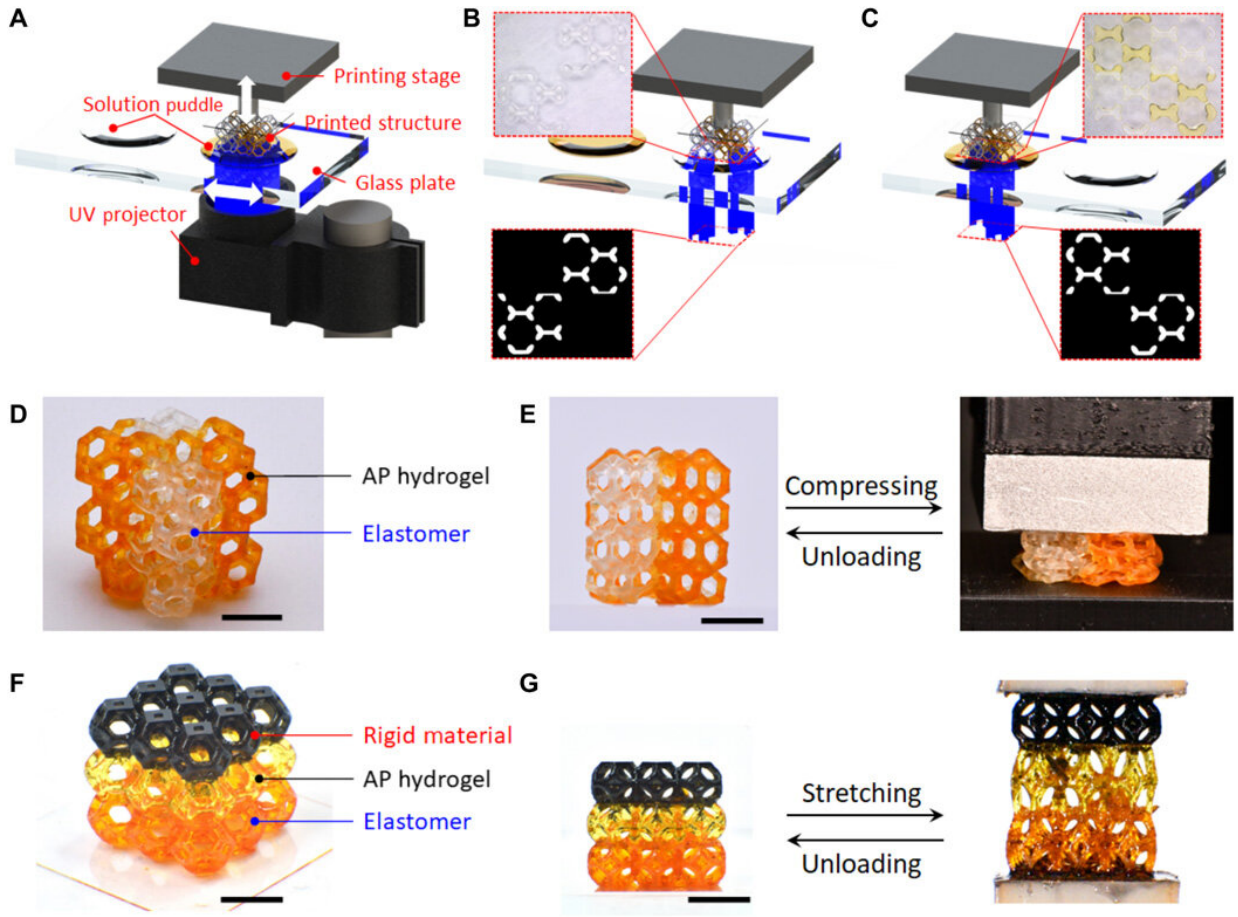
3-D printing highly stretchable hydrogel with diverse UV curable polymers

January 20 2021, by Thamarasee Jeewandara



Multimaterial 3D printing hydrogel with other polymers. (A) Illustration of the DLP-based multimaterial 3D printing apparatus. (B and C) Processes of printing elastomer and hydrogel structures, respectively. (D) Snapshot of a diagonally symmetric Kelvin form made of AP hydrogel and elastomer. (E) Demonstration of the high deformability of the printed diagonally symmetric Kelvin form. (F) Snapshot of a printed Kelvin foam consisting of rigid polymer, AP hydrogel, and

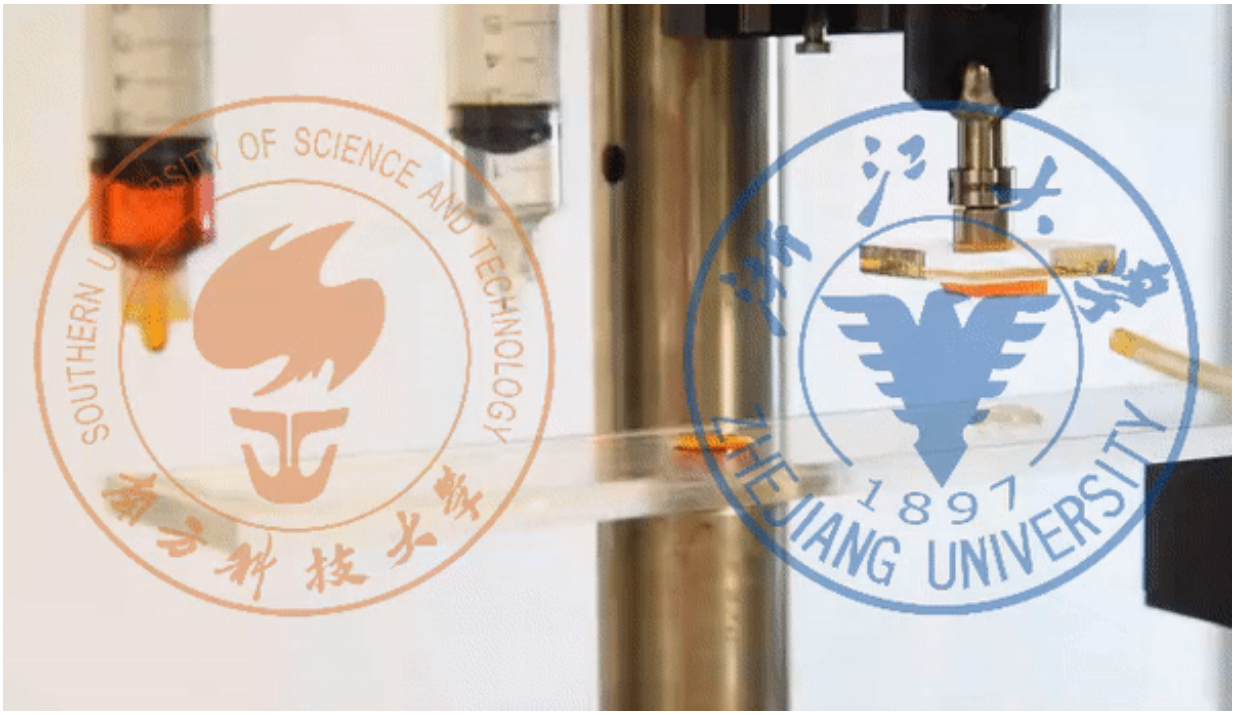
elastomer. (G) Demonstration of the high stretchability of the printed multimaterial Kelvin foam. Scale bar, 5 mm. (Photo credit: Zhe Chen, Zhejiang University.) Credit: Science Advances, doi: 10.1126/sciadv.aba4261

Hydrogel-polymer hybrids are widely used across a variety of applications to form biomedical devices and flexible electronics. However, the technologies are presently limited to hydrogel-polymer hybrid laminates containing silicone rubbers. This can greatly limit the functionality and performance of hydrogel-polymer-based devices and machines. In a new study, Qi Ge, and a team of scientists in mechanics, mechatronic systems, flexible electronics, chemistry and advanced design in China, Singapore and Israel demonstrated a simple and versatile multi-material three-dimensional (3-D) printing approach. The method allowed the development of complex hybrid 3-D structures containing highly stretchable and high water content acrylamide—poly(ethylene glycol)diacrylate (PEGDA) abbreviated as AP hydrogels, covalently bonded with diverse ultraviolet (UV) curable polymers. The team printed the hybrid structures on a self-built digital-light processing (DLP)-based multi-material 3-D printer. They facilitated covalent bonding between the AP hydrogel and other polymers through incomplete polymerization initiated by a water-soluble photoinitiator. The team displayed a few applications based on this approach to propose a new way to realize multifunctional soft devices and machines by bonding hydrogel with diverse polymer in 3-D forms. The work is now published on *Science Advances*.

The new 3-D printing approach

Hydrogels are water containing polymer networks that have a variety of applications across biomedical devices and flexible electronics. Many applications in materials engineering combine hydrogels with other

polymers to design hybrid structures to protect, reinforce or add new functionalities to hydrogel constructs such as hydrogel-based lubricant skin and elastomeric antidehydration coating. However, most polymers that form hybrids with hydrogels are mostly limited to silicone rubbers and laminate structures that constrain the functionality and performance of such devices and machines. As a result, materials scientists aim to develop effective alternative strategies. In this work, Ge et al. reported a simple and versatile multi-material 3-D printing approach to develop highly complex, hybrid 3-D structures. The new method will pave an efficient path to develop soft devices and machines with greatly extended functionalities and performances.



The DLP (digital-light printing)-based multimaterial 3D printing system. Credit: Science Advances, doi: 10.1126/sciadv.aba4261

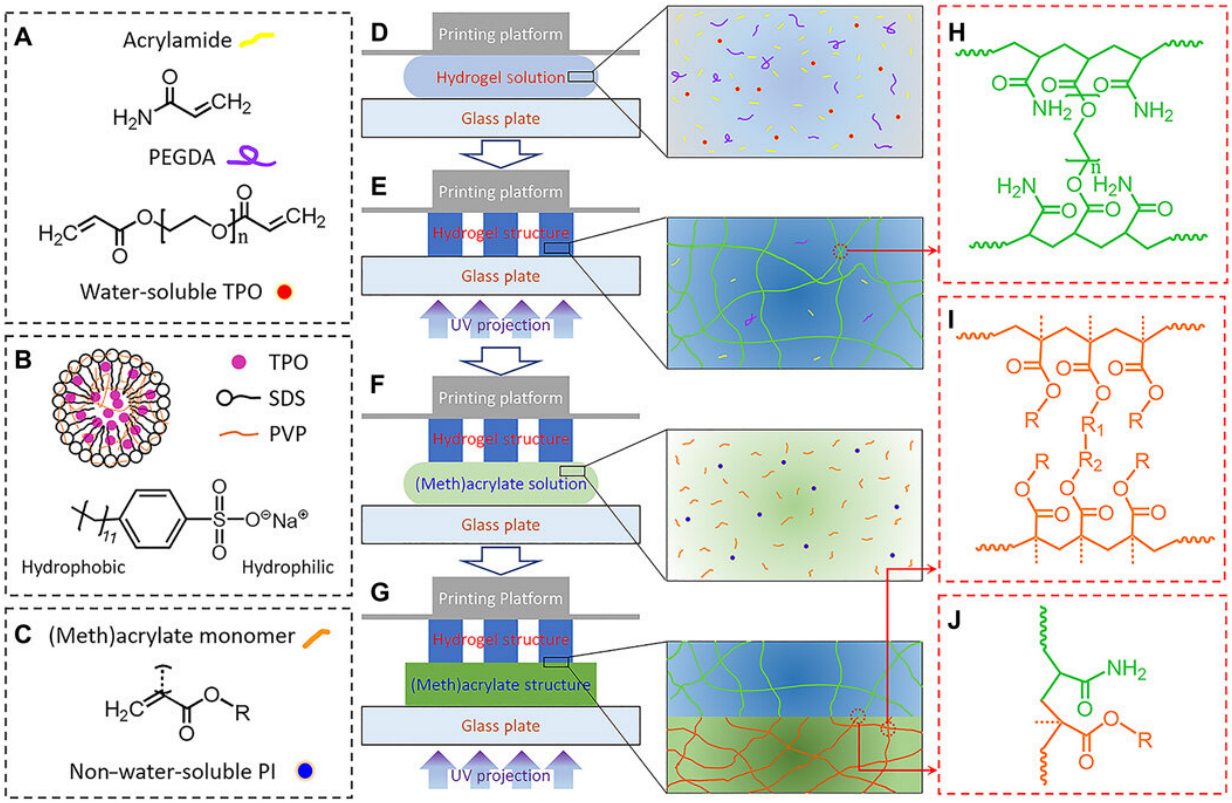
Multi-material 3-D printing with other materials

The materials contained highly-stretchable hydrogels with a high-water content, covalently bonded with diverse water-insoluble UV curable polymers such as elastomers, rigid polymers, shape memory polymers and UV-cured methacrylate networks. As proof of concept, they used the multi-material 3-D printing approach and demonstrated a number of applications including 4-D printing cardiovascular stents for drug delivery and 3-D printing ionic conductors. Ge et al. first printed the hydrogel-polymer structures on a self-built, high-resolution, high-efficiency digital-light-processing-based multi-material 3-D printer using a "bottom-up" approach. During the process, digitalized UV-light irradiated from the UV projector was placed below the printing stage and could be moved vertically to control the layer thickness of each printed layer. A glass surface between the printing stage and UV projector supported two or three polymer precursor solution puddles to deliver a precursor solution as required. The scientists used highly stretchable and high-water content UV curable acrylamide-poly(ethylene glycol) diacrylate (PEGDA), known as the AP hydrogel. They obtained the UV curable polymers as commercially available methacrylate-based 3-D printing polymers.

Materials bonding mechanism

The team explored the mechanisms that allowed the AP hydrogel to firmly bond with other methacrylate-based UV curable polymers. For this, they prepared the AP hydrogel precursor solution by mixing the acrylamide powders, PEGDA polymer and water-soluble photoinitiators in water. They tuned the mechanical behavior of the material by changing the ratio of hybrid polymers and by regulating the water content. The self-prepared water soluble photoinitiator (2,4,6-trimethylbenzoyl diphenylphosphine oxide abbreviated as TPO) formed a key component of the AP hydrogel precursor solution,

rendering it highly UV curable and 3-D printable. To 3-D print a hybrid structure containing the AP-hydrogel and other polymers, Ge et al. also chose a number of commercially available polymer precursor solutions such as methacrylate-based monomers, crosslinkers and oligomers.

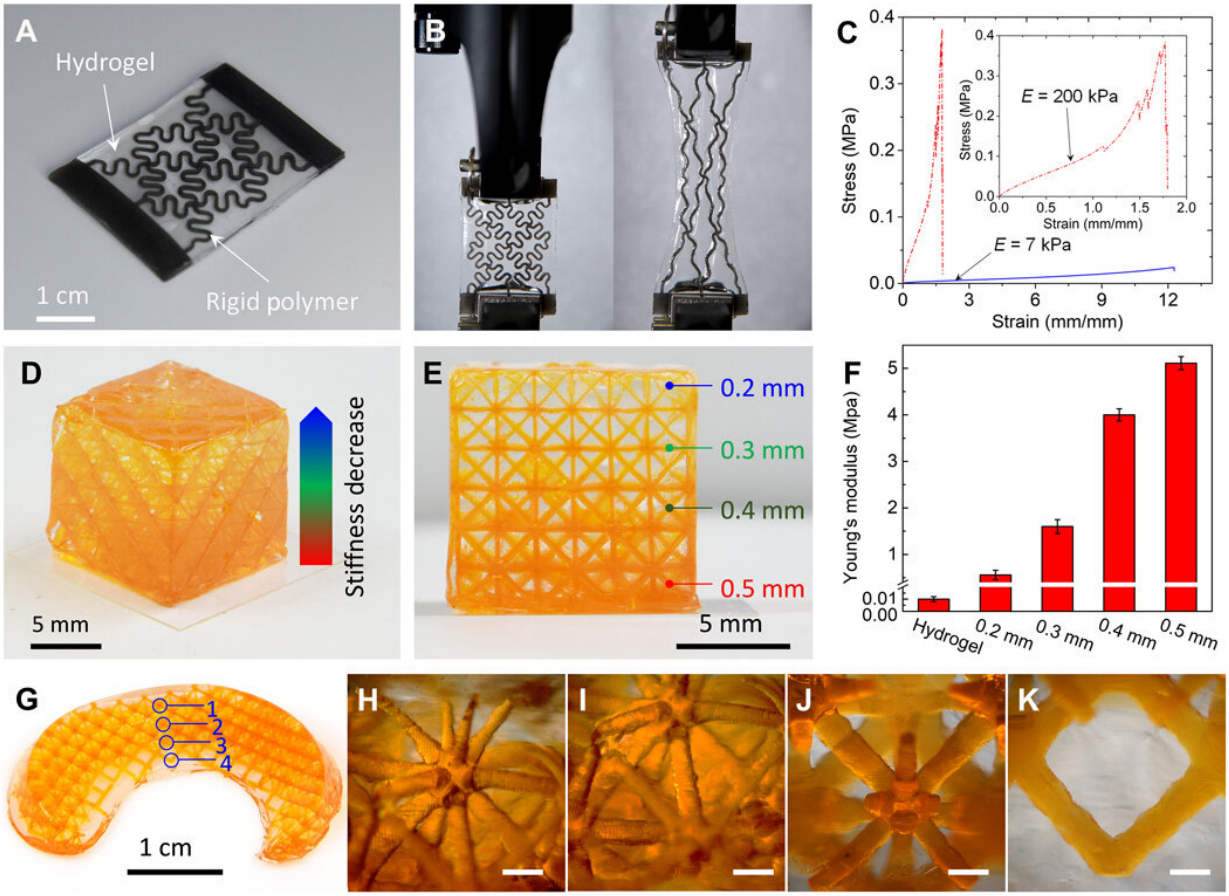


Materials and bonding mechanism. (A) Chemicals used to prepare the AP hydrogel solution. (B) Illustration of the water-soluble TPO nanoparticle. PVP, polyvinylpyrrolidone. (C) Possible chemical structure of the (meth)acrylate-based polymer solution. PI, photoinitiator. (D to G) Schematics of the process of printing hydrogel-polymer multimaterial structure. (H to J) Chemical structures of cross-linked AP hydrogel, AP hydrogel–(meth)acrylate polymer interface, and cross-linked (meth)acrylate polymer, respectively. R, R1, and R2 are the possible middle chains in (meth)acrylate polymer. Credit: Science Advances, doi: 10.1126/sciadv.aba4261

The multi-material 3-D printing method produced chemical structures with the proposed interface bonding mechanism between AP hydrogel and the methacrylate monomer. The reactive radicals at the material interface allowed chemical bonding between the polymer and hydrogel layers. To validate the proposed mechanism of interfacial bonding, Ge et al. conducted Fourier transform infrared (FTIR) spectroscopy and compared the conversion and kinetics of polymerization between the materials. Ge et al. then investigated the interfacial toughness between the hydrogel and the UV curable polymer by performing 180 degrees peeling tests. The results showed the energy needed to break the hydrogel-polymer interface to be greater than the energy needed to break the hydrogel itself.

Proof of concept: 3-D printed, rigid polymer-hydrogel composites, cardiovascular stents and flexible electronic devices

Based on the properties of new materials, Ge et al. easily developed rigid polymer-reinforced hydrogel composites with superior mechanical performance and design flexibility. The team designed a series of microstructures to reinforce rigidity and explored the existing challenge of stiffness mismatch between hydrogels and human tissues, which they demonstrated by printing a meniscus consisting of AP hydrogel reinforced by a Vero rigid polymer. They mechanically tuned the material by varying the rigid microstructures to translate the material for enhanced functionality and performance for 3-D printed biological materials and tissues. The scientists next used shape memory polymers (SMPs) as an ideal 4-D printing material to 3-D print shape cardiovascular stents that can expand in blood vessels with stenosis. They used multi-material 3-D printing to convey drug releasing functionality into the cardiovascular SMP stent by including hydrogel into the construct.



3D printed rigid polymer–reinforced hydrogel composites. (A to C) Hydrogel composite reinforced by horseshoe rigid polymer structure. (A) Isotropic picture of a printed composite. (B) Snapshots of the composite before uniaxial tensile test (left) and after stretched by 175% (right). (C) Comparison of the stress-strain behavior between pure hydrogel and composite. (D to F) Hydrogel composite reinforced by rigid polymer lattice structure. (D) Isotropic picture of a printed composite cube with gradient stiffness. (E) Front view of the printed composite cube where the diameter of truss rod decreases from 0.5 to 0.2 mm. (F) Measured compressive modulus for pure hydrogel and rigid polymer lattice structure–reinforced hydrogel with different rod diameters. (G) Snapshot of a printed meniscus made of hydrogel reinforced by rigid lattice structure. (H to K) The corresponding microscopic images of the microstructures at locations 1 to 4 within the printed meniscus (scale bars, 500 μm). (Photo credit: Zhe Chen, Zhejiang University.) Credit: Science Advances, doi: 10.1126/sciadv.aba4261

They programmed the SMP stent into a compact shape and recovered its original shape upon implantation at a different programmed temperature. Using a multi-material DLP (digital-light processing) printer, they developed the SMP-hydrogel stent and loaded a red dye into the construct to mimic drug release. The team conducted the experiment in a plastic tube to show stent expansion upon implantation and hydrogel-based drug release. Thereafter, they employed the ionic conductivity of hydrogels as a promising property for flexible electronics. For this, they printed a soft pneumatic actuator with a hydrogel strain sensor and conducted finite element analysis (FEA) to simulate bending of the structure to form a printed flexible electronic device with a 3-D ionic conductive hydrogel lattice structure and water-proof elastomeric protective skin.

The shape-memory polymer/hydrogel stenting procedure followed by drug

delivery via hydrogel skins. Credit: Science Advances, doi: 10.1126/sciadv.aba4261

Outlook

In this way, Qi Ge and colleagues developed a simple and versatile multi-material 3-D printing approach to fabricate highly complex, hybrid 3-D architectures. They then used a self-built digital-light processing multi-material 3-D printer to form hydrogel-polymer hybrid 3-D structures. The team displayed a series of applications including a 3-D printed meniscus, 4-D printed cardiovascular stent and a 3-D printed ionic conductor, as advantages of the approach.

More information: Ge Q. et al. 3D printing of highly stretchable hydrogel with diverse UV curable polymers, *Science Advances*, DOI: 10.1126/sciadv.aba4261

Grigoryan B et al. Multivascular networks and functional intravascular topologies within biocompatible hydrogels. *Science*, 10.1126/science.aav9750

Kim Y. et al. Ferromagnetic soft continuum robots, *Science Robotics*, 10.1126/scirobotics.aax7329

hydrogel-diverse.html