

3D Printed Self-Healing Elastomers for Modular Soft Robotics

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Abstract

Advances in materials, designs, and controls are propelling the field of soft robotics at an incredible rate; however, current methods for prototyping soft robots remain cumbersome and struggle to incorporate desirable geometric complexity. Herein, a vat photopolymerizable self-healing elastomer system capable of extreme elongations up to 1000% is presented. The material is formed from a combination of thiol/acrylate mixed chain/step growth polymerizations and uses a combination of physical processes and dynamic-bond exchange via thioethers to achieve full self-healing capacity over multiple damage/healing cycles. These elastomers can be 3D printed with modular designs

capable of healing together to form highly complex and large functional soft robots. Additionally, these materials show reprogrammable resting shapes and compatibility with self-healing liquid metal electronics. Using these capabilities, sub-components with multiple internal channel systems were printed, healed together, and combined with functional liquid metals to form a high-wattage pneumatic switch and a humanoid-scale soft robotic gripper. The combination of 3D printing and self-healing elastomeric materials allows for facile production of support free parts with extreme complexity, resulting in a paradigm shift for the construction of modular soft robotics.

Introduction

Soft robotics aim to provide safe, adaptable, and articulate robots by replicating biological form and function through the use of compliant and responsive materials.¹⁻⁴ The fabrication of soft robotic components has traditionally relied on soft lithography through molding, which limits object complexity, heterogeneous material integration, size, and throughput.^{5,6} However, innovations in fields of additive manufacturing (AM) have begun to displace cast and mold steps in the production of soft robots.⁷⁻¹¹

AM encompasses a wide variety of fabrication techniques to construct 3-dimensional objects layer-by-layer. The fabrication of soft robotic components using direct-write, ink-jetting, selective laser sintering, and vat photopolymerization (VP) processes have all been recently demonstrated, but no one technique can overcome trade-offs in speed, resolution, design complexity, scale, and materials integration.⁷ For example, VP, which uses patterned light to sequentially photopolymerize layers of resin, is a technique with excellent potential for the fabrication of soft robots. VP can expose entire layers at a time to achieve both high speed and resolution, while also having the capacity to form challenging geometries (e.g. overhangs, cavities, channels). Unfortunately, VP still faces many limitations as few options exist for multi-material printing,¹² integrating conductive materials,¹³⁻¹⁵ printing tough materials with high strain capacity,¹⁶⁻¹⁹ and printing large area structures.²⁰ Additionally, building

large soft robotic objects via VP is challenging due to the need for structural supports, limited directions for resin to drain from cavities, and insufficient build area.^{10,21,22}

Modular soft robotics (MSR) joins smaller sub-components to form integrated parts, which is a strategy that addresses many of the barriers to fabricating macroscale soft robotic structures.^{23–25} Sub-components remain easy to design and may be fabricated on smaller printers with less concern for orientation for resin drainage and structural support. MSR typically uses adhesive or mechanical connectors to merge sub-components, however such methods are not always ideal due to adhesive compatibility for soft robots and added complexity of connectors can hinder the final design.²⁶

Self-healing materials are a promising and underutilized option for MSR that could remove the need for adhesives or complicated connectors. Self-healing materials integrate chemical modalities into polymer chains that bond materials after synthesis. Self-healing materials generally consist of two distinct categories that rely on either intrinsic or extrinsic self-healing mechanisms. While extrinsic self-healing relies on capsules or channels of reactive compounds that burst and then react, intrinsic mechanisms also offer the opportunity to reconfigure whole components because they can be reorganized numerous times without the need of being fractured to release healing agent. These materials typically use thermal, photonic, or chemical energy to overcome the activation energy needed to initiate dynamic bonds to provide on-demand reconfigurability²⁷ and damage repair.^{1,28–30} Unfortunately, few self-healing materials are reported for VP and amenability to soft robotics has been limited by material synthesis, mechanical properties, and healing capacity.^{29,31}

In this work, we have developed a soft robotic manufacturing approach based on 3D printed, self healing materials, that combines the advantages of both VP and MSR. This approach promises significantly increased design complexity, scale, and facile fabrication all while removing the need for cumbersome adhesives, supports, and connectors that often hinder robot designs. This advance is made possible through a tunable self-healing elastomer photoresins with dynamically exchangeable thioether moieties amenable to VP 3D print-

ing. These resins exhibit ultrastretchability (500-1000+% strain), repeatable self-healing capacity (>3 cycles), the ability to reprogram resting shape, and compatibility with self-healing stretchable electronics. To demonstrate a platform for MSR, sixteen sub-components (centimeter-scale) were printed with multiple internal channels and cavities without the need for external supports and fused together post-printing into large (decimeter-scale) soft robots. The final robots contained long internal channel networks and pneumatic cavities that are otherwise impractical to produce in a single part. After fabrication, heterogeneous materials such as low melting point liquid metals were integrated via the internal channel networks for additional mechanical and electrical functionality. These results lay the groundwork for a paradigm of soft robot fabrication combining self-healing materials, AM, and MSR.

Results and discussion

Material Formulation

The chemical components, dynamic bond exchange mechanism, and fabrication strategy of the 3D printable self-healing elastomer systems are illustrated in Figure 1. An elastomeric hydrogel forming monomer, 2-hydroxyethyl acrylate (HEA), was used as the base material component and tuned by adding small amounts of difunctional thiol 2,2-(ethylenedioxy)diethanethiol (EDDT) and dynamic thioether containing cross-linking agent 2-((3-(2-(acryloyloxy)ethoxy)-3-oxopropyl)thio)ethyl acrylate (TMADA). These components were mixed with a photoinitiator and dye to form photopolymerizable resins which were both casted into molds and printed into complex parts with internal cavities and channel networks using a digital light processing (DLP) 3D printer. These modular parts were then combined and grafted together with heat to form large scale soft robotic systems with relative ease.

Previous reports have utilized TMADA, and related thiol-Michael linkers, to imbue HEA polymer systems with self-healing capacity.^{32,33} These systems proceed through thermally induced retro-Michael reactions which in turn yield free thiol and acrylate moieties that

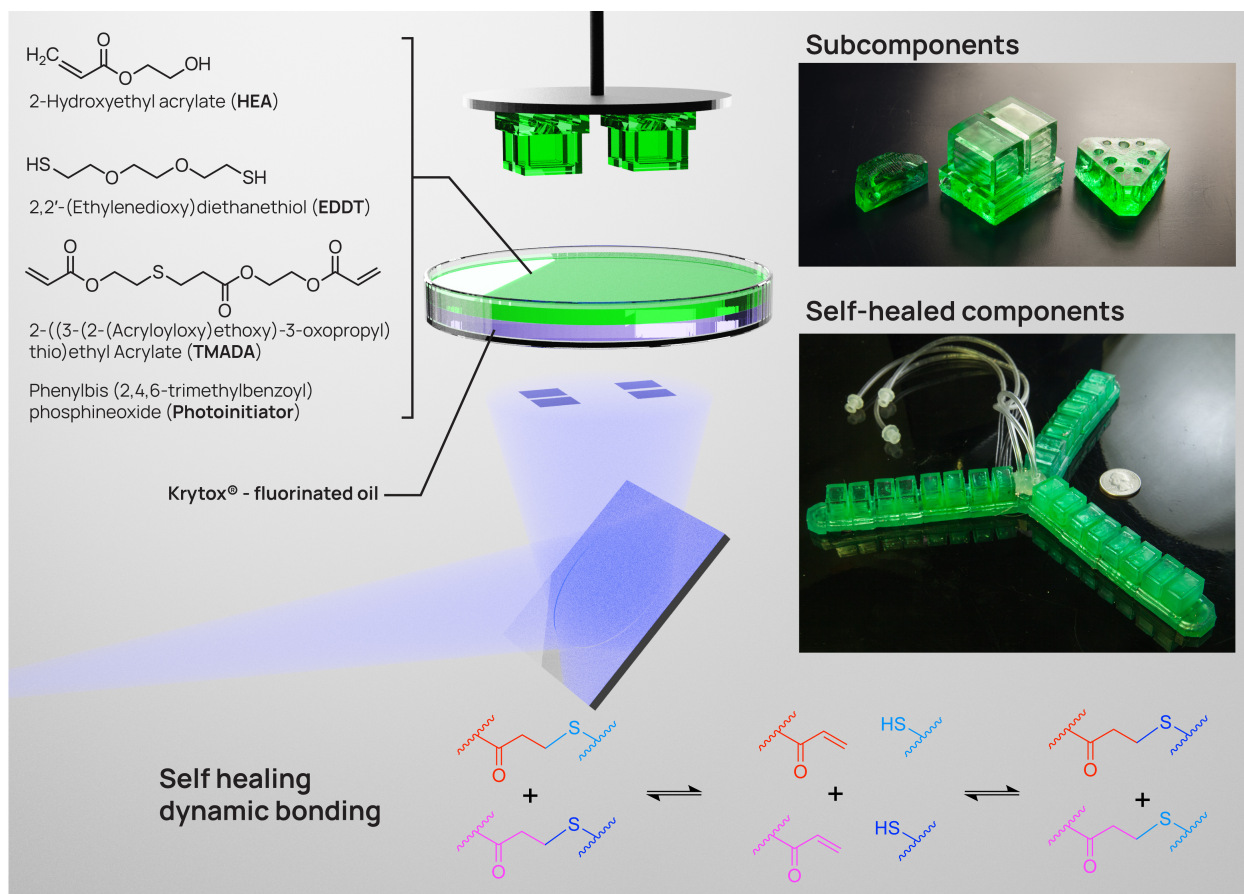


Figure 1: **DLP printed self healing modular robotics.** Photopolymerizable mixed thiol/acrylate resins enable 3D printing of self-healable parts using dynamic exchange of thioether moieties. Components can be combined together to enable facile construction of large parts with complex internal structures.

quickly associate to form new thioether bonds.³⁴ Our attempts to adapt this procedure³² using photo polymerization instead of the thermal polymerization method resulted in materials which were too stiff to enable effective polymer diffusion and self-healing (see Supplemental Figure S2). In an attempt to both lower the modulus and add additional dynamic thioether moieties, EDDT was added to the formulations. With a mixture of thiols and acrylates undergoing free-radical polymerization, step-growth thiol-acrylate polymerization occurs simultaneously with chain-growth acrylate homopolymerization. Reports on similar mixed mode polymerizations have demonstrated that thiols act as chain transfer agents, increasing both thioether connections and termination events from chain transfer to thiols.³⁵

Functionally, the addition of small amounts of EDDT to the rapid, bulk free radical acrylate polymerization used for VP serves to form additional thioethers, which widen the distribution of polymer molecular weights, and reduce cross-linking by patching abstraction-based intermolecular side reactions (see Scheme S1 and Figure S1).³⁶⁻³⁸

Material Properties and Characteristics

The mechanical properties of thiol/acrylate mixtures which produce tailorable ultrastretchable self-healing elastomers are evaluated in Figure 2. An image of one such elastomer stretching to over 1000% strain is shown in Figure 2a. For tensile testing, elastomer dogbones were cast and photopolymerized in molds. A comparison study between 3D printed and cast dogbones showed similar mechanical properties and can be observed in Supplemental Figure S6. The effects of independently increasing the content of either TMADA or EDDT in an HEA polymer system is shown in the tensile strain to break curves of Figure 2b. Increasing the amount of cross-linking agent TMADA (without EDDT) increased the modulus an order of magnitude. Contrarily, small additions of 0.125 to 0.25 wt% EDDT to a photopolymerizable mixture of HEA substantially lowered the modulus, decreased ultimate tensile strength from about 750 kPa to about 450 kPa, and increased strain at break from about 400% to over 900%. Increasing the EDDT content beyond 0.25 wt% without adding additional cross-linking agents created a sticky gel of linear polymer unable to hold its shape. HEA polymer systems with both EDDT and TMADA were needed to produce materials with properties appropriate for pneumatic soft robotic actuators. Formulations were evaluated as shown in Figure 2c by keeping TMADA cross-linker constant at 1 wt% while increasing the content of EDDT up to 1 wt%. Optimized materials increased the total content of dynamic thioether groups to enable self-healing while exhibiting strain-stiffening and high stretchability upwards of 1500%.

An investigation of self-healing capacity is shown in Figure 2d with uncut samples depicted in solid shapes against their cut and rejoined counterparts in open form. All samples

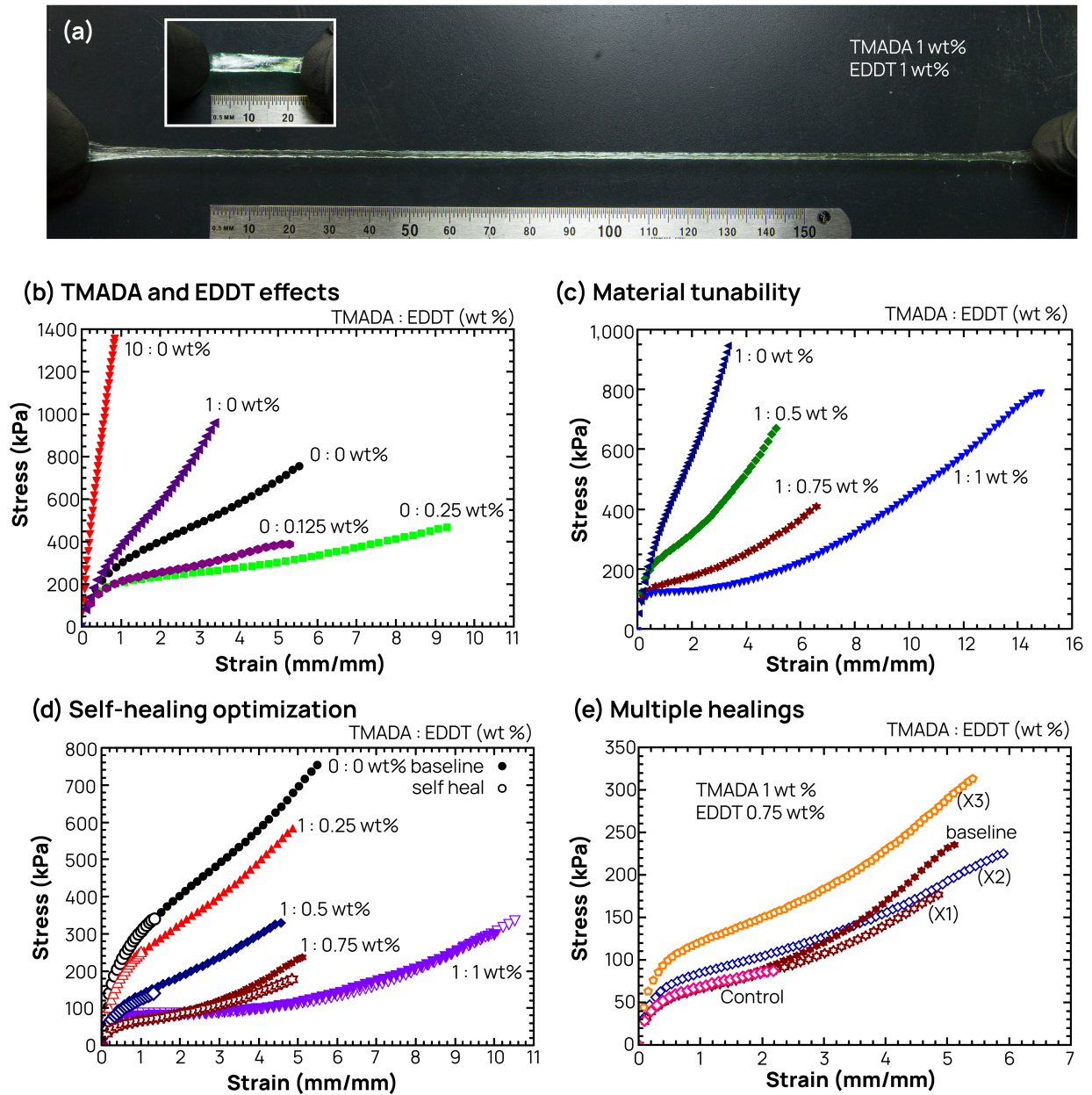


Figure 2: **Mechanical characterization of photopolymerized resins.** (a) Photo of elastic properties of HEA based 1:1wt% TMADA:EDDT material with over 1000% strain. (b) Effects of TMADA and EDDT concentration on tensile properties of HEA based elastomers strained to failure. (c) Tensile properties of HEA elastomers with both TMADA and EDDT strained to failure. (d) Tensile properties of self-healed dogbones (open symbols) compared with uncut baseline dogbones (closed symbols) strained to failure. (e) Tensile properties of multiply cut and healed dogbones (X1 = 1 cut/heal cycle, X2 = 2 cut/heal cycles, X3 = 3 cut/heal cycles) and of cut a dogbone healed at room temperature (Control) strained to failure.

shown in Figure 2d have undergone a thermal treatment at 90 °C for 24 hours. A significant decrease in toughness (approximately 50%) is consistently observed with heat treatment of these materials. It is hypothesized that the removal of plasticizing species largely accounts for this change (see Supplemental Figure S3). Some self-healing capacity is observed in pure HEA systems, which is attributed to hydrogen bonding.³² Only when systems had a substantial amount of EDDT did they begin to exhibit self-healing capacity approximating baseline performance. This is likely due to the softening effect of adding EDDT allowing for greater polymer mobility.

It is potentially advantageous for soft robots to heal damage or be reconfigured multiple times during their lifecycle. The results of multiple self-healing cycles wherein a specimen was cut and healed in the same location up to three times is presented in Figure 2e with no apparent degradation of mechanical properties observed. Control experiments were also performed such that dogbones were cut and placed back together without heating. A representative result is shown in Figure 2e as the "Control", showing that minimal healing occurs without the addition of heat (some room-temperature healing is expected due to hydrogen bonding).

With the capacity for repeated healing and shape reprogrammability, these self-healing elastomer systems are excellent candidates for reconfigurable devices. A demonstration of this potential is shown in Figures 3a and b where two samples are 1) grafted together, 2) cut apart, reconfigured, and grafted together again, and 3) heated while under strain to reprogram the permanent shape. The ability to program new permanent shapes is enabled by the dynamic exchange of thiol-Michael bonds and polymer chain diffusion, which reconfigure polymer chains to relieve stresses incurred during shape programming. This relaxes the internal stress in the material to reset the resting shape. A strong correlation between self-healing capacity and shape retention after shape reprogramming was observed through experiments with various resin formulations.

Liquid metals have been demonstrated to be potent materials in functional soft devices

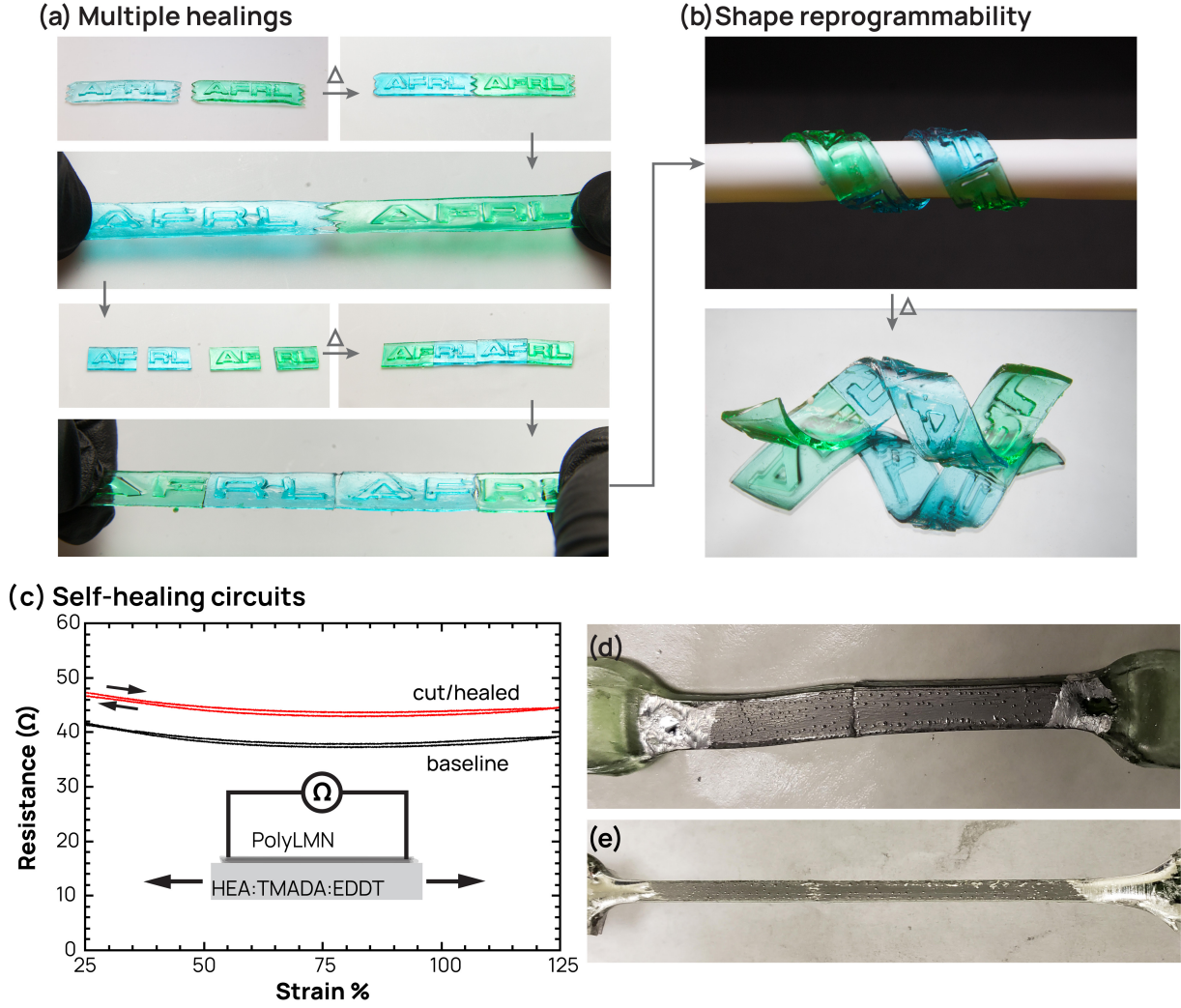


Figure 3: Material Capabilities. (a) A demonstration of sequential grafting and reconfiguration of HEA based elastomer pieces with 1:0.75wt% TMADA:EDDT. (b) Shape reprogramming of the piece from Figure 3a is shown by wrapping the piece around a rod while heating. Dynamic bond exchange relieves programmed stress, allowing the piece to adopt a new resting shape. (c) Polymerized liquid metal networks (PolyLMN) deposited on top of a 1:1wt% TMADA:EDDT HEA based elastomer and strained while measuring resistance versus strain before and after cutting/healing. (d) PolyLMN and elastomer after healing without strain and (e) maintaining electrical connectivity under strain.

and self-healing electronics.^{39–43} In continuation of this trend, three different liquid metal systems were integrated with these elastomer materials. Eutectic Gallium Indium (EGaIn), Field’s Metal, and Polymerized Liquid Metal Networks (Poly-LMNs) were exploited for electrical conductivity, structural support, and self-healing electronics respectively. Poly-LMNs are a new class of nano-structured liquid metal conductors which maintain stable

resistances under strain.^{44,45} They are constructed from polymerized core-shell liquid metal particles where the shell can be ruptured via mechanical force allowing particle-particle connections to be made. This ultimately forms a highly tortuous network of liquid metal held in shape by the remaining polymer and metal oxide. As Poly-LMNs are comprised mostly of liquid metal, they have great potential for self-healing electronics.^{40,43} The result of applying a Poly-LMN trace to a self-healing elastomer dogbone is shown in Figures 3c-e. Initially, the resistance across the Poly-LMN trace was 40 Ω and predictably stable over the observed range of strain. After cutting, the elastomer dogbone could be rejoined to reconnect the Poly-LMN trace and healed to restore mechanical integrity. A small 8 Ω increase in resistance was likely due to reduced contact area at the site of damage was observed, however, it is notable that the shape of the resistance over strain curve remained unchanged after cutting and healing the stretchable electronic system. We anticipate that the combination of 3D printable self-healing elastomers and Poly-LMNs will be of great use for soft robotics and reconfigurable electronics applications.

Modular Soft Robotics

DLP 3D printing allows parts with advanced soft robotic features, such as internal cavities and channel networks, to be quickly fabricated at high resolution in a single step. Optimization for DLP 3D printing required increasing the initiator content (0.5 to 1 wt%) and adjusting exposure time to ensure material solidification without overgrowth. For ease of use, the resin was suspended on a bed of immiscible fluorinated oil (Krytox GLP 101), as shown in Figure 1, to remove any interfacial adhesion to the glass vat.²⁰ Several interchangeable pieces were designed to leverage the advantages of VP and self healing chemistry (Figure 4) for soft robot fabrication. A modular unit with two pillars for pneumatic expansion connected to a center channel and two outer auxiliary channels is shown in Figure 4a(i). Pieces intentionally had small footprints to avoid supports and enable proper resin drainage. The auxiliary channels were filled post-assembly with either electrically conducting or structurally sup-

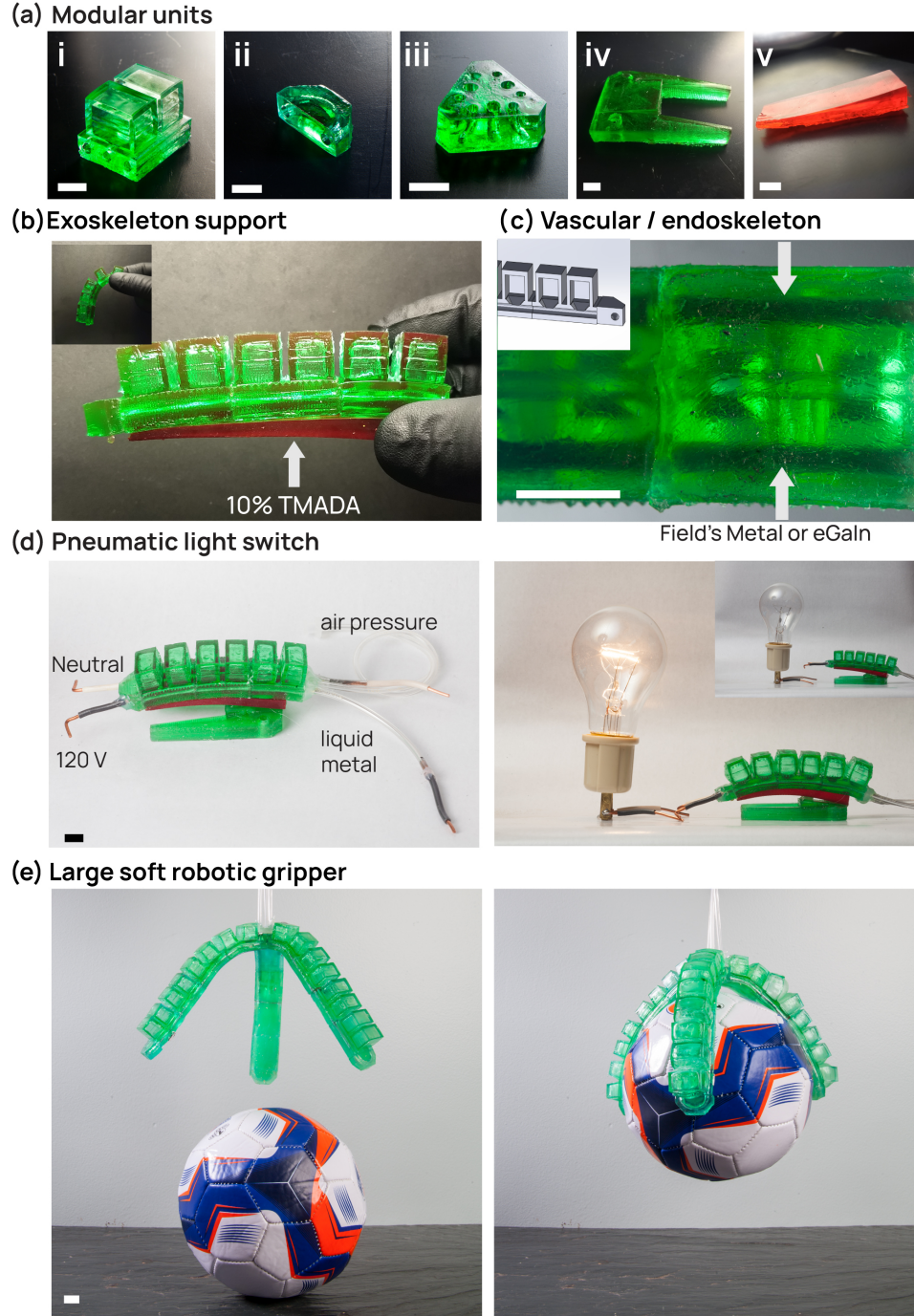


Figure 4: Modular Soft Robotic Demonstrations (a) 3D printed modular units. (b) (inset) Unsupported soft robotic actuator. Exoskeleton support with healed 10:0wt% TMADA:EDDT (red) base piece to 1:1wt% TMADA:EDDT (green) materials. (c) Healed unit cells containing liquid metal inside channels for either conducting vascular network or endoskeleton support. (d) Pneumatic switch with EGaIn filled channels powering a light bulb. (e) A large soft robotic gripper with three independently controlled arms containing Field's metal for structural support picking up a soccer ball (diameter=12.7cm, mass=142g). All scale bars are 1 cm.

portive metal. The end cap unit (Figure 4a(ii)) sealed the center pneumatic channel while connecting the auxiliary channels. The center connector (Figure 4a(iii)) interfaces with the channels and provides a center support for a robotic actuator with three connected arms. We then take sixteen individual pieces and, utilizing their self-healing behavior, assemble them into a larger structure by pressing them together and heating.

Mechanically supportive structures, such as polymer films integrated into bending regions, are often necessary in soft robotics. A method to provide mechanical support through fusing materials of different moduli (Supplemental Figure S8) was explored. From this, supportive pieces were designed as shown in Figures 4a(iv) and (v) where the red unit (Figure 4a(v)) was printed with 10 wt% TMADA cross-linker for structural support. The contrast between supported and unsupported structures can be seen in Figure 4b where a soft material was grafted to a hard material exoskeleton. Alternatively, the internal auxiliary channels of the actuator shown in Figure 4c were filled with Field’s metal to provide support as a functional endoskeleton.

The combination of VP-3DP, self-healing, and MSR enables facile construction of macroscale soft actuators as demonstrated in Figure 4d with a pneumatic light switch and in Figure 4e with a large gripper. Liquid metal filled internal channels could provide high wattage conduction, which is desirable for pumping, heating, lighting, or powering electronics in a soft robotic system. Further, the strain stiffening and high strain capacity of these materials allows for stable pneumatic control with minimal risk of over-pressurization. Exploiting this design paradigm, a sizable (250 mm diameter) pneumatic gripper capable of grasping a soccer ball was constructed without complicated connectors, printing supports, messy adhesives, all on a printer with a 90 mm diameter build area (see Figure S9 for additional detail). This pneumatic gripper was able to grasp and lift a 12.7 cm diameter, 142 g ball, which would be a challenging task for other vat photopolymerized pneumatic actuators.^{9,11,18,46}

This work represents several advances in 3D printed modular soft robotics. We demonstrate an acrylic elastomer with chain and network architecture tuned through small amounts

of dithiol and dynamic thioether cross-linking agent. The developed materials were versatile, with tunable properties and amenability to VP-3DP. A modular approach to combine 3D printed components was utilized to construct macroscale robotic units. Extensive channel systems were printed, fused together, and exploited for auxiliary materials such as EGaIn or Field’s metal. The complimentary advantages of self-healing, 3D printing, and modular units expand the ability to fabricate soft robots with high degrees of complexity and functionality.

Experimental

Elastomer Polymerization The photoinitiator phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Sigma-Aldrich) was combined with 2-hydroxyethyl acrylate (TCI America) as a 0.5 wt% additive and mixed until fully dissolved. TMADA was synthesized according to previous documented procedures.³² TMADA and EDDT (Sigma-Aldrich) were added to HEA by weight percent (0-10 wt% and 0-1 wt%, respectively) and thoroughly mixed in amber vials. Solutions were cast into 2 mm deep silicone dogbone molds, and subsequently photopolymerized using 365 nm UV light (36 W) for 15 min. Samples were then left to rest for 24 hours.

Mechanical Characterization Dogbone specimens were 45.5 mm long and 2mm thick, with a 17 mm gauge length and 7 mm gauge width tapering up to an overall width of 14 mm over a 9 mm radius. Testing was completed on an Instron 3344 universal testing system with a 100 N load cell and custom self-tightening grips. Initial sample lengths were measured as the distance between grips when testing. Stress was calculated as force divided by cross sectional area. Samples were strained at a rate of 50 mm/min until torn. Cast elastomers were divided into groups to observe mechanical properties with each test group containing a minimum of 3 samples. After air drying, the self-healing samples were cut with a razor and then re-joined and placed in an oven at 90 °C for 24 hours, along with the uncut baseline samples. The control samples were cut, re-joined, and placed in room temperature for 24

hours. All samples were then removed from the oven and let to rest at room temperature for 3 days to allow samples to equilibrate. Samples with multiple healing were cut, re-joined and placed in the oven at 90 °C for 24 hours, after removing from the the oven and cooled, the samples were cut again in the same spot, re-joined, and placed in the oven. Samples were cut either 1X, 2X, or 3X before testing.

Self-healing Electronics Poly-LMNs were fabricated and tested according to previously reported methods,⁴⁴ with the exception that they were cast onto an elastomer substrate comprising 97.75 wt% HEA, 1 wt% TMADA, 1 wt% EDDT, and 0.25 wt% initiator which were prepared as described above. Self-healing was executed as described above, with a slight amount of compression applied at the interface in order to reconnect the Poly-LMN material.

Reconfigurability Materials of 98.025 wt% HEA, 1 wt% TMADA, 0.75 wt% EDDT, 0.125 wt% initiator, and 0.1 wt% dye were prepared as described above. Samples were wrapped around a Teflon coated rod and held in place while heated at 90 °C for 24 hours. After samples were allowed to cool and released from the rod, their twisted geometry remained even after stretching and temporary heating.

3D Printing DLP printing was accomplished using a 3DLP9000 Light Engine from Digital Light Innovations using a 405 nm LED light source, a custom z-stage, and open source NanoDLP software. Several calibrations prints altering exposure time, layer thickness, and initiator content confirmed the following parameters for all resin formulations. Initiator content was increased to 1 wt% and food coloring dye was added at 0.1 wt% or methyl red at 0.01 wt% to prevent light scattering. Approximately 30 mL of Krytox oil (GPL 101) was added to the glass lid of a 90 mm diameter petri dish and resin was poured on top. The stage was lowered to the resin/oil interface. Three burn-in layers consisting of 50 μ m where exposed for 7 seconds onto an anodized aluminium build plate. Each layer after that was is exposed

for 5 s. The build plate is raised up 3 mm and down 2.95 mm for each layer to recirculate the resin. After prints are complete, the sub-components are removed from the build plate and thoroughly rinsed with isopropyl alcohol to wash any unpolymerized resin. Parts were post-polymerized under 365 nm UV light (3 minutes at 1.5 mW cm²) and permitted to rest for a minimum of 8 hours before self healing units together. Several calibration prints confirmed that channels printed parallel to the build plate (i.e. poor resin drainage) were possible if the channels were short in length and no less than 1 mm in diameter.

Soft Robot Fabrication All of the green units were printed with 1:0.75 material, (1 wt% TMADA, 0.75 wt%EDDT, 1 wt% initiator, and the remainder HEA) mixed in a rotary mixer. Red units were printed using 10 wt% TMADA, 0 wt% EDDT, 0.5 wt% Irgacure 819 and the remaining HEA. Parts were joined together and placed in the oven for 24 hours at 90 °C. The auxiliary channels were filled with either EGain or Field’s metal (32.5% Bi, 16.5% Sn, 51% In by weight) which melts around 62 °C. To fill with Field’s metal, the gripper and the Field’s metal were heated to 80 °C and two syringes, one with positive pressure and the other with negative pressure, were used to fill the channels. EGaIn was filled in a similar manner with a syringe/needle inserted through the end. After the syringes were removed a 14 AWG copper wire was inserted into the end cap and the tubing and sealed with hot melt adhesive.

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Supporting Information Available

Additional experimental data and material characterization is available online in the supplementary information file.

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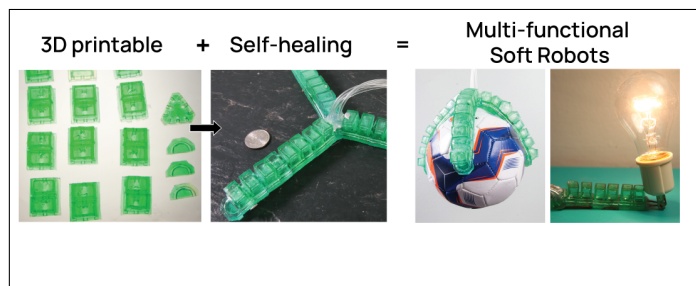
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Graphical TOC Entry



A photopolymerizable self-healing elastomer was created for soft robotics. The material is capable of extreme strain (1000%) and self-heals with temperature. Elastomer parts were 3D printed with vat polymerization into subcomponents and assembled with self-healing to create large soft robotic actuators with internal channels filled with supportive and conductive metal.