Plant-inspired strategy uses photosynthesis to strengthen 3D printed polymers

The mechanical properties of engineering materials constantly decline during service life, owing to fatigue or degradation. Plants, by contrast, harness their metabolism to enhance their strength and stiffness by remodeling parts of their structures. For instance, glucose produced during photosynthesis can be transported to specific sites in the plant, such as tree trunks and branches, to generate rigid polysaccharide structures. Recently, inspired by this natural process, researchers from the University of Southern California designed a series of three-dimensional (3D)-printable polymers that can be remodeled and strengthened by the photosynthesis of embedded living chloroplasts (**Figure a**). This work was reported in a recent issue of the *Proceedings of the National Academy of Sciences* (<https://doi.org/10.1073/pnas.2016524118>).

“Typical engineering materials do not communicate with living biological processes. Here, we construct a communication channel between the

engineering materials and the living photosynthesis of chloroplasts,” say Qiming Wang and Nicholas X. Fang, the work’s principal investigators. “Through this communication channel, the engineering materials can be modulated [on-demand] via living biological processes and endowed with living functions that previously only belonged to living creatures.”

A polymeric network was created by combining spinach-extracted chloroplasts with a polymer resin containing both acrylate and isocyanate distal (NCO) groups. The resin can be used in techniques such as stereolithography, to 3D print various geometries based on the photopolymerization of the acrylate groups. Printing speeds of 75–400 $\mu\text{m/s}$ and resolutions of $\sim 25 \mu\text{m}$ were achieved. Subsequent production of glucose during photosynthesis results in additional cross-linking, where the free NCO groups strongly react with the hydroxyl groups on the glucose to generate urethane linkages ($-\text{NO}-\text{CO}-\text{O}-$). This greatly enhances the mechanical properties of the 3D printed materials (**Figure b**).

“We harness the photosynthesis of chloroplasts to produce glucose within the 3D printed material matrix to remodel the material [properties],” the researchers tell *MRS Bulletin*.

The photosynthesis-assisted mechanical enhancement could be modulated with patterned light. Local strengthening was achieved by exposing the sample to light of a specific shape. This capability makes it possible to fabricate engineering materials with stiffness gradients. It can also be applied to detour crack paths in the material.

The photosynthesis-assisted strengthening can also be adjusted through external mechanical preload. Materials showed higher strength and stiffness when they were stretched with mechanical loads while being illuminated (i.e., when photosynthesis occurred). A possible reason for this is that the external forces deform the primitive network, and the additional glucose-NCO cross-links maintain the compact architecture. This may potentially be utilized to design materials that conform to external pressures. For instance, this photosynthesis-assisted strategy could be used to fabricate shoe soles with a nonuniform stiffness distribution corresponding to the inhomogeneous stress distribution applied by the foot, given that the forces on the foot are not uniform, making the footwear more comfortable.

Notably, the photosynthesis-assisted remodeling and strengthening process can be stopped by temporarily freezing the samples at $0-4^\circ\text{C}$ to inhibit the activity of the chloroplasts. After returning to room temperature, the photosynthesis process is restored, and the material can be strengthened again. “This is a critical difference between this hybrid synthetic-living material and existing synthetic materials,” says Xianlei Li, a research fellow from the National University of Singapore, who was not involved in this study. “The properties of this material can be controlled through modulating the living activity of the embedded chloroplast.” Also, the mechanical enhancement can be reversed by periodic acid (HIO_4) through cleaving the glucose cross-linkers (HIO_4 can cleave the carbon–carbon bonds

(a) Schematic illustration of photosynthesis-assisted remodeling of the synthetic polymer and (b) its self-strengthening capability. Credit: Qiming Wang.

in the carbohydrate through oxidation cleavage).

Further, due to the additional cross-linking between glucose and free NCO groups in the polymer matrix, photosynthesis enables healing of the fractured polymer materials. The healed

samples exhibited tensile properties including stretching up to 1.8 times the original length without breakage.

“This hybrid synthetic-living material has great potential applications due to its great functions such as self-strengthening, self-healing, and

temporary freezing.” For the next step, the researchers say, “we continue to work on inventing new communication channels between living chloroplasts and 3D printed engineering materials for new functions/properties.”

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