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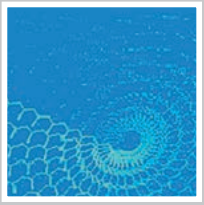

Polymer and Colloid Highlights

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Double Network Granular Hydrogels

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Hydrogels are polymeric networks filled with water. Their ability to retain water and thereby moisture, the possibility to render them biocompatible and modify them with biologically relevant functionalities render them attractive for biomedical applications.[1] Certain hydrogels respond to external stimuli, a feature that makes them particularly attractive for soft robotic applications.[2] Unfortunately, the limited stiffness and/or toughness of many hydrogels prevent their use in this field. These parameters can be increased if hydrogels are formulated as double networks.[3] However, the multi-step fabrication of these double network hydrogels prevents their 3D printing. 3D printing, however, would enable nonlinear changes in the composition and hence, stiffness and toughness of hydrogels, which would be key for their use as soft actuators or robots. To address this limitation, we introduced 3D printable double network granular hydrogels (DNGHs) composed of hydrogel-based microparticles, so-called microgels made of poly(2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) that are connected through a second poly(acrylamide) (PAM) hydrogel network that interpenetrates and covalently crosslinks them, as shown in Fig. 1a.[4]

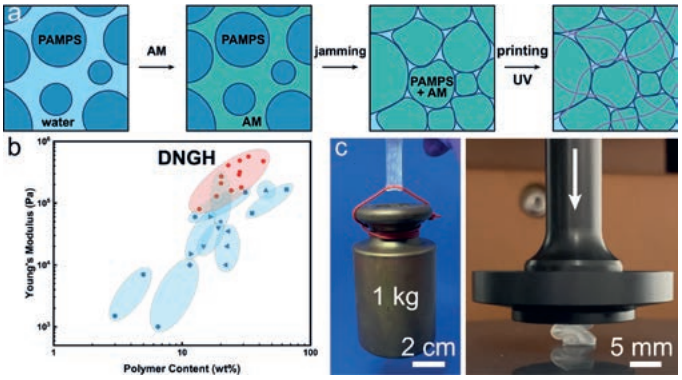

Fig. 1. (a) Process flow for the fabrication of DNGHs. (b) Ashby plot of 3D printed hydrogels that have previously been published (blue) and our recently published DNGHs (red).[4] (c) DNGH strip holding a 1 kg weight (left). A DNGH 3D printed cylinder is compressed at 80% strain (right).

Certain hydrogels can be 3D printed from bulk solutions. However, hydrogels formed from precursor solutions that fulfill the rheological requirements to be 3D printed are soft, as summarized in Fig. 1b. This limitation can be overcome if the precursor solution is first processed into microgels that are up-concentrated to form a shear thinning ink that exhibits a low yield stress. This two-step process offers the distinct advantage that it decouples the rheological properties of the hydrogel precursor solution from those of the ink. As a result, many more hydrogels, including strong or tough ones, can be 3D printed.[5] Unfortunately, the inter-particle connections of the resulting granular hydrogels are weak such that their Young's moduli do not exceed 10–100 kPa, even if adjacent microgels are connected through host–guest chemistries,[6] ionic interactions,[7] or covalent bonds.[8] We overcame this problem by connecting microgels through a percolating network that interpenetrates and simultaneously crosslinks them.[4] Thereby, this network distributes the stress more homogeneously such that the stiffness of these 3D printable hydrogels is at least 4-fold higher than that of any previously reported 3D printable hydrogel, as shown in Fig. 1b. As a result of the firm inter-particle connections, DNGHs can repetitively bear loads of over 1 MPa under tension and compression without appreciable damage, as shown in Fig. 1c.

Key to the high stiffness our DNGHs display is the percolating network. Its formation is enabled by the sponge-like structure of microgels that allows loading them with a high concentration of monomers without risking that the monomers flow after they have been 3D printed. Thereby, we ensure a good shape retention of the 3D printed material while maintaining the mobility of the monomers that allows the formation of a percolating network after 3D printing. Importantly, because the percolating network is formed after completion of the 3D printing process, the stiffness and toughness of the DNGHs are isotropic and independent of the printing direction, in stark contrast to many previously reported 3D printed polymers.

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