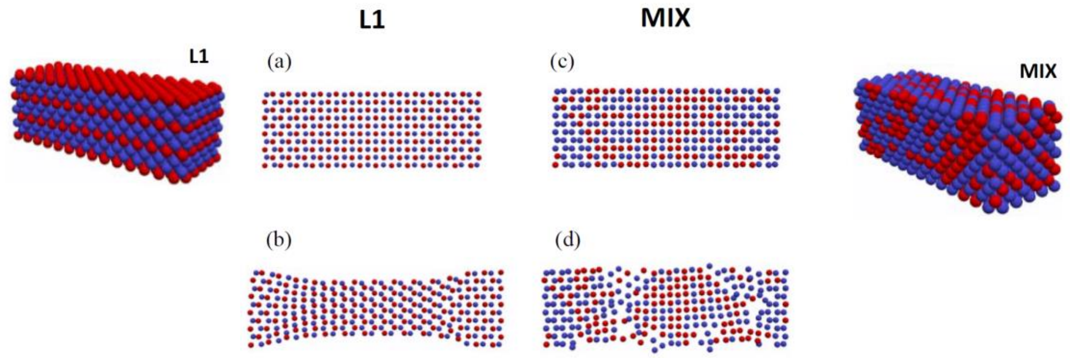
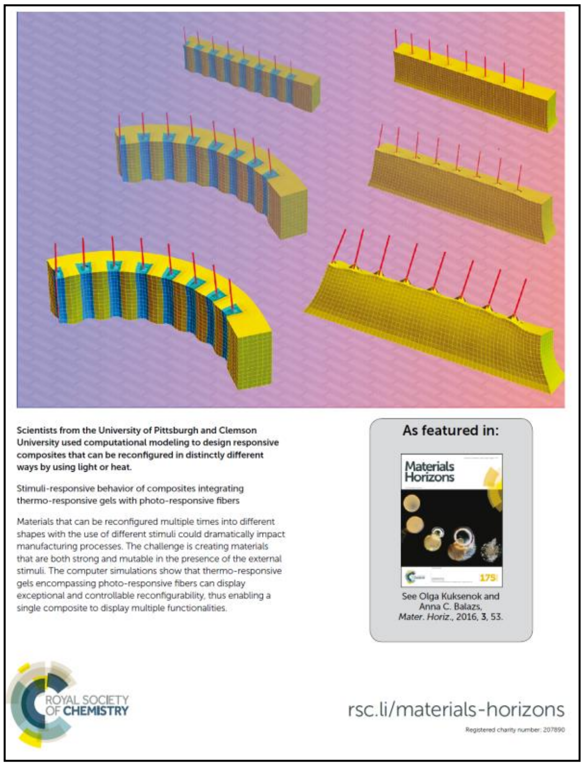


Fig. 5. Layered structure (L1) and mixed structure (MIX) are subjected to tensile deformation. The images in (a)-(d) are the top down views of the two central layers of the system. The images in (a) and (c) are the initial states and (b) and (d) show the respective systems after they have been strained to the same extent. The mixed system clearly shows distinct voids, indicating the failure of the composite. On the other hand, the layered system stays intact, showing a distinctive and stable restructuring of the material.

networks having an alternating layered structure of A and B particles (L1 in **Fig. 5**) and networks that encompassed randomly mixed A and B particles (MIX in **Fig. 5**). Using our computer simulations, we compared the ultimate tensile properties (strength, toughness, ductility), the strain recovery properties and cyclic loading properties for these structures. We demonstrated that the layered structures could be designed to obtain highly resilient self-healing materials. Namely, under tensile deformation and a fixed value of strain, the layered structures underwent a morphological transition to another ordered structure (**Fig. 5(a)-(b)**), while the mixed structure underwent failure (**Fig. 5(c)-(d)**).

Stimuli-responsive Behavior of Composites Integrating Thermo-responsive Gels with Photo-responsive Fibers P 6

Materials that could be reconfigured multiple times into different shapes with the use of different stimuli could dramatically impact manufacturing processes. As a step toward creating such useful, adaptive materials, we used computational modeling to design a composite that integrates a thermo-responsive polymer gel and photosensitive fibers. The gel displays a lower critical solution temperature (LCST), and thus, shrinks at elevated temperatures. The elastic fibers are functionalized with spirobenzopyran (*SP*) chromophores, which become hydrophobic under blue light. If these chromophores are uniformly distributed in this LCST gel (without the embedded fibers), then both light and heat produce the same effect on the sample, causing the gel to undergo a uniform collapse. When the *SP*-functionalization is confined to fibers that are embedded in the gel, the material displays distinctly different behavior in the presence of light and heat. In particular, samples anchored to a surface bend in one direction when illuminated and in the opposite direction when heated. When the sample is detached from the surface, then the composites shrink like an accordion when heated and bend like a caterpillar when illuminated. Common to both the tethered and untethered samples, one material displays a distinct response to the different stimuli. Hence, our findings indicate how a given sample can be fashioned into different shapes through the use of separate stimuli. Overall, our results point to a robust method for controllably reconfiguring the morphology of compliant composites and amplifying the effects of external environmental cues (light or temperature) on the behavior of these systems. Our findings were featured on the back cover of *Materials Horizons* (see **Fig. on the right**) for the issue containing our paper.



Scientists from the University of Pittsburgh and Clemson University used computational modeling to design responsive composites that can be reconfigured in distinctly different ways by using light or heat.

Stimuli-responsive behavior of composites integrating thermo-responsive gels with photo-responsive fibers

Materials that can be reconfigured multiple times into different shapes with the use of different stimuli could dramatically impact manufacturing processes. The challenge is creating materials that are both strong and mutable in the presence of the external stimuli. The computer simulations show that thermo-responsive gels encompassing photo-responsive fibers can display exceptional and controllable reconfigurability, thus enabling a single composite to display multiple functionalities.

As featured in:

Materials Horizons

See Olga Kuksenok and Anna C. Balazs, *Mater. Horiz.*, 2016, **3**, 53.

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Embedding Flexible Fibers into Responsive Gels to Create Composites with Controllable Dexterity P 7

Using computational modeling, we designed a composite that encompasses a thermo-responsive gel and photo-responsive fibers that extend from the surface of the gel. By simulating the effect of light and heat on the sample, we isolated scenarios where cooperative interactions within the system allow the gel to actuate the “finger-like” motion of the embedded fibers. To achieve this distinctive behavior, we considered a gel formed from poly-N-isopropylacrylamide (pNIPAAm), which shrinks when heated above the lower critical solution temperature (LCST). The fibers are functionalized with spirobenzopyran (SP) chromophores that extend a finite region into the polymer network. The application of heat causes the entire gel to shrink, while the application of light causes the regions around the functionalized fibers to collapse. With the fibers arranged in a square or circular pattern in the center of the gel, heating the non-illuminated samples drives the fibers to move apart as they bend outward (away from the center). With the application of light, the tips of fibers come together as the fibers bend inward. In this configuration, the fibers could act as grippers that bind objects in the presence of light. With the illumination turned off, the grippers could controllably release the objects. By placing the fibers closer to the edge of the sample, the combination of heat and light could be harnessed to bind and release larger objects. We also show that by illuminating the fibers separately, we can manipulate the motion of the individual finger-like objects, and thus, potentially expand the utility of the system. Overall, our findings provide guidelines for controllably reconfiguring the shape of soft materials and thus, tailoring the material to display different functionalities in different environments. Our work was featured on the cover of *Soft Matter* (see **Fig. to the right**) containing our paper.

Finally, we note another set of studies that are currently in progress. Namely, the fibers are now completely embedded in the gel and different layers of the system can encompass different orientations of the fibers. For example, in **Fig. 6,** 16 relatively short, closely spaced fibers are localized in the horizontal direction of the top layer and 16 fibers of these fibers are arranged in the vertical direction of the bottom layer. When the thermo-responsive LCST gel is heated, it undergoes a non-uniform contraction due to the presence of the stiff fibers. We are currently undertaking studies that exploit this behavior to tailor the dynamic 3D reconfiguration of the composite.

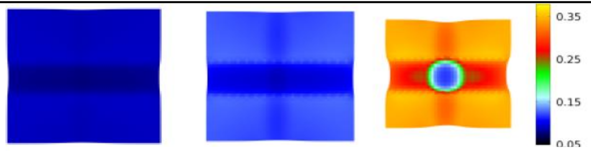

Fig. **6** Computer simulations of a portion of the fiber-filled composite. 16 fibers are arranged in a horizontal direction in the top gel layer and 16 are placed in vertical arrangement in the bottom gel layer (as visible in the middle image). Gel collapses as the heat is increased (going from left to right). Color bar indicates the polymer volume fraction ϕ and shows that the gel is less collapsed near the fibers (i.e., ϕ is smaller near the fibers).

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Papers acknowledging funding from previous grant period

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