Highly compliant and self-healable 3D architected polyelectrolyte complexes via projection stereolithography

Amylynn Chen[1], Daryl Yee[2], Widianto Moestopo[1], Julia R. Greer[1]

1. California Institute of Technology, Pasadena, CA, United States.
2. Massachusetts Institute of Technology, Cambridge, MA, United States.

Additive manufacturing (AM) has been demonstrated as an efficient method to produce high-accuracy and isotropic parts with complex geometries. Projection micro-stereolithography (PμSL) is a rapid AM technique based on photo-induced polymerization of liquid photoresin, which is capable of fabricating complex 3D structures in a layer-by-layer fashion. Currently, the established photolithography-compatible materials are high crosslinked brittle and inert polymers, which limits their applications. There has been a growing effort to seek compliant materials for AM with advanced functionalities, such as stimuli-responsiveness, self-healing, deformability, degradability, and recyclability.

Polyelectrolyte complexes (PECs) are a class of supramolecular polymers that consist of oppositely charged polyions interconnected by electrostatic interactions. Generally, the synthesis of PECs involves multiple steps, such as polyanion/polycation synthesis, purification and mixing of the polymer components to achieve desirable properties. These systems are notable for their high compliance and rapid self-healing at the hydrated state but require multistep processes that are unsuitable for AM. To maintain their properties, these materials are often stored in water. This raises concerns for the consistency of the mechanical properties and long-term stability in ambient environment and limits the potential applications. In this work, we demonstrate the a “one-pot” approach to fabricate 3D structures of PECs via PμSL, where the material obtains >450% strain at break and ~3MPa failure strength through tensile testing. After equilibrating in ambient environment for more than 20 days, our ASTM D638 standard type-V tensile specimens still exhibit 100% of the original strain. We have also investigated the tunability, cyclability, reproducibility, strain-rate dependency and self-healing properties of the additively manufactured PECs. This simple and versatile approach opens up a new space for 3D printing of self-healable and responsive polymers with tunable properties.