

Starch granules transform hydrogels into dynamic tissue mimics

Dynamic and Programmable Cellular-Scale Granules Enable Tissue-like Materials

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Matter **2**, 948 (2020)

Recommended with a Commentary by Rae M Robertson-Anderson 

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Living tissues, composed of dense cellular ensembles and an extracellular matrix (ECM), display highly complex properties like strain-stiffening, self-healing, and mechanical memory. However, a major challenge in soft matter biomimetics is that conventional synthetic polymers and hydrogels typically lack the necessary dynamic, hierarchical structure to replicate these coupled cellular- and ECM-level behaviors simultaneously (1).

Fang and co-workers present a significant leap in the design of synthetic soft materials to address this engineering challenge. By incorporating cellular-scale hydrated starch granules into conventional hydrogel matrices comprising polyacrylamide (PAA) and alginate (Alg), they achieve a suite of highly desirable, emergent mechanical properties including strain-stiffening, self-healing, and mechanical memory (**Fig 1**).

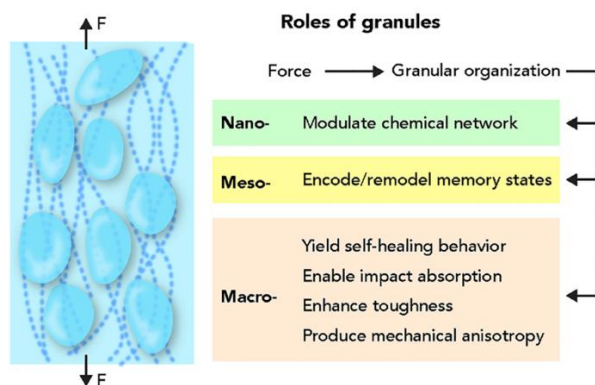


Figure 1. Summary of key features across multiple length scales enabled by starch granules for tissue-like materials. Reproduced from the recommended paper.

The novelty lies in recognizing that the starch granules are not passive, inert fillers but rather dynamic, mesoscopic, interacting particles suspended within a soft medium. Specifically, the

alpha-glucan chains on the semi-crystalline starch surface are key, enabling dynamic hydrogen bonding (H-bonding) between the hydroxyl groups on the starch granule surface and the amide groups within the PAA matrix. This rapid, reversible starch-matrix interaction acts as the fundamental energy dissipation and structure-tuning mechanism, which is key to the composite's unique behavior (**Fig 2**).

The dynamic nature of these bonds, which allows them to rupture under stress and spontaneously reform, is what enables both the excellent energy dissipation and the self-healing capability (2). The reversible nature is essential for the material to dissipate mechanical energy without permanent failure (allowing high stretchability) and to recover its initial state after damage (enabling self-healing and mechanical memory).

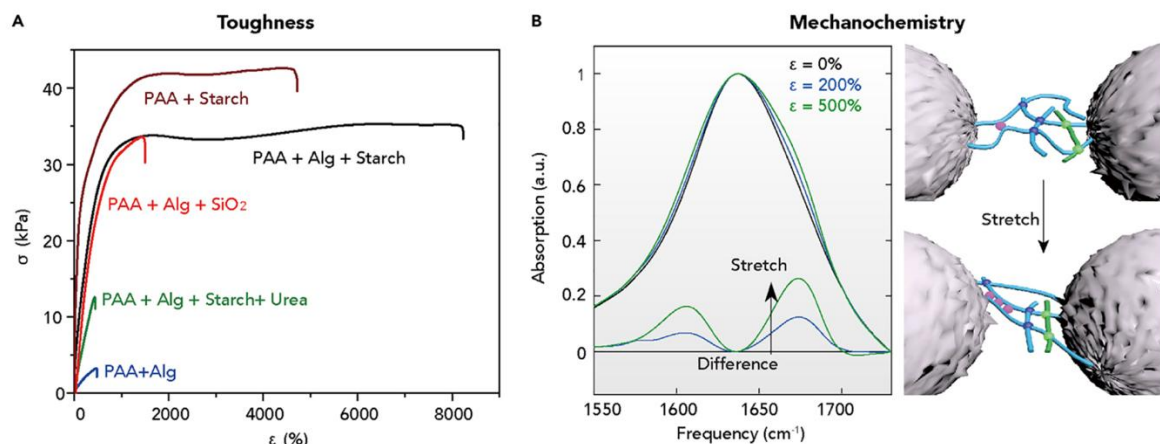


Figure 2. Hydrogen bonding enables toughness and stretchability. (A) Toughness. Stress-strain curves illustrate the roles of individual components in determining material stretchability. Urea disrupts hydrogen bonding; alginate (Alg) reduces PAA crosslinking density to support starch reorganization; silica (SiO₂) particles of similar size as starch granules but without H-bonding capability do not recapitulate mechanical toughness of starch composites. (B) Mechanochemistry. Left: attenuated total reflectance Fourier transform infrared spectra of starch-Alg-PAA composite at different strain levels. Difference spectra (scale factor, 3) are plotted at the bottom with respect to the unstrained sample (black trace). Blue and green traces represent data from $\epsilon = 200\%$ and $\epsilon = 500\%$, respectively. Right: schematic depicting enhancement of interchain hydrogen bonds (magenta dots) between adjacent PAA side chain (blue lines) upon stretching. The purple and green dots are the covalent crosslinking points in the PAA (blue lines) and Alg (green lines) network. Reproduced from the recommended paper.

The composites also exhibit emergent stress-stiffening from dynamic reinforcement of the hydrogel by the granules. The pronounced strain-stiffening observed arises not just from particle contact, but from the reorganization and stabilization of dynamic H-bond-mediated force chains. Under load, the starch granules are forced into closer proximity. The dynamic H-bonds on the granule surfaces and with the PAA chains rapidly break and reform, effectively increasing the local cross-linking density only in the highly strained regions. This transient, self-reinforcing network of bonds is the primary cause of the non-linear stiffening response (3). The material's ability to dissipate energy (low hysteresis in the first few cycles) through bond rupture further supports this interpretation.

Composites also exhibit mechanical memory and programmability. Namely, by applying a large uniaxial strain (i.e., programming), the material's mesoscopic structure is driven to a new, stable, anisotropic state. The granules align along the loading direction, and the density of inter-granular H-bonds is maximized in this new configuration. This structural reorganization is stable because the system settles into a lower energy state defined by the new network geometry.

Finally, the dynamic and reversible nature of the H-bonding mechanism provides an efficient pathway for structural restoration and self-healing (**Fig 3**). When a cut is introduced, the broken polymer and granule surfaces expose free hydroxyl and amine groups, allowing the H-bonds to spontaneously re-establish connections across the interface, restoring mechanical integrity.

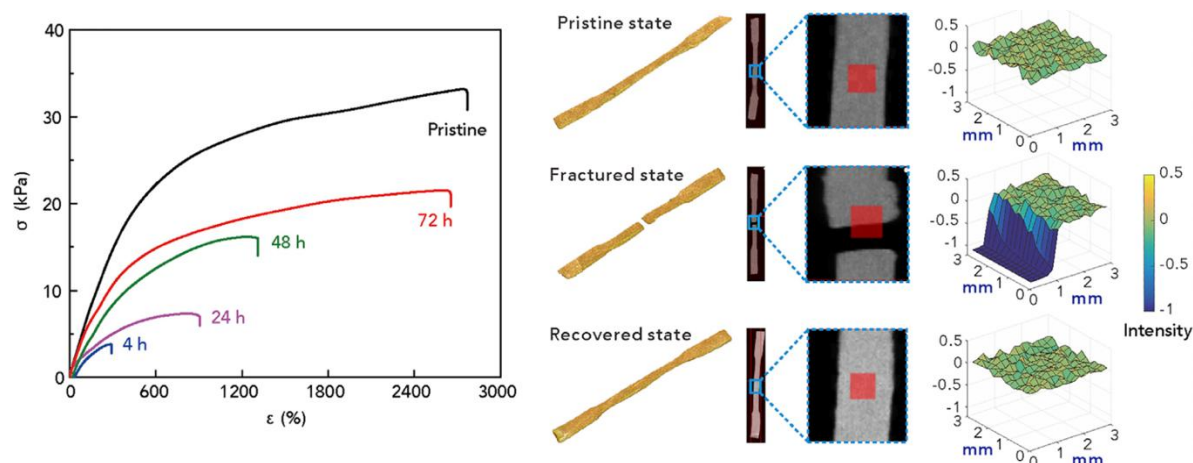


Figure 3. Starch composites exhibit tissue-like self-healing. (Left) Stress-strain curves demonstrate the self-healing behavior of the starch-PAA-Alg composites. Initial malleability and Young's modulus were gradually recovered after extended healing under ambient conditions. (Right) X-ray tomography data (3D volume rendering, 2D view and surface profiles) from pristine, fractured, and recovered states of a composite. Red squares mark regions used for profile analysis. Reproduced from the recommended paper.

This work introduces starch granules as a powerful material to sculpt biomimetic soft matter systems and opens the door to expand the emergent mechanical and structural properties of this platform (4). For example, modeling the effective, strain- and temperature-dependent interaction potential between the granules and matrix as a function of local strain and polymer concentration could predict and more completely map the phase space of composition-structure-mechanics relations. Additionally, determining the effect of particle size, shape, and surface chemistry on the observed memory and stiffness would enable more precise tuning of mechanical programmability. Finally, the current system is passive, but one could imagine making granules and/or the matrix active via responsiveness to light, pH, or electric fields to enable non-mechanical sculpting. For example, granules with anionic or cationic surface charges could be oriented via electric fields to locally modulate the composite mechanics, and photo-responsive polymers, such as poly(ethylene glycol) diacrylate could be incorporated to spatiotemporally pattern the matrix structure surrounding the granules and alter starch-matrix interactions.

References:

1. Tahmasebi, Pejman. A state-of-the-art review of experimental and computational studies of granular materials: Properties, advances, challenges, and future directions. *Progress in materials science* 138 (2023): 101157.
2. Han, Liujia, Wenhao Qi, Kai Liu, and Peiyi Wu. "Multi-Armed Molecule Drives High Energy Dissipation and Stiffness via Physically Cross-Linking." *Small* 21, no. 25 (2025): 2503823.
3. Shi, X., Shivers, J. L., MacKintosh, F. C., & Janmey, P. A. (2025). Tissue-like compression stiffening in biopolymer networks induced by aggregated and irregularly shaped inclusions. *bioRxiv*, 2025-06.
4. Lin, Y., Gao, X., Yue, J. *et al.* A soil-inspired dynamically responsive chemical system for microbial modulation. *Nat. Chem.* **15**, 119–128 (2023). <https://doi.org/10.1038/s41557-022-01064-2>