4D-printable thermoresponsive hydrogel exhibits high mechanical properties

Thermoresponsive hydrogels are soft materials that can change physical properties with variations in ambient temperature, and show great potential in biomedical applications. However, conventional temperature-responsive hydrogels such as poly(*N*-isopropylacrylamide) (PNIPAM) commonly show weak mechanical performance and lack an energy-dissipating mechanism, which impedes their use in practical applications. Some strategies, including double networks, dual-cross-linking, and compositing, can be used to improve the toughness, but these reduce the thermoresponsive capabilities. Creating thermosensitive hydrogels that maintain their mechanical performance is still a major and urgent challenge.

Recently, researchers from the University of California, Los Angeles, have designed hydrogels that couple thermoresponsive and tough components into a single network, yielding high toughness and temperature-actuation performance. This work was reported in a recent issue of *ACS Applied Materials & Interfaces* (<https://doi.org/10.1021/acsami.0c17532>).

Through UV-light irradiation, temperature-responsive PNIPAM was grafted onto the tough polymer backbone of poly(vinyl alcohol) (PVA) and its methacrylate derivatives (PVA-MA). After the one-pot synthesis, the sample was immersed in a Na_2SO_4 salt solution to further strengthen the hydrogel network where the PVA aggregates and crystallizes under these conditions (**Figure a**). Notably, due to the single-network architecture, this strengthening process does not weaken the stimuli-responsive properties.

“Molecularly integrating a tough component and a stimuli-responsive component in a single polymer network can yield hydrogel actuators with simultaneous high strength and toughness, and stimuli responsiveness,” says Ximin He, the work’s principal investigator. After heating, the volumetric contraction of the hydrogel (i.e., PVA/(PVA-MA)-g-PNIPAM) could reach ~50% with change in transparency, and recover to its original size by cooling.

Thanks to the distinct toughness and crystallinity of the PVA backbone, this hydrogel showed excellent mechanical performance and exhibited 100 times higher toughness (~10 MJ/m³) than conventional PNIPAM hydrogels. As shown in **Figure b**, with the physical

deformation of the hydrogel from 25°C to 40°C, it was able to behave as a linear actuator capable of lifting a weight while the regular PNIPAM sample fractured.

“The actuation force of a hydrogel actuator is limited by its strength/modulus, as the passive deformation of the actuator during actuation would relax the tension in the material,” He tells *MRS Bulletin*. “Therefore, improving strength and toughness of hydrogel actuators also promotes higher actuation force.” The mechanical toughness is considerably regulated by the concentration of a salting-out agent (i.e., Na_2SO_4) and solid content of the hydrogel.

Interestingly, based on the four-dimensional (4D) printing technique, bilayer actuators of multifarious geometry were easily manufactured. These bilayer actuators were composed of a passive layer of PVA-based hydrogel and an active layer of PVA/(PVA-MA)-g-PNIPAM hydrogel with potential to be utilized in several applications. For example, the bilayer gripper could perform a fold-unfold motion under thermal actuation and could be used to pick up objects (**Figure c**). In addition, with structural design and the aid of the 4D printing technique, the contraction ratio and actuation speed of the printed hydrogel geometry could be controlled. Printed lattice-architected hydrogels, as shown in **Figure d**, exhibited three times the contraction ratio and four times the actuation speed compared to the bulk sample.

“For the next step, we plan to print underwater soft robots with more complex structures and explore ways to alternatively modify PVA to have other stimuli responsiveness,” He says. “We envision its broad potential applications including printing underwater robots with high toughness and various stimuli responsiveness, and printing shape-morphing structures (metamaterials) with higher toughness.”

Yufeng Shou

Four-dimensional printable PVA/(PVA-MA)-g-PNIPAM hydrogel. (a) Illustration showing the structure and composition, (b) linear actuator, (c) bilayer gripper, and (d) printed lattice-structure hydrogel. NIPAM is *N*-isopropylacrylamide; PVA is poly(vinyl alcohol); PVA-MA is PVA and its methacrylate derivatives. Credit: Ximin He.