



MULTI-MATERIAL 3D PRINTING OF STRETCHABLE ELECTRONICS VIA FILAMENTARY AND DROPLET-BASED DEPOSITION OF VISCOELASTIC INKS

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MULTI-MATERIAL 3D PRINTING OF STRETCHABLE ELECTRONICS VIA
FILAMENTARY AND DROPLET-BASED DEPOSITION OF VISCOELASTIC INKS

A dissertation presented by

TRAVIS ALEXANDER BUSBEE

To The John A. Paulson School of Engineering and Applied Sciences

In partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

in the subject of

Engineering Sciences

Harvard University

Cambridge, Massachusetts

August 2025

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Multi-Material 3D Printing of Stretchable Electronics via Filamentary and Droplet-Based Deposition of Viscoelastic Inks

ABSTRACT

As the boundary between digital and biological systems continues to blur, the seamless integration of electronic devices with living tissue has emerged as a technological imperative. Yet most electronic devices contain materials with elastic moduli exceeding 100 GPa, while biological tissues are inherently soft with moduli ranging from 0.1 to 1000 kPa. This pronounced mechanical mismatch fundamentally impedes electronics-human tissue integration. Current soft electronics fabrication strategies deploy rigid materials that are geometrically patterned to facilitate stretchability, or soft materials that are intrinsically stretchable. Both strategies fail to robustly integrate rigid electronic components within stretchable matrices, as stress concentrations at rigid-soft interfaces inevitably cause delamination and electrical failure under cyclic loading. This challenge is particularly critical given that high performance rigid components lack soft analogues with comparable functionality and cost.

My PhD dissertation establishes multi-material 3D printing via filamentary and droplet-based approaches, as transformative manufacturing platforms for robust electromechanical integration of rigid components within soft matrices with programmable mechanics. First, a hybrid direct ink writing (DIW) platform is developed, combining printable thermoplastic polyurethane (TPU) elastomers and conductive silver-TPU inks achieving conductivities up to 3×10^6 S/m with robotic pick-and-place assembly. This approach enables fabrication of soft electronic devices including wearable strain sensors and microcontroller systems. Systematic characterization reveals

that selective TPU reinforcement around rigid components extends their composite electromechanical strain tolerance sevenfold, from 17% to 120%.

Building upon these insights, a novel droplet-based viscoelastic ink printing (DVIP) method is introduced, capable of spatially patterning multiple photocurable thiol-ene elastomers, with moduli spanning three orders of magnitude, through raster image processing. Integration of robotic assembly and printable liquid metal inks enables scalable fabrication of personalized stretchable devices with spatially programmable mechanical gradients surrounding embedded components. Devices incorporating zonally graded strain relief demonstrate 100-fold improvement in electrical fatigue life compared to uniform matrices, surviving 5000 strain cycles versus 50. The versatility of DVIP is further demonstrated through multi-layer architectures incorporating printed variable capacitance sensors, vertical interconnects, and selectively encapsulated circuit modules, establishing a scalable pathway for the digital printing of next-generation biointegrated electronics.

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CHAPTER 1

INTRODUCTION

Human-machine interfaces are of growing interest for applications ranging from neural interfaces and cardiac monitoring to wearable health sensors and neuromuscular prostheses [1-3].

However, commercial electronics are fundamentally rigid, constructed from crystalline semiconductors and metals with elastic moduli exceeding 100 GPa, and often surface mounted on fiber-reinforced epoxy substrates. By contrast, biological tissues exhibit elastic moduli spanning from 0.1 kPa (brain tissue) to 1 MPa (epidermis) resulting in a mechanical mismatch of up to six orders of magnitude between electronic devices and living systems [4-6]. Hence[1-3], there is an urgent need to create soft electronic devices that can mechanically conform to, and dynamically interface with, human tissues.

Current strategies for fabricating stretchable electronic devices generally fall into two categories: 1) harness geometric patterns composed of rigid materials to enable stretchability or 2) use soft materials, such as conductive polymers, polymer composites, liquid metals, and ionic conductors, which are intrinsically stretchable [7, 8]. Unfortunately, neither strategy provides a scalable solution for robust integration of rigid components within soft matrices. These hybrid systems inevitably concentrate stress at rigid-soft interfaces, leading to delamination, cracking, and electrical failure under mechanical loading [9-11]. This challenge is particularly critical given that state-of-the-art stretchable materials [8] cannot approach the computational density of modern integrated circuits ($>300,000,000$ transistors per mm^2) [12]. Hence, embedding rigid silicon components within stretchable systems appears essential for achieving practical performance at reasonable cost. Furthermore, current fabrication methods rely heavily on complex multi-step

lithographic processes, limiting the production of personalized devices [8, 13] that conform to a given anatomy.

Despite significant advances in material chemistry and device architectures, existing manufacturing approaches for stretchable electronics remain constrained by two fundamental challenges: (1) the inability to robustly integrate rigid electronic components within soft matrices and (2) the lack of scalable methods for creating patient-specific devices with arbitrary geometries. My PhD research addresses these challenges through the development of novel materials and transformative manufacturing platforms based on multi-material 3D printing. Both stretchable conductive inks composed of silver particle-filled elastomers and anhydrous eutectic gallium-indium emulsions as well as photo-curable thiol-ene elastomers with tunable stiffness spanning three orders of magnitude have been created for filamentary direct ink writing (DIW) and droplet-based viscoelastic ink printing (DVIP), each of which are capable of co-printing multiple materials to create soft electronic devices. Each method is further augmented via robotic pick-and-placement of rigid electrical components that are interconnected via stretchable interconnects to yield soft electronic devices. Inspired by natural systems, such as tendon-bone interfaces, DVIP is used to generate stretchable devices with zonally graded matrices that distribute mechanical loads that arise due to pronounced stiffness mismatches at the interfaces between rigid electronics and these soft materials [14-16]. Using these materials sets and novel printing modalities, we have fabricated stretchable electronic devices with unprecedented mechanical robustness for use in instrumented heart-on-a-chip models, stretchable LED arrays, body-mounted strain sensors, and variable capacitance sensors.

1.1 DISSERTATION SCOPE

The first aim of my dissertation focused on creating soft biocompatible materials for multi-material direct ink writing (DIW) of instrumented cardiac micro-physiological devices. Such devices enable one to continuously collect real-time tissue contractility data. These multilayered, printed devices consist of cardiac tissue layers seeded on top of micropatterned cantilevers with embedded strain sensors. The second aim focused on developing a hybrid printing platform that combines direct ink writing with robotic assembly of surface mount electronics to create stretchable electronics. This advancement recognizes that practical soft electronics require both the computational power of silicon-based components and the mechanical compliance of stretchable interconnects. The third aim introduces droplet-based viscoelastic ink printing (DVIP), a transformative digital manufacturing approach that spatially controls material properties around rigid components. By enabling zonal modulation of matrix stiffness and extensibility, DVIP overcomes a fundamental failure mechanism of stretchable electronics—namely stress concentration at rigid-soft interfaces—thereby enabling unprecedented mechanical robustness during cyclic deformation.

The principal outcome of my PhD dissertation establishes digital manufacturing of stretchable electronics with spatially graded architectures and functionality, through systematic advances in material chemistry, design principles, and scalable fabrication methods. Specifically, my research has led to: 1) novel stretchable electronic ink formulations maintaining conductivity under extreme deformation 2) UV-curable elastomers with tunable mechanics spanning three orders of magnitude in modulus 3) anhydrous liquid metal emulsions eliminating electromechanical hysteresis and 4) a new scalable multi-material printing platform, known as

DVIP. These advances provide both the fundamental understanding and practical tools necessary for next-generation human-machine interfaces.

1.2 DISSERTATION ORGANIZATION

In Chapter 2, a review of relevant literature for stretchable electronics fabrication strategies and materials sets is provided. In Chapter 3, the design of printable inks for direct ink writing of instrumented cardiac-on-chip devices with 10^{-6} N force detection for cardiac monolayer contractility is described. In Chapter 4, a hybrid 3D printing method combining direct ink writing of a highly conductive stretchable silver ink with robotic pick-and-place of rigid electronic components to create stretchable electronic devices is reported. In Chapter 5, a new droplet-based viscoelastic ink printing method is established, which allows one to rapidly print robust stretchable electronic devices with zonally graded interfaces. Finally, the principal findings of my Ph.D. work are summarized in Chapter 6.

CHAPTER 2

LITERATURE REVIEW

2.1 MOTIVATION AND SCOPE

The design and fabrication of soft electronics capable of mechanically conforming to dynamic and complex biological surfaces represents a transformative advancement with diverse applications ranging from wearable health monitoring and human-machine interfaces to implantable medical devices. Achieving the integration of electronics with soft, deformable substrates requires overcoming inherent mismatches between conventional electronic materials, which are inherently rigid, and the compliant properties of biological tissues. This chapter presents a focused review of literature relevant to the field of stretchable electronics, with particular emphasis on key material strategies, fabrication methods, and seminal research contributions. The initial sections discuss foundational concepts behind soft electronics, exploring the dichotomy between intrinsically stretchable materials and geometrically engineered stretchability. Subsequent sections introduce prominent material sets and device fabrication methods central to advancing stretchable electronic systems. Finally, the rationale for employing multi-material 3D printing, integrated with robotic pick-and-place of individual electronic components, as a scalable and customizable manufacturing platform for soft electronic devices is discussed to motivate my core research objectives.

2.2 INTRODUCTION TO SOFT ELECTRONICS

Conventional electronics devices, known as printed circuit boards, are composed of silicon-based microchips, surface mounted components (e.g., resistors, capacitors, etc.), metallic interconnects, and fiber-reinforced epoxy substrates. This combination of material choices along with significant advances in automated fabrication and assembly techniques has enabled remarkable progress in

device capabilities alongside substantial reductions in production costs. However, their structural rigidity imposes a critical limitation for emerging applications involving human-machine interfaces.

There is a growing impetus to achieve a deeper integration of electronic devices with the human body. Realizing this vision could unlock transformative applications across diverse domains, including wearable health monitoring and treatment, implantable medical devices, robotic control interfaces, virtual reality enhancements, and brain-machine interfaces [3]. A fundamental barrier to such intimate integration remains the inherent compliance mismatch between rigid electronic materials and the inherently soft, stretchable nature of biological tissues. This mismatch presents significant challenges, ranging from everyday discomfort such as carrying rigid smartphones, to critical functional failures exemplified by implantable electronics intended for continuous and unobtrusive monitoring that fail due to scarring caused by modulus mismatch [17].

The field of soft electronics aims explicitly to resolve this mechanical incompatibility by developing electronic systems that harmoniously integrate with soft biological tissues. Addressing this challenge involves highly interdisciplinary research that encompasses materials science, mechanical engineering, electrical engineering, and bioengineering. Successful devices must retain the advantageous electronic properties and cost efficiencies associated with traditional rigid electronics, while simultaneously incorporating mechanical compliance and resilience necessary for enduring functionality in dynamic biological environments.

Two primary strategies have emerged to overcome these mechanical compliance challenges: geometrically engineered stretchability and intrinsically stretchable materials [7, 8]. Geometrically engineered stretchability leverages structural design principles to impart

stretchability to otherwise rigid materials [7]. Employing sophisticated structural configurations, such as serpentine patterns, mesh-like designs, or origami-inspired structures, strategically redistributes stress across the device, thereby significantly enhancing effective stretchability and mechanical resilience. Although these approaches often necessitate intricate fabrication processes, they preserve compatibility with existing high-performance electronic materials.

Conversely, intrinsically stretchable materials inherently possess mechanical flexibility and elasticity, typically achieved through innovative polymer chemistries and conductive polymer composite formulations [18]. These materials can deform extensively without catastrophically compromising electrical performance, allowing robust and direct integration with biological tissues. Both strategies, intrinsic stretchability and geometric engineering, offer distinct advantages while presenting unique implementation challenges. Hybrid approaches combining these methods can yield optimized systems that harmonize mechanical compliance with exceptional electrical performance. Selecting and developing the most appropriate approach requires careful consideration of specific application demands, underscoring the importance of comprehensive literature reviews and thoughtful analysis of existing solutions and their associated trade-offs.

2.3 MATERIALS AND FABRICATION METHODS FOR SOFT ELECTRONICS

2.3.1 GEOMETRICALLY STRETCHABLE ELECTRONIC MATERIALS

Rigid materials, when patterned into thin layers of appropriate geometry, can exhibit stretchability [19, 20]. This concept was first demonstrated by Rogers and co-workers, who showed that microscale, periodic wave-like geometries of silicon, bonded to pre-stretched silicone elastomer substrates, could enable electronics-grade silicon (a notoriously brittle material) to withstand tensile strains over ten times greater than its intrinsic breaking strain (**Fig. 2.1**) [21]. Importantly, most rigid electronic materials can be made stretchable via geometric engineering (**Fig. 2.2**) [22].

The key to unlocking this multi-modal stretchability is through the selective bonding of the electronic material onto pre-strained elastomeric substrates followed by the selective release in unbonded areas during relaxation of the elastomer, leading to out of plane serpentine and curvilinear structures that can absorb high tensile strains in the elastomer, without transferring that strain to the electronic materials [7, 23].

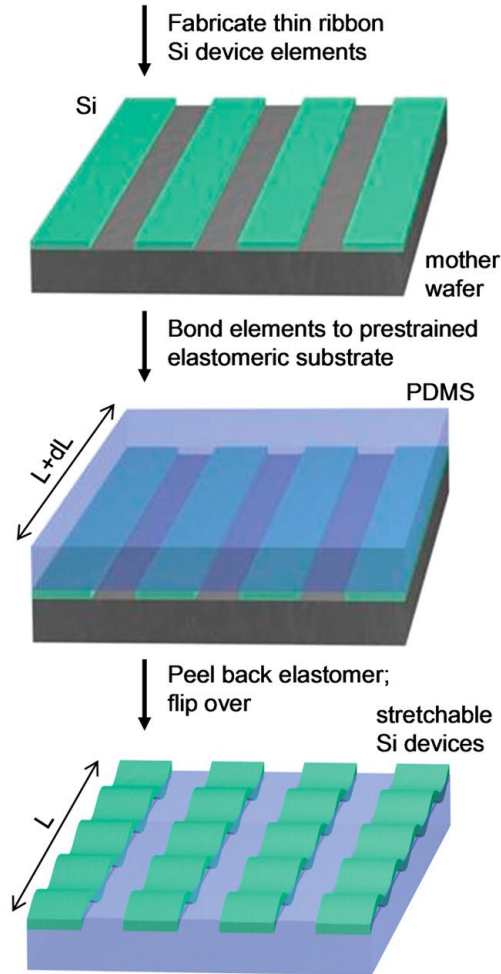


Figure 2.1: Building stretchable single-crystal Si devices on elastomeric substrates. The first step (**top**) involves fabrication of thin (thicknesses between 20 and 320 nm) elements of single-crystal Si or complete integrated devices (transistors, diodes, etc.) by conventional lithographic processing, followed by etching of the top Si and SiO₂ layers of a SOI wafer. After these procedures, the ribbon structures are supported by, but not bonded to, the underlying wafer. Contacting a pre-strained elastomeric substrate (PDMS) to the ribbons leads to bonding between these materials (**middle**). Peeling back the PDMS, with the ribbons bonded on its surface, and then releasing the pre-strain, causes the PDMS to relax back to its unstrained state. This relaxation leads to the spontaneous formation of well-controlled, highly periodic, stretchable wavy structures in the ribbons (**bottom**). [adapted from Ref. [21]]

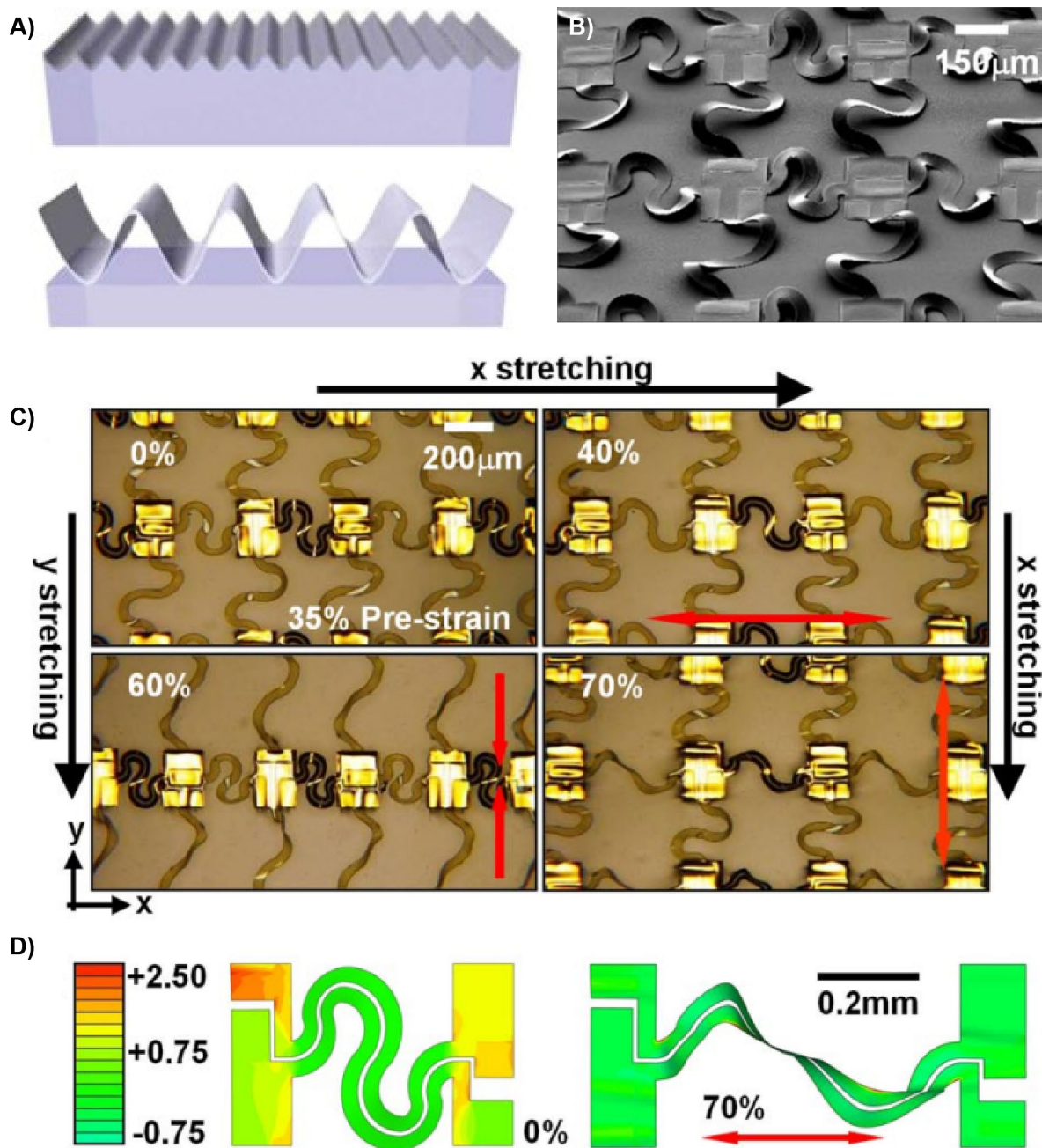


Figure 2.2: Stretchable inorganic films through selective bonding of thin rigid semiconductors to pre-stretched elastomeric films. A) A model of an inorganic film bonded to a pre-stretched elastomer, then relaxed; when the full film is bonded (top) and when only selected portions of the film are bonded (bottom). [adapted from Ref. [22]] B) An SEM image of an array of stretchable CMOS inverters with noncoplanar bridges that have serpentine layouts. C) Optical images of CMOS inverters stretching tests in the x and y directions. D) FEM simulation before (35% pre-strain) and after (70% applied strain) stretching. [adapted from Ref. [23]]

The concept of geometric control for expanded elongation of intrinsically rigid materials has been widely implemented to create devices of increasing complexity, including solar cells (**Fig 2.3A**) [24], multiplexed biosensing arrays [25], and NFC antennas (**Fig. 2.3B-D**) [26].

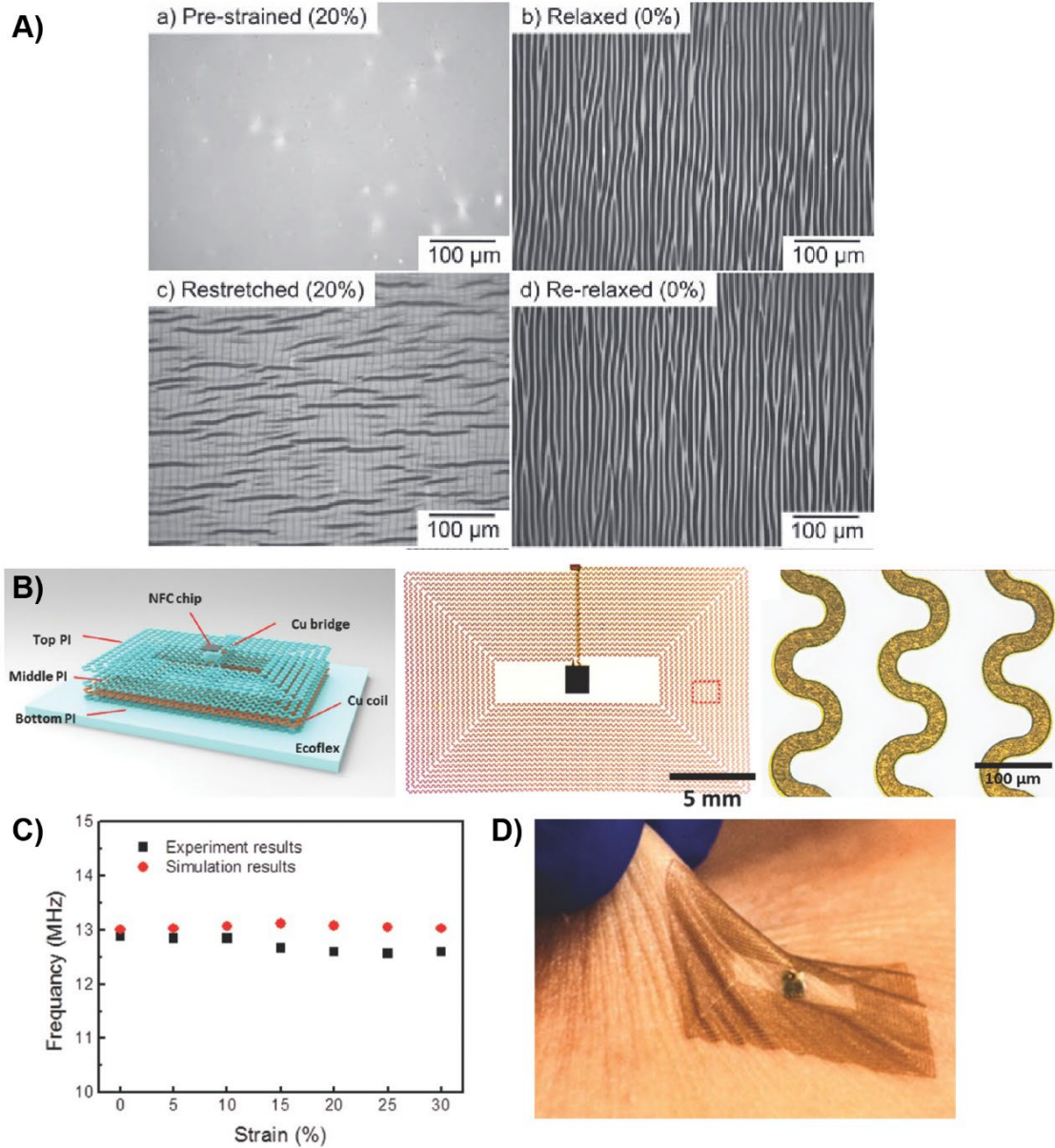


Figure 2.3: Stretchable solar cells and NFC antennas. A) Stretchable solar cells composed of poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl- C_{61} -butyric acid methyl ester (PCBM) + poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS) on a pre-stretched PDMS support. [adapted from Ref. [24]] B) Stretchable NFC Antenna based on serpentine pattern of Copper and Polyimide. C) RF resonant frequency of the antenna as a function of strain. D) A photo of the stretchable device on deformed skin. [adapted from Ref. [27]]

While serpentine, wavy, or rigid island interconnects have enabled stretchability in otherwise stiff materials, such architectures have several critical limitations. Principally, these geometric designs restrict device integration density [10], concentrate strain at the interfaces between rigid and compliant regions (which can lead to delamination and mechanical failure or electromechanical fatigue under cyclic loading) [10, 28], and constrain multiaxial deformability [29]. Collectively, these limitations hinder true conformal integration and limit the scalability of such systems for complex, multifunctional and multi-layer applications.

2.3.2 INTRINSICALLY STRETCHABLE ELECTRONIC MATERIALS

Materials designed for intrinsic stretchability are characterized by their inherent ability to deform significantly without failure, regardless of their geometry or orientation, given a sufficiently high load. A common analogy is a rubber band, capable of stretching linearly beyond 200% strain and reliably returning to its original shape upon release. However, unlike elastomers, most high-performance electronic materials are fundamentally rigid, making the pursuit of intrinsically stretchable electronic materials a compelling frontier in materials science.

The successful development of intrinsically stretchable electronic materials capable of matching the electrical performance of their rigid counterparts would unlock several transformative advantages for device fabrication. Such advances may open new avenues for increased device integration density by utilizing straight, parallel interconnect lines rather than complex serpentine designs. Furthermore, intrinsically stretchable materials would enable the stacking of multiple functional layers without compromising mechanical compliance, dramatically simplifying fabrication processes and improving manufacturing efficiency. The inherent strain tolerance of these materials eliminates constraints imposed by geometric patterns, providing

superior overall device robustness during mechanical deformation. Moreover, the use of intrinsically stretchable materials could reduce the risk of mechanical failure at interfaces between rigid and compliant components. Rigid-soft interfaces typically experience substantial stress concentrations due to mismatched mechanical properties, often leading to device delamination or interconnection failure under repeated mechanical loading [9, 30]. By reducing the modulus mismatch, thereby reducing the stress concentration, intrinsically stretchable materials inherently enhance device longevity and reliability.

Despite these clear advantages, developing intrinsically stretchable materials with adequate electrical performance presents substantial scientific challenges. Current research efforts focus on creating novel conductive elastomer composites, liquid metal-based conductors, ionically conductive liquids, and semi-conducting polymers, capable of maintaining high electrical conductivity under significant mechanical deformation. Innovations in polymer chemistry, molecular engineering, and composite material design are essential for overcoming the trade-off between mechanical compliance and electrical performance. Hence, the design and digital fabrication of intrinsically stretchable materials represent a crucial research direction, promising to drive significant progress in the field of stretchable electronics. Advancements in these materials will likely pave the way for next-generation, soft electronic devices capable of seamless and durable integration with complex biological systems. The remainder of the section will highlight key classes of intrinsically stretchable electronic materials as well as their applications.

2.3.2.1 *Conductive Polymer Composites*

One prominent strategy for making intrinsically stretchable conductors is to combine elastomeric polymers with electrically conductive particles. Multiple types of conductive particles have been explored as fillers, including carbon nanotubes (CNT) [31, 32], carbon black [33], graphene [34], silver nanowires [35, 36], [37], nanoparticles [38], and flakes [39]. There are several considerations when choosing the best conductive filler. High aspect ratios are preferred for increasing conductivity, while minimizing the loading level required to exceed the percolation threshold. **Eq. 2.1** shows the relationship between percolation threshold Φ_C and excluded volume fraction $\langle V_{ex} \rangle$, as it applies to cylindrical particles with high aspect ratio $\eta = L/W$, where length (L) $\gg$ width (W) [40].

$$\Phi_C \sim \frac{V}{\langle V_{ex} \rangle} = \frac{W}{2L} = 1/(2\eta) \quad (2.1)$$

The percolation threshold is inversely proportional to the particle aspect ratio. This theoretical model was later validated for CNT composites by comparing its predicted values to experimental data from multiple independent studies [41]. Another key consideration is the electrical conductivity of the filler, since conductivity of a composite composed of an insulating matrix may never exceed the conductivity of the conductive filler itself. The conductivity of a percolating network can be described by the power-law theory **Eq. 2.2**. [42]

$$\sigma = \sigma_o(V_f - V_c)^S \quad (2.2)$$

where σ is the conductivity of the conductive composite, σ_o is the bulk conductivity of conductive filler, V_f is the volumetric fraction of conductive filler (assuming all solvent removed), V_c is the critical volume fraction at percolation (in dried form), and S is the power law exponent. An additional pertinent consideration is the resistance of the conductive filler to oxidative damage. Carbon particles are extremely resistant to oxidative changes in conductivity in mild conditions. Silver is prone to oxidation under mild conditions, but readily forms thin passivated layers of silver oxide, which themselves are intrinsically conductive [43], making it a good option for stretchable conductive inks (**Fig 2.4A,B**). Alternative metals, like copper, while attractive from a cost perspective, form electrically insulating oxide layers over time [44], leading to degraded electrical performance with aging. A final consideration is the mechanical robustness of the percolating filler network over time. Networks composed of brittle particles, such as carbon black, are prone to interfacial degradation when mechanically strained in a repeated manner [45]. While the same effect occurs with metallic [46] and carbon nanotube [47] networks, the effect is less pronounced due to their increased ductility and higher contact area relative to carbon black nanoparticle.

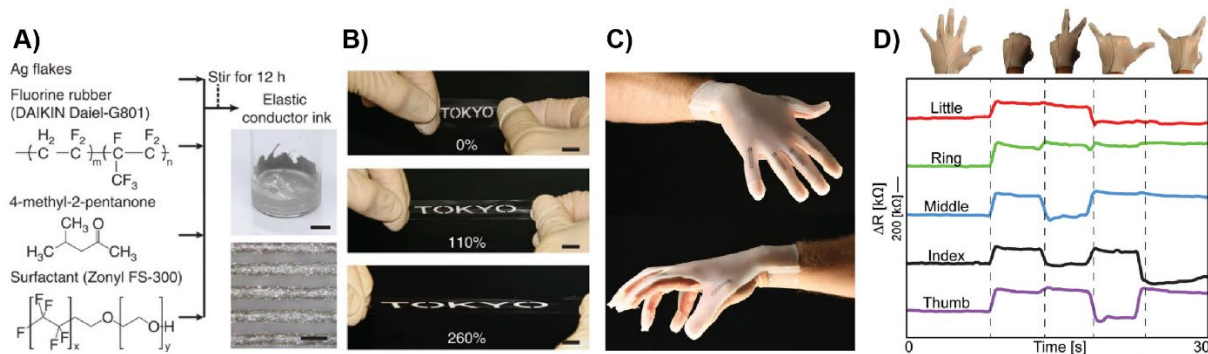


Figure 2.4: Stretchable conductive composites formed from conductive particles dispersed in an insulating matrix. A) The chemical components making up a stretchable silver ink based on silver flakes. B) Photo of screen printed structures of the stretchable ink under varying degrees of stretch. [adapted from Ref. [39]] C) A photo of a printed stretchable strain sensing device based on a carbon ink. D) The resistance change of the five strain sensors of the device in response to finger motions of the device wearer. [adapted from Ref. [48]]

2.3.2.2 Eutectic-Gallium Indium (eGaIn) Liquid Metal

Even the highest reported bulk conductivity of highly stretchable conductive composites is less than 1% of that of bulk copper [39]. Conductive composites face the additional challenge of non-linear piezoresistivity and electro-mechanical hysteresis, to varying degrees, when repeatedly stretched and relaxed beyond their elastic limit [46]. While high piezoresistivity is an attractive quality for a strain sensor (**Fig. 2.4 C,D**), it is far less desirable for an electrical interconnect material. To solve these issues, the use of room temperature liquid metals as an electrical interconnect material has emerged as a compelling solution for stretchable electronics applications [10, 49]. Eutectic Gallium-Indium (eGaIn) is the most widely used alloy, due to its eutectic liquidus temperature of 15 °C (**Fig 2.5A**).

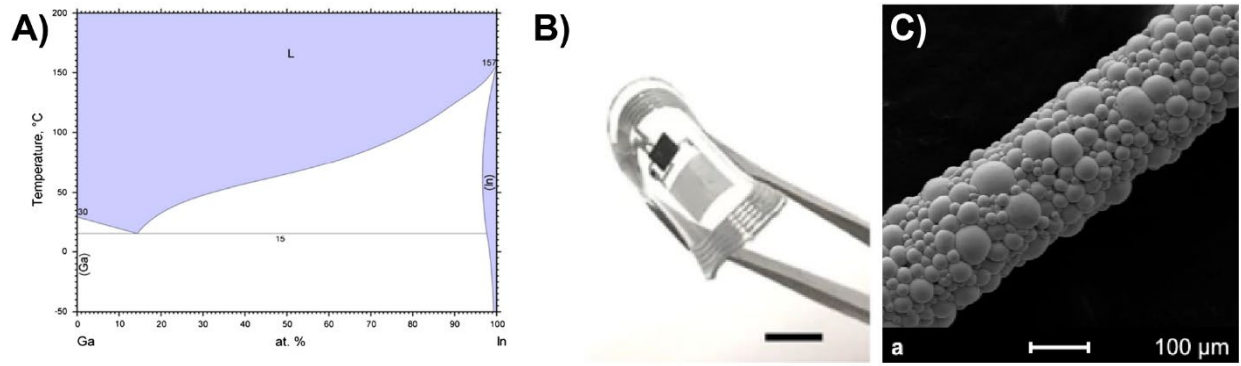


Figure 2.5: eGaIn liquid metal. (A) Gallium-indium phase diagram. [adapted from Ref. [50]] (B) A photo of a near field communication antenna with strain sensor, made by patterning eGaIn onto an evaporated metal pattern. [adapted from Ref. [51]] (C) A micrograph of a printed trace of eGaIn emulsion. [adapted from Ref. [52]]

In addition to eGaIn's low melting point, this alloy is considered non-toxic and has an electrical conductivity of 3.4×10^6 S/m [53], making it an attractive candidate for wearable electronic applications (**Fig 2.5B**). While this electrical conductivity is only 5.9% of bulk copper, it is more than 50x higher than many filled composites. eGaIn also has a negligible electrical hysteresis in response to shape change, since it is a particle-free liquid that can readily flow. However, given this flow behavior, eGaIn must be fully encased in an elastomeric structure. Under these conditions, eGaIn mimics the mechanical hysteresis of the polymeric encapsulant, which can be designed to be negligible compared to the hysteresis of highly filled conductive composites [51, 54, 55]. Notably, eGaIn exhibits a very high surface tension (~ 624 mN/m), which can be both advantageous and disadvantageous depending on the application [53]. Its high surface tension hinders deposition using techniques such as direct ink writing or screen printing due to droplet formation. However, it also enables precise patterning via surface activation methods [51]. Similar to the way solder paste selectively wets metal pads on a printed circuit board, while avoiding the solder mask, eGaIn can be selectively deposited on metal-coated regions, enabling

high-fidelity patterning without spreading [51]. eGaIn also readily forms a thin solid oxide layer upon exposure to oxygen. Once again, this feature also presents both advantages and challenges. In applications where eGaIn is encapsulated and repeatedly deformed in an oxygen-permeable matrix such as silicone, the oxide can continue to grow over time. This gradual buildup can lead to increased electrical resistance and a decline in performance, particularly in long-term or high-sensitivity devices. However, oxide stabilization layers also enable the emulsification of eGaIn to form stable, low surface tension inks (**Fig. 2.5C**) [52, 56] as well as specialty printing methods that control the oxide formation [57, 58].

2.3.2.3 *Stretchable Ionic Conductors*

Another important class of intrinsically stretchable conductors with negligible electromechanical hysteresis is ionically conducting liquids and gels [59]. These materials fall into two main categories: ionic liquids and dissolved salt solutions [60]. Ionic liquids are room-temperature molten salts composed entirely of free-moving cations and anions, enabling efficient ionic charge transport largely decoupled from mechanical strain. They are characterized by high thermal stability, low volatility, and excellent deformability. In contrast, salt solutions, such as aqueous NaCl, are composed of high-melting-point salts dissolved in a solvent. While functionally similar, these solutions contain a lower density of charge carriers and are more prone to solvent evaporation. Both types of ionically conducting fluids can sustain large deformations without cracking, delaminating, or introducing electromechanical hysteresis, making them especially well-suited for compliant electronic systems [60]. Their fluid nature allows them to endure repeated mechanical cycling without degradation, as they lack the rigid interfaces or fragile percolation networks found in particle-filled composites. Like liquid metals, these fluids must be encapsulated inside of a polymeric matrix to contain their flow. However, swollen polymer networks can also

be built inside of these liquids, to form ionogels [60]. Ionogels are viscoelastic solids that preserve the liquid's high ionic conductivity while providing improved mechanical integrity.

Despite these advantages, ionically conducting systems exhibit key limitations. Their electrical conductivity is typically lower than that of electronic conductors, particularly in dilute salt solutions [60]. Water-based electrolytes suffer from evaporation through polymeric encapsulants, while more stable ionic liquids are often costly and may raise biocompatibility concerns. Furthermore, ionic conductors rely on ion transport rather than electron flow, necessitating interfacial mechanisms, either Faradaic or non-Faradaic, for coupling to conventional electronics [61]. Faradaic processes involve redox reactions that can cause gas evolution or fouling of electrodes, while non-Faradaic processes rely on the formation of electrical double layers, effectively creating ionic capacitors [61]. These characteristics limit the use of ionically conducting materials in applications demanding DC conductivity or high-frequency signal transmission. Nonetheless, their exceptional mechanical compliance, cycling stability, and low hysteresis make them compelling candidates for stretchable sensing and actuation platforms where such trade-offs are acceptable. Researchers have even leveraged the unique ionic transport phenomena to make stretchable devices ranging from actuators and speakers [60], sensors [62], capacitors [63], and energy harvesters [64].

2.3.2.4 *Semiconducting Polymers*

Semiconducting polymers are another important class of intrinsically stretchable electronic materials. These materials typically exhibit elongations at break below 50% and can be processed into highly flexible thin films. However, their electrical conductivity is substantially lower than those of metallic conductors, generally below 3000 S/m [65]. Despite their limited stretchability and conductivity, semiconducting polymers play a crucial role in printed electronic devices due to

their utility as organic electrochemical transistors (**Fig. 2.6A**) [18] and their capacity for mixed-mode ionic and electronic conduction [66].

Poly(3,4-ethylenedioxythiophene) (PEDOT) electrically stabilized with poly(styrenesulfonate) (PSS) is the most extensively studied conducting polymer within this category, notable for its biocompatibility and ease of processing (**Fig. 2.6B**) [66]. PEDOT undergoes oxidative doping, involving the removal of electrons from its π -conjugated backbone, generating positively charged holes that function as mobile electronic carriers [66]. These charges are balanced by stationary, negatively charged sulfonate groups in PSS, which concurrently enhance the polymer's hydrophilicity. Electrical conduction in PEDOT:PSS occurs by hopping along holes between PEDOT chains when a drain voltage is applied. Due to its intrinsic doping, PEDOT:PSS behaves as a depletion mode semiconductor in a normally-on state, conducting electricity without an applied gate voltage (**Fig 2.6C**). In this state, it functions as a conductive polymer, and is often used in this way [49]. Application of a positive gate bias induces ionic migration from an electrolyte into the polymer, neutralizing the sulfonate counterions and effectively de-doping the polymer, thereby inhibiting hole hopping, and transitioning the device into an off-state [66]. Conversely, other semi-conducting polymers can exhibit a normally-off state (accumulation mode) and are activated by applying a negative gate voltage (**Fig. 2.6D**) [67].

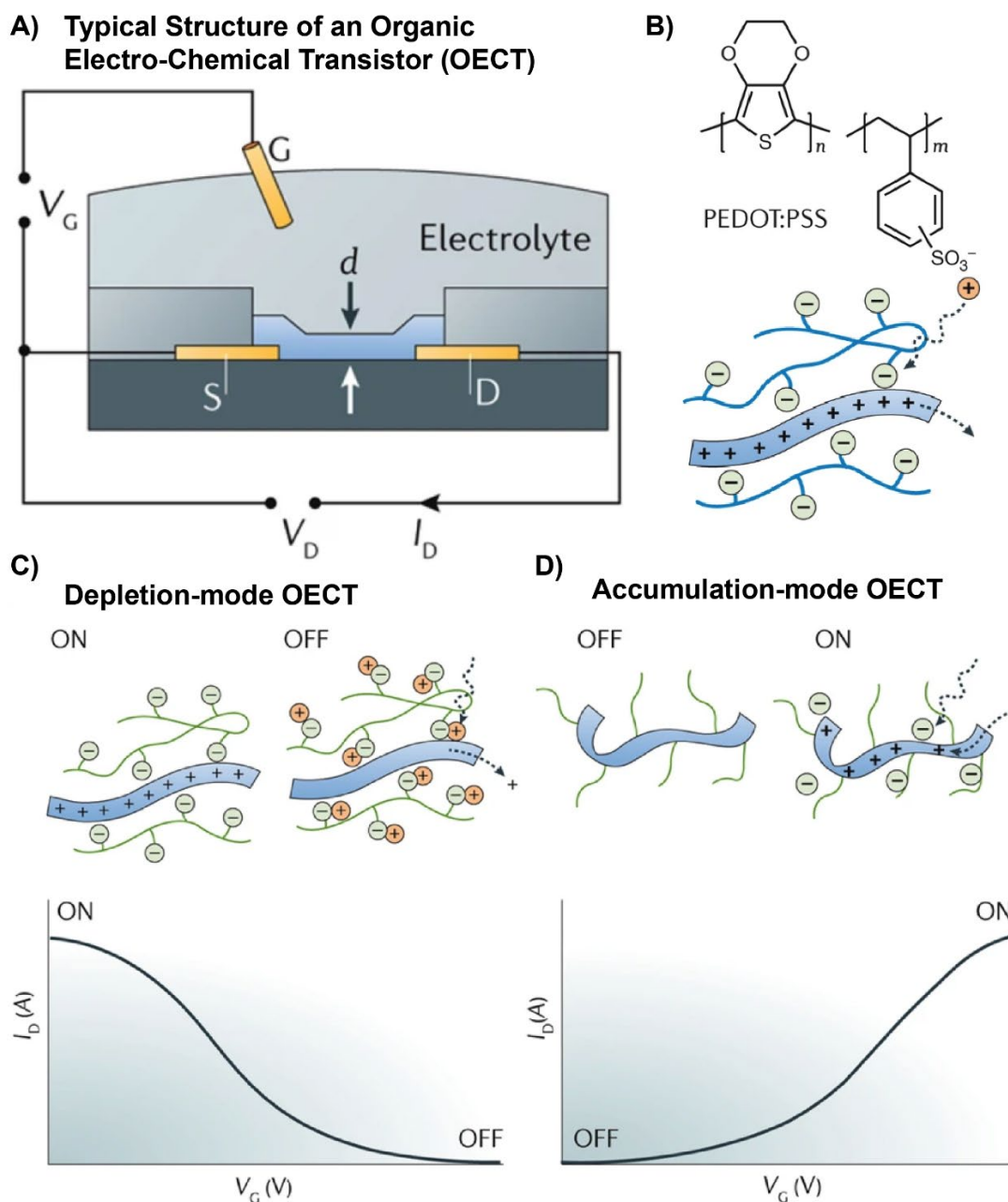


Figure 2.6: Structure and operation of organic electrochemical transistors. (A) The typical structure of an organic electrochemical transistor (B) Top: The chemical structure of PEDOT:PSS Bottom: A diagram of PEDOT:PSS roles in the depletion mode semi-conducting polymer. (C) A diagram of the functioning principle of a depletion mode OECT and a typical relationship for drain current I_D as a function of gate voltage V_G . (C) A diagram of the functioning principle of an accumulation mode OECT and a typical relationship for drain current I_D as a function of gate voltage V_G . [adapted from Ref. [66]]

Although pristine PEDOT:PSS films have a limited elongation at break ($\sim 5\%$), numerous strategies have emerged to enhance their mechanical properties. For instance, incorporating polyvinyl alcohol into PEDOT:PSS has successfully increased elongation at break beyond 100%, although this enhancement typically occurs alongside reduced conductivity [49]. Additionally, dual-network hydrogels composed of a polyacrylic acid scaffold infiltrated with PEDOT:PSS achieve remarkable elongation, exceeding 600%, while maintaining a conductivity of approximately 24,700 S/m. Nevertheless, these hydrogel-based materials remain vulnerable to dehydration [68]. To address this limitation under non-hydrated conditions, researchers have engineered customized PEDOT:PSS-based co-polymers, achieving elongations at break surpassing 75% [69]. Alternative semiconducting polymers with tailored molecular structures aimed at reducing crystallinity have reached elongation at break values of approximately 40%. Notably, laminating these polymers onto elastomeric substrates like PDMS has facilitated significant enhancements, pushing elongation at break beyond 100% [70].

2.3.3 INTRINSICALLY STRETCHABLE INSULATING MATERIALS

Both geometrically and intrinsically stretchable electronic materials are typically bonded to or encapsulated within elastomeric insulating matrices. These matrices provide the mechanical framework of the device and serve to insulate the electronic components from external interference. Because they constitute the majority of the device volume, they largely determine its bulk mechanical properties. To match the mechanical behavior of biological tissues, ideal elastomers should exhibit a low elastic modulus, high elongation at break, high toughness, and high elastic resilience. In both intrinsically and geometrically stretchable systems, devices are often engineered to localize and limit strain in critical regions to prevent failure and ensure reliable operation [9, 18]. Inclusion of materials with increased elastic modulus within a substrate material

with a significantly lower elastic modulus, as a rigid-island, is one demonstrated way to achieve this [18, 30, 71-73]. From this perspective, it is advantageous to design material systems in which both stretchable and rigid components are compatible in terms of processing and integration. Below, the most widely used insulating matrix materials in contemporary stretchable electronics are introduced.

2.3.3.1 *Silicone Elastomers*

Polydimethylsiloxane (PDMS) elastomers are widely used across many industries, with especially broad adoption in stretchable electronics [7, 48]. Their prevalence in this field is due to a unique combination of favorable material properties and versatile processability. From a performance standpoint, PDMS offers a low and tunable elastic modulus, exceptionally high resilience, unmatched thermal stability among elastomers, resistance to UV and chemical degradation, intrinsic biocompatibility, and low surface energy [74]. A key advantage of PDMS is its formulation from easy-to-handle liquid oligomers that are cross-linked via an addition-curing reaction, resulting in elastomers with minimal shrinkage during curing (**Fig. 2.7A**) [74]. The pot life and curing rate can be tailored by adjusting the catalyst type and concentration [74]. Rheological behavior and mechanical properties can also be tuned by incorporating various forms of silica, enabling mechanical reinforcement and process optimization [74]. These features make PDMS compatible with a wide range of manufacturing methods, including spin coating, injection molding, casting, knife coating, screen printing, and direct ink writing, enabling its use in varying form factors and fabrication processes (**Fig. 2.7B & Fig. 2.4C**). However, PDMS does have some limitations. Once mixed, its pot life is relatively short and bonding to cured PDMS is challenging due to its low surface energy [74]. Additionally, its elastic modulus is inherently limited, typically tunable only within the range of a few hundred kilopascals to several megapascals. The difficulty

of bonding other material chemistries to silicones creates major challenges for mechanically tuning the devices with additional strain relief, and in fabricating complex multi-layered devices out of multiple material chemistries. Silicones are also prone to cure inhibition due to the sequestration of the platinum catalyst by thiols, amines, alkenes, or other reactive contaminants, which further exacerbate incompatibilities in multi-chemistry systems [74].

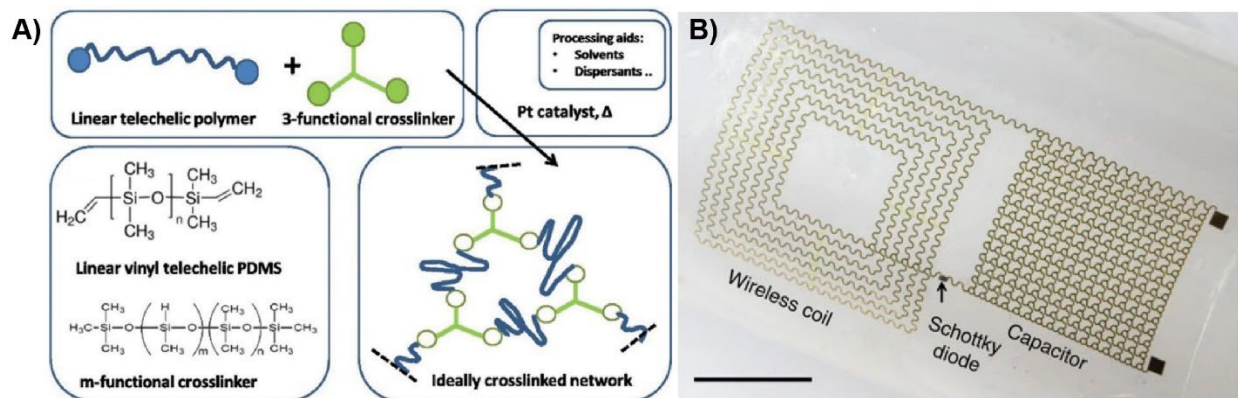


Figure 2.7: PDMS-based stretchable electronics. A) A diagram showing the core constituents of a PDMS elastomer and the resulting polymer network that is formed. [adapted from Ref. [74]] B) A stretchable wireless recharging module for an intrinsically stretchable battery, with PDMS as the substrate material. [adapted from Ref. [13]]

2.3.3.2 Thermoplastic Elastomers

Thermoplastic elastomers (TPEs), including styrene-ethylene-butylene-styrene (SEBS) [10, 18] and thermoplastic polyurethanes (TPUs) [75-78], are increasingly utilized in stretchable electronics due to their broad mechanical tunability and processing resilience. TPEs combine the elasticity of chemically cross-linked rubbers with the reprocess-ability of thermoplastics, owing to their phase-separated block structures that form reversible physical crosslinks (**Fig. 2.8 A-C**). Materials, like SEBS, can be created with a wide range of tunable elastic moduli, from <100 kPa to over 10 MPa [18], by controlling their hard and soft block composition, molecular weight, and additives, such as oils or fillers (**Fig. 2.8B, D**) [18, 79]. TPUs (**Fig. 2.8C**) similarly offer high

toughness, durability, and tunable mechanical behavior, with greater chemical resistance and load-bearing capacity than SEBS [78]. Both classes of materials can be engineered to exhibit high elongation at break, low hysteresis, and fatigue resistance, enabling use in mechanically demanding, bio-integrated, or load-bearing applications where PDMS is often inadequate. However, these advantages come at the cost of more complex processing. Unlike PDMS, which begins as a flowable liquid, TPEs require either melt processing or solution casting from organic solvents, both of which limit compatibility with common patterning techniques such as soft lithography, screen printing, or direct ink writing. Achieving fine features and multilayer assemblies is more challenging, and substrate compatibility can be an issue due to the higher processing temperatures or solvent use. Additionally, while TPEs are more easily bonded than PDMS [78], solvent welding or adhesion promoters are sometimes required for robust interfacial adhesion. Despite these drawbacks, the ability to finely tune mechanical properties and reprocess materials without chemical curing makes SEBS, TPU, and related TPEs strong candidates for applications requiring tunable elasticity and improved interfacial bonding.

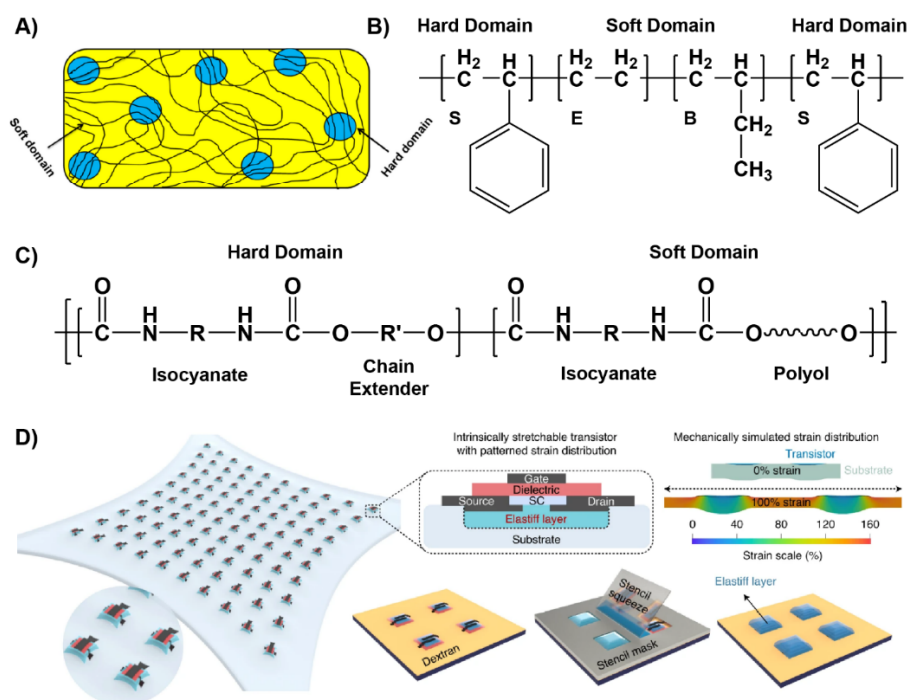


Figure 2.8: Design and composition of thermoplastic elastomers for stretchable electronics. A) A diagram of the macroscopic organization inside of a TPE, showing hard domains that assemble to form physical cross-links, and soft domains that remain amorphous, providing stretchability. [adapted from Ref. [80]] B) The chemical structure of Styrene Ethylene Butylene Styrene co-polymer (SEBS). C) The chemical structure of a thermoplastic polyurethane polymer. D) A schematic showing the structure and working principle of an intrinsically stretchable transistor with patterned strain distribution, where both the Elastiff and substrate layers are composed of SEBS copolymer of varying elastic modulus. [adapted from Ref. [18]]

2.3.3.3 *Thiol-ene Elastomers*

Thiol-ene elastomers are gaining traction in stretchable electronics due to the versatility and efficiency of the thiol-ene click reaction; a highly selective, fast addition reaction that can be initiated thermally or photochemically, depending on the initiator (**Fig. 2.9**) [81]. A broad range of thiol- and alkene-functional oligomers are commercially available [81]. Notably, di-vinyl-polydimethylsiloxane (a staple in PDMS formulations) is intrinsically alkene-functional and can be cross-linked with thiol-functional PDMS via the thiol-ene reaction to form photocurable elastomers with mechanical properties comparable to those of platinum-catalyzed hydrosilylation-cured PDMS, one of the most widely used materials in stretchable electronics [82].

Beyond PDMS-based systems, thiol-ene chemistry enables the use of various alkene-functional oligomers derived from natural oils [81], rubber resins [81], and synthetic glycols [83]. This broadens the material palette and allows fine-tuning of mechanical properties and surface energy, making thiol-ene systems particularly attractive for multi-material, multi-layer device fabrication [83].

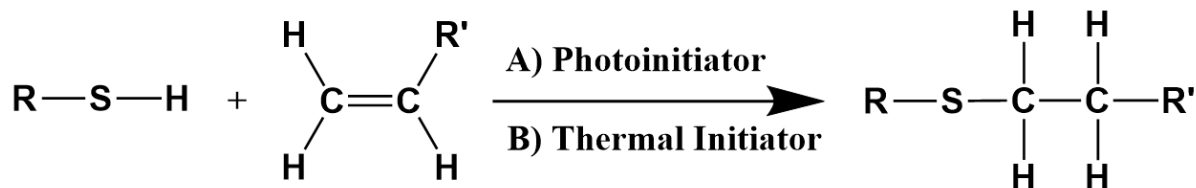


Figure 2.9: The thiol-ene click reaction by either thermal or photoinitiation

In addition to compositional flexibility, thiol-ene systems offer processing advantages. Their step-growth addition curing mechanism yields uniform high molecular weight polymer networks with low shrinkage starting with low viscosity oligomeric feedstocks [81]. Compared to acrylates, which are currently the most common UV-curable resins, thiol-enes offer greater control over stiffness and resilience, improved biocompatibility, reduced oxygen inhibition, and more predictable mechanical performance, all from low-viscosity precursors suitable for digital light patterning or rapid global UV curing [83].

2.3.4 PREFABRICATED ELECTRONIC MATERIALS

Semiconducting devices are central for wearable stretchable electronics, as they form the basis of all computing logic. To date, researchers have made tremendous strides towards stretchable organic logic-based devices. Zhong and Bao et al recently reported the capability to fabricate 1000 stretchable organic transistors on a 1 mm² area [8], an impressive feat. However, by contrast, leading industrial silicon microchip manufacturers have achieved >300 million transistors per mm² using a 2 nm fabrication process [12]. Fundamental differences in the driving mechanism of organic semiconducting polymers compared to silicon semiconductors are likely to prevent organic semiconductors from ever achieving the density and performance of modern computer chips, namely the 3 order of magnitude difference in charge carrier mobility and the structural and energetic disorder caused by irregular polymeric packing [84]. Hence, we envision that stretchable organic semi-conductors will be used only in applications where silicon microchips have major drawbacks, such sensing and stimulation at soft biological interfaces. For other applications, it is essential to develop strategies to robustly integrate rigid electronic devices such as silicon chips and modules into stretchable electronic devices.

2.4 STRETCHABLE ELECTRONIC DEVICES AND FABRICATION METHODS

Fabrication methods used to produce intrinsically stretchable electronic devices share many similarities with that of geometrically stretchable devices, i.e., they both rely on multi-step combinations of material deposition and photolithographic patterning techniques. The primary distinction lies in their material handling approaches. Geometrically stretchable devices typically begin with pre-fabricated laminated material sheets, selectively masking regions to preserve and etching away the remainder. By contrast, intrinsically stretchable devices are built up layer by layer, using photoresist to define areas for selective material removal during each etching cycle.

One of the most complex and exciting intrinsically stretchable devices in recent years was demonstrated by Zhong et al. [8]. This device, consists of an integrated electronic skin composed of thousands of organic transistors, embedded in a TPE matrix, and interconnected by liquid metal wiring (**Fig 2.10**). Their team demonstrated several core circuit architectures typically associated with rigid silicon electronics, including 2000-transistor arrays with >98% functional yield, ring oscillators operating up to 41 kHz, and NAND/NOR logic gates. In addition to replicating these traditional electronic functions, they also showcased capabilities unique to intrinsically stretchable platforms. For example, they fabricated a finger-conformable, tactile reader that can sense and decode Braille patterns, demonstrating direct interfacing with soft and textured surfaces. They demonstrated that not only can intrinsically stretchable electronics rival the capabilities and complexity of conventional semiconductor systems in certain applications, but that these novel form factors and mechanics give rise to new applications not accessible using rigid electronics.

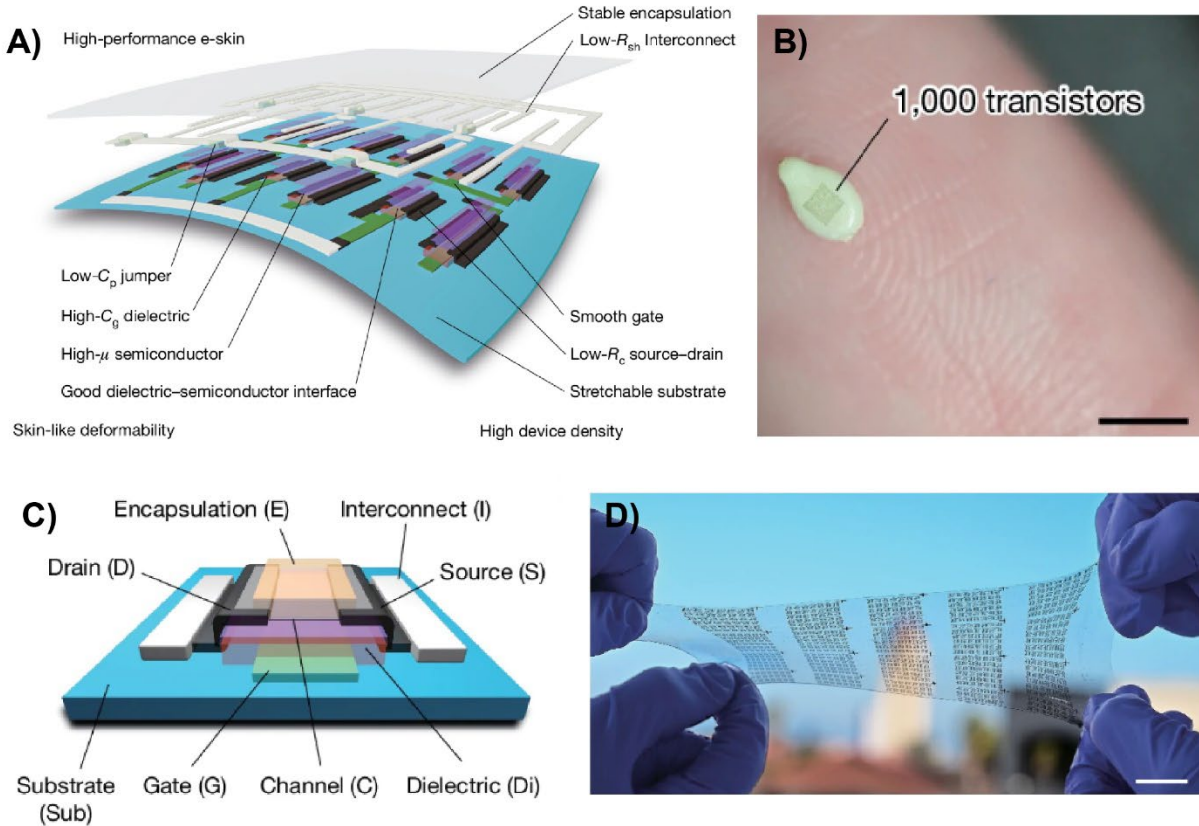
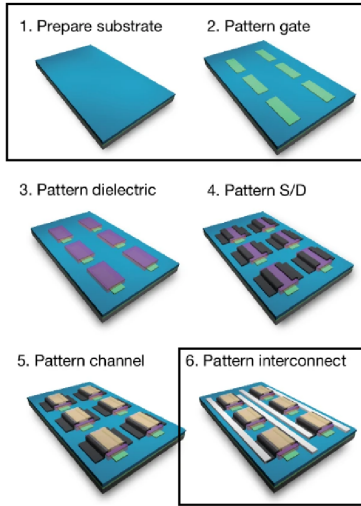


Figure 2.10: High-speed and large-scale intrinsically stretchable integrated circuits. A) Three-dimensional diagram of the high-performance intrinsically stretchable electronics, consisting of the stretchable substrate, gate electrode (bottom electrode), gate dielectric, S/D electrodes, semiconductor, channel encapsulation, jumper dielectric, top electrode (interconnect) and top encapsulation. B) Photo of a high-density transistor array attached to a single white sesame seed with 1,000 transistors in an area of 1 mm^2 on a fingertip. C) Schematic of an intrinsically stretchable transistor. D) Photo of intrinsically stretchable electronics under large deformation after being released from the supporting substrate. Each block is a three-stage ring oscillator with 16 transistors. [adapted from Ref. [8]]

One of the most striking aspects of their approach is the sheer complexity and number of steps required for fabrication. Although not all steps are illustrated, the ones shown clearly reveal the time- and labor-intensive nature of the process (Fig. 2.11). To underscore this complexity, there are 38 major steps used in their device fabrication, each of which consists of multiple sub-steps [8]. Moreover, there are at least 17 distinct fabrication techniques used, including spin-coating, wet and dry transfer printing, drop casting, blade coating, photoresist exposure, optical alignment,

oven baking, plasma treatment, oxygen plasma etching, FeCl_3 etching, solvent dissolution, sonication, centrifugation, vacuum desiccation, dry ice chilling, and e-beam evaporation. While such process complexity has been successfully demonstrated for commercial semiconductor fabrication, they are not conducive to customization and do lead to substantial material waste. Rigid semiconductors are designed to interface with printed circuit boards through a small number of standardized formats, allowing a single scale-up process to yield millions of identical components that can be integrated into thousands of varying devices. Human bodies, by contrast, vary infinitely in form. Soft electronic devices that conform to, sense, or stimulate are uniquely tailored to each individual. Hence, new manufacturing methods are needed for fabricating stretchable electronics based on digital and modular designs that enable customization “on-the-fly”.

A) Simplified Fabrication Steps

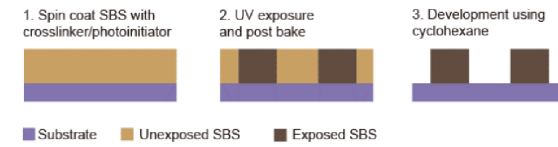
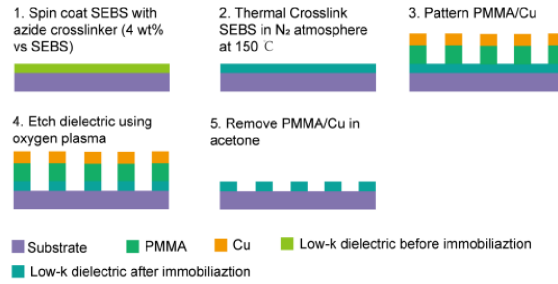


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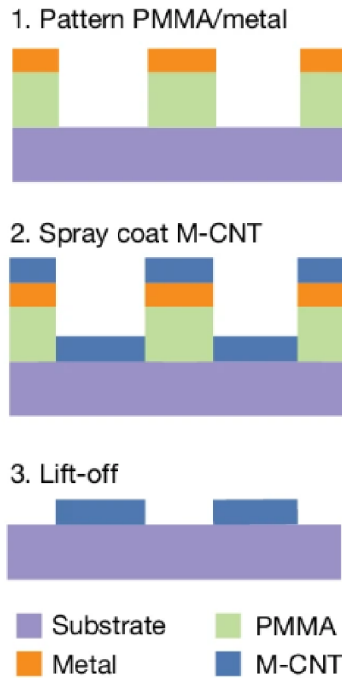
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B)

3. Dielectric



C) 4. Source/Drain



D)

5. Channel

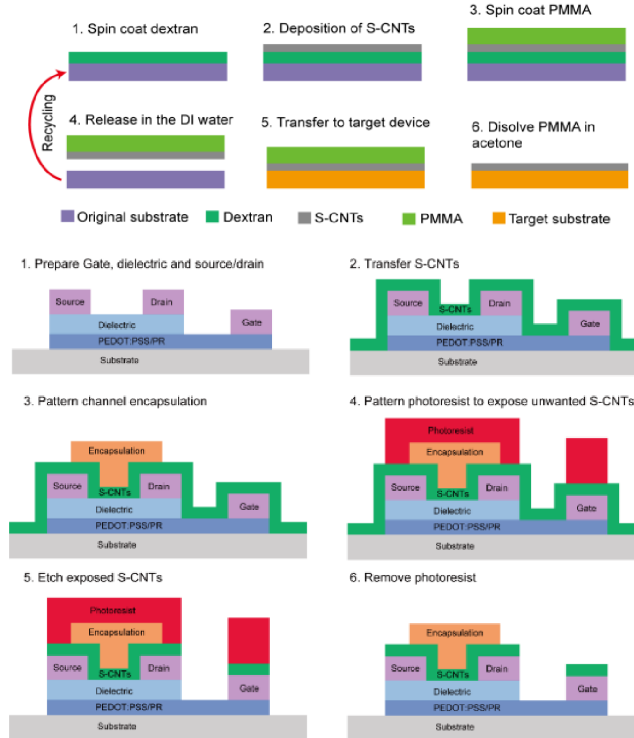


Figure 2.11: Simplified fabrication steps for manufacturing intrinsically stretchable integrated circuits. A) An overview of device manufacturing steps. B) An overview of the major steps required to pattern the dielectric. C) An overview of the major steps required to pattern the source and drain electrodes. D) An overview of the main steps required to pattern the channel (semiconductor material). [Adapted from Ref. [8]]

2.5 DIGITAL PRINTING

As demonstrated throughout this chapter, stretchable electronic devices rely on the integration of multiple material types working in concert to achieve their function. The combination of diverse materials and overall dimensions (mm-to-cm in area) of body-integrated devices results in the need to define thousands of intricate features within each device. An ideal digital printing process for manufacturing such systems must therefore be capable of depositing multiple materials with sufficient resolution at a high volumetric throughput. Although multiple printing technologies have emerged over the past two decades, only a few are well-suited for multi-material applications. Amongst these, the three most prominent are inkjet printing, direct ink writing, and fused deposition modeling. The remainder of this section will review each of these candidate technologies in detail.

2.5.1 INKJET PRINTING

Inkjet printing is a non-contact, drop-on-demand digital fabrication method that has found widespread use in industrial printed electronics [85]. The technology operates by ejecting small volumes of ink through micron-scale nozzles in response to an applied electrical signal, enabling precise deposition of materials onto a substrate [86]. The process is digitally controlled, allowing high-resolution patterning without the need for physical masks or stencils. In the context of stretchable electronics, inkjet printing offers a compelling approach for depositing conductive, dielectric, and functional inks with micron-level precision [87].

One of the primary advantages of inkjet printing is its high resolution and material efficiency. Inks are dispensed in 10-100 picoliter droplets, allowing the definition of fine features and complex interconnects with minimal overspray or bleeding [86]. This makes it particularly well suited for patterning conductive traces, sensing elements, and thin dielectric layers in

multilayer device architectures. Inkjet systems are also highly reconfigurable, enabling pattern changes on demand and direct additive printing from digital files, which reduces development time and prototyping costs.

Inkjet printing supports multi-material deposition, provided the inks are appropriately formulated for compatibility. Different materials can be deposited in adjacent or stacked layers through multi-nozzle printheads using either multiple printheads or sequential print passes. This capability is particularly useful in stretchable systems, where spatial variation in material composition is often necessary to balance mechanical compliance with electronic functionality [18]. Additionally, inkjet systems are compatible with large-area substrates and can be integrated into roll-to-roll processing workflows, where thousands of nozzles operate in parallel, making them well suited for scalable manufacturing.

Despite these advantages, inkjet printing has significant limitations. The range of printable materials is tightly constrained by requirements on ink viscosity, surface tension, density, and particle size. The most widely accepted criterion for assessing ink jet-ability is the inverse of the Ohnesorge number (Oh), defined as Z :

$$Z = Oh^{-1} = \frac{\sqrt{\rho\gamma a}}{\eta} \quad (2.3)$$

where ρ is the ink density, γ is the surface tension, a is the characteristic length (typically the nozzle diameter), and η is the dynamic viscosity. A jettable ink generally falls within the range $2 < Z < 10$ [86]. This dimensionless group describes the ratio of inertial forces to viscous forces in the fluid. When inertial forces dominate ($Z > 10$), droplets tend to fragment and cause satellite formation or splattering. When viscous forces dominate ($Z < 2$), the droplet may fail to detach cleanly from the nozzle and pool at the printhead.

In practice, commercial inkjet systems operate within a narrow range of nozzle diameters, and the surface tension and density of printable polymers do not vary widely. Viscosity is the most influential parameter controlling jettability. Most inkjet systems are limited to low-viscosity fluids in the range of 12–60 mPa·s and require particle sizes below 1 μm [88-90]. As such, many high-performance conductive pastes, nanoparticle suspensions, and elastomeric inks simply cannot be patterned via inkjet printing. Although emerging droplet formation methods are compatible with inks exhibiting broader Z ranges and higher viscosity, they are either not yet commercially scalable or not well suited for large nozzle arrays [91, 92]. Another limitation of inkjet printing is that the deposited features are typically thin and low in volume, which restricts mechanical robustness unless multiple layers are built up. For devices that require many layers, throughput is somewhat limited by the need to sequentially print each layer. This printing method is less suitable for applications requiring thick features or mechanically durable structures. Despite these constraints, inkjet printing is widely deployed for fabricating printed electronics, especially for applications where high resolution, design flexibility, and material minimization are prioritized.

2.5.2 DIRECT INK WRITING

Direct ink writing (DIW) is a highly versatile, extrusion-based digital printing technique that has become foundational in the additive manufacturing of soft functional materials. In DIW, viscous inks are extruded through a nozzle along a programmed toolpath, depositing material layer-by-layer, only where it is needed (**Fig 2.13 A-C**). This enables the fabrication of intricate three-dimensional structures with minimal waste. DIW is especially well suited for stretchable electronic devices due to its compatibility with a broad range of functional inks due to its unique ability to deposit highly viscous, shear-thinning fluids, particularly those with a rheological yield stress (**Fig. 2.13B**). These materials can be deposited in a liquid-like state and rapidly recover to a solid-like

form, preserving fine features immediately after printing (**Fig 2.12A,C**) [93]. Unlike printing methods that rely on droplet formation, DIW accommodates a wide range of materials that would otherwise be unprintable. This makes it ideal for printing conductive pastes [94], particle-filled elastomers [48], and high-performance dielectric materials [95], many of which naturally display viscoelastic shear thinning behavior.

DIW can be conducted under ambient conditions, although other temperatures can be used to modulate ink rheology and post-deposition behavior [96]. DIW supports true multi-material printing, either by sequential deposition of different inks [97, 98] or by using multi-input systems [99], enabling spatially defined material architectures essential for integrated stretchable electronics. Parallelization strategies using multi-nozzle arrays or multiple independent printheads have also been developed, though they either require multi-axis actuation for each nozzle or are restricted to periodic patterns [94]. Complex printheads capable of co-extruding multiple inks within a single filament have also been implemented to create stretchable sensors and dielectric elastomer actuators (**Fig. 2.12C**) [62, 100].

Despite its flexibility, DIW has important limitations. Unlike projection-based methods that cure entire layers simultaneously, or drop-on-demand techniques that use arrays of nozzles in simple raster patterns, DIW is a serial process in which every point of material must be deposited through a translating nozzle following curvilinear toolpaths (**Fig 2.12E**) [101]. Throughput therefore scales poorly with part complexity or size. This becomes a significant challenge in body-scale stretchable devices, where tens of thousands of features must be patterned over large areas. The resulting long print times and limited scalability remain key obstacles to broader adoption in high-throughput manufacturing. Nevertheless, for applications where material functionality, structural integration, and design flexibility outweigh speed or resolution, e.g., larger devices with

simple geometries [48] or microscale structures with complex architectures [97], DIW remains a powerful and adaptable platform for fabricating stretchable electronic systems.

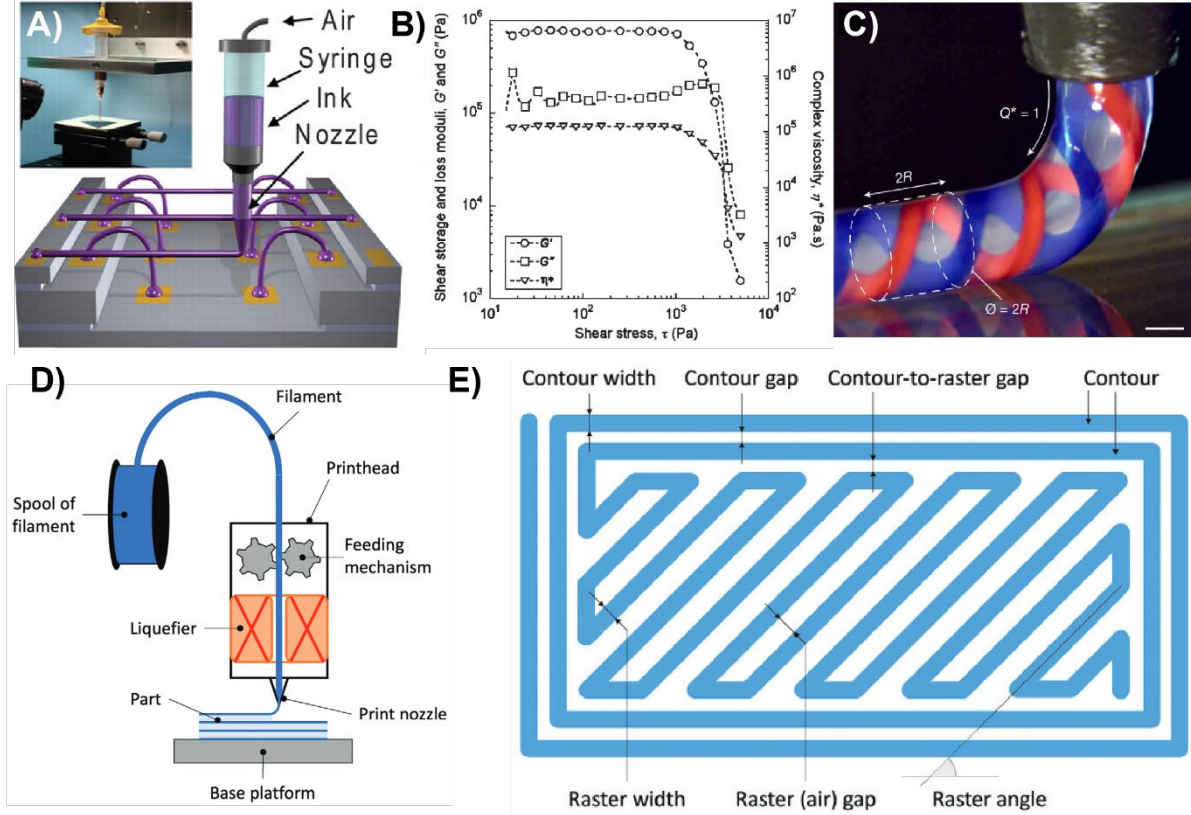


Figure 2.12: Direct Ink Writing (DIW) and Fused Filament Fabrication (FFF). A) A schematic illustration of a direct ink writing system. (inset) A photo of a silver nanoparticle ink being deposited via direct ink writing. [adapted from Ref. [102]] B) A plot of shear storage modulus (G') and shear loss modulus (G'') as a function of shear stress for an ideal ink for direct ink writing, showing the yield stress behavior and shear thinning nature of the ink. [adapted from Ref. [103]] C) A photo of a rotational multimaterial 3D printing nozzle depositing a multi-material filament containing 3 materials. [adapted from Ref. [100]] D) A diagram showing the key components of an FFF printer. E) A diagram of a representative machine toolpath that would be used to create a rectangular part using either FFF or DIW. [adapted from Ref. [104]]

2.5.3 FUSED FILAMENT FABRICATION

Fused filament fabrication (FFF), also known as fused deposition modeling, is a widely used extrusion-based printing technique in which a thermoplastic filament is fed into a heated nozzle, melted, and deposited layer by layer to form three-dimensional structures (Fig. 2.12D) [101]. It is

similar to DIW in that it is a filamentary extrusion method. While traditionally associated with rigid polymers like polylactic acid or acrylonitrile butadiene styrene, FFF has gained increasing relevance in stretchable electronics through the development of high-performance thermoplastic elastomers, such as thermoplastic polyurethanes (TPUs) and styrenic block copolymers.

A major advantage of FFF is its ability to process these elastomers in their melt state, eliminating the need for solvent casting or curing. This thermal processing route simplifies materials handling, avoids drying or post-processing steps, and allows for direct patterning of mechanically robust, solvent-free elastomeric structures. Because molten thermoplastics solidify rapidly upon cooling, thick (or thin) layers can be deposited in a single pass, enabling fast build-up of mechanically durable features. This makes FFF particularly well suited for printing substrates, stretchable housings, and structural layers in wearable or conformal devices. FFF also benefits from a mature ecosystem of low-cost hardware and open-source control systems, making it widely accessible for prototyping and custom fabrication. Some systems can be adapted for multi-material printing through multiple extruders or tool-changing mechanisms, which can facilitate limited functional integration within elastomeric structures.

FFF does have several key limitations. Like direct ink writing, it is a serial process that relies on the mechanical movement of the printhead, resulting in modest throughput and long print times for large or complex parts (**Fig 2.12E**). The technique is also limited to thermoplastic materials [104], which excludes many important classes of inks used in stretchable electronics, such as liquid metals, highly filled conductive pastes, silicone elastomers, and photopolymerizable resins. Additionally, the method typically requires filament feedstock. Filaments made from soft or very flexible elastomers can be difficult to manufacture accurately, and are prone to dimensional changes, kinking, or buckling during feeding into the printhead, leading to inconsistent extrusion

and reduced reliability [104]. Despite these constraints, FFF remains a valuable approach for building structural and insulating components in stretchable electronic systems, particularly when durability, simplicity, and solvent-free processing are priorities [76, 105].

2.6 CONCLUSIONS

The field of soft electronics has advanced through two distinct approaches: geometrically engineered stretchability and intrinsically stretchable materials. While geometric strategies have enabled impressive demonstrations, they face fundamental limitations in integration density, interface reliability, and scalability. Intrinsically stretchable materials, such as conductive composites, liquid metals, ionic conductors, and semiconducting polymers, offer compelling advantages by providing mechanical compliance without complex patterning. However, in practice, organic semiconductors simply cannot match the computational density of silicon microchips (1000 vs. 300 million transistors per mm^2). We posit that the future lies in devices based on hybrid architectures, which combine intrinsically stretchable materials for sensing, interconnects, and bio-interfacing with rigid silicon chips and other surface mounted electrical components. However, their successful integration requires new manufacturing paradigms. While digital printing methods offer distinct capabilities, none are sufficient for complete device fabrication. The path forward requires: (1) continued development of intrinsically stretchable materials with improved electrical and mechanical performance, (2) innovative strategies for integrating and protecting rigid components within compliant systems, and (3) automated, multi-material digital fabrication platforms capable of producing customized multi-material devices with a broad range of materials efficiently. Only by establishing this integrated approach can one seamlessly merge stretchable electronics with biological systems.

CHAPTER 3

DIRECT INK WRITING FOR INSTRUMENTED HEART-ON-CHIP

MODELS

This chapter has been adapted from the following manuscript:

J. U. Lind*, T. A. Busbee*, A. D. Valentine, F. S. Pasqualini, H. Yuan, M. Yadid, S.-J. Park, A. Kotikian, A. P. Nesmith, P. H. Campbell, J. J. Vlassak, J. A. Lewis, K. K. Parker, “Instrumented cardiac microphysiological devices via multimaterial three-dimensional printing.” *Nature Materials* 16 (3), 303 (2017).

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3.1 INTRODUCTION

Biomedical research has relied on animal studies and conventional 2D cultures of human cells for human drug discovery and safety screening for decades. Microphysiological systems (MPS), also known as organs-on-chips, that recapitulate the structure and function of native tissues *in vitro*, have recently emerged as a promising alternative [106]. However, most organ-on-chip models lack integrated sensors for *in situ* measurement of cell function [107]. Models developed for human cardiac tissue rely on microscopy coupled with optical tracking analysis for assessing tissue contractile stress. For instance, muscular thin-film (MTF) assays track changes in curvature of soft cantilever substrates induced by the contraction of a laminar tissue [108], while micro-post assays allow one to measure the deflection of pillars supporting a micro-tissue [109]. Although these assays have proven valuable for short-term modelling of human disease and small-scale drug screening applications [106, 110, 111], they are not well suited for higher-throughput, longitudinal studies. Moreover, biomimetic microsystems are at present fabricated using soft material lithography-based techniques that require multiple steps, masks and dedicated tools [109, 112-

114], which hinders rapid prototyping and tissue specific customization. By contrast, multi-material 3D printing of viscoelastic inks enables a wide range of functional, structural and biological materials to be patterned and integrated in a single programmable manufacturing step [99, 115-117].

Here, we introduce a fully 3D printed and instrumented microphysiological device that provides continuous electronic readout of the contractile stress of multiple laminar cardiac micro-tissues (**Fig. 3.1A,B**). Each device contains three key features: multilayer cantilevers, composed of a base layer, an embedded strain sensor, and a tissue-guiding layer; electrical interconnects for readout; and eight independent media wells (**Fig. 3.1C–I**). The tissue-guiding layer promotes self-assembly of engineered physio-mimetic laminar tissues from neonatal rat ventricular myocytes (NRVMs) and human induced pluripotent stem cell derived cardiomyocytes (hiPS-CMs). To create this integrated device, six materials are patterned sequentially via direct ink writing (DIW) multi-material 3D printing. Our microphysiological device facilitates tissue culture and non-invasive analyses of tissue contractile strength over several weeks, and facilitates drug studies inside a controlled incubator environment.

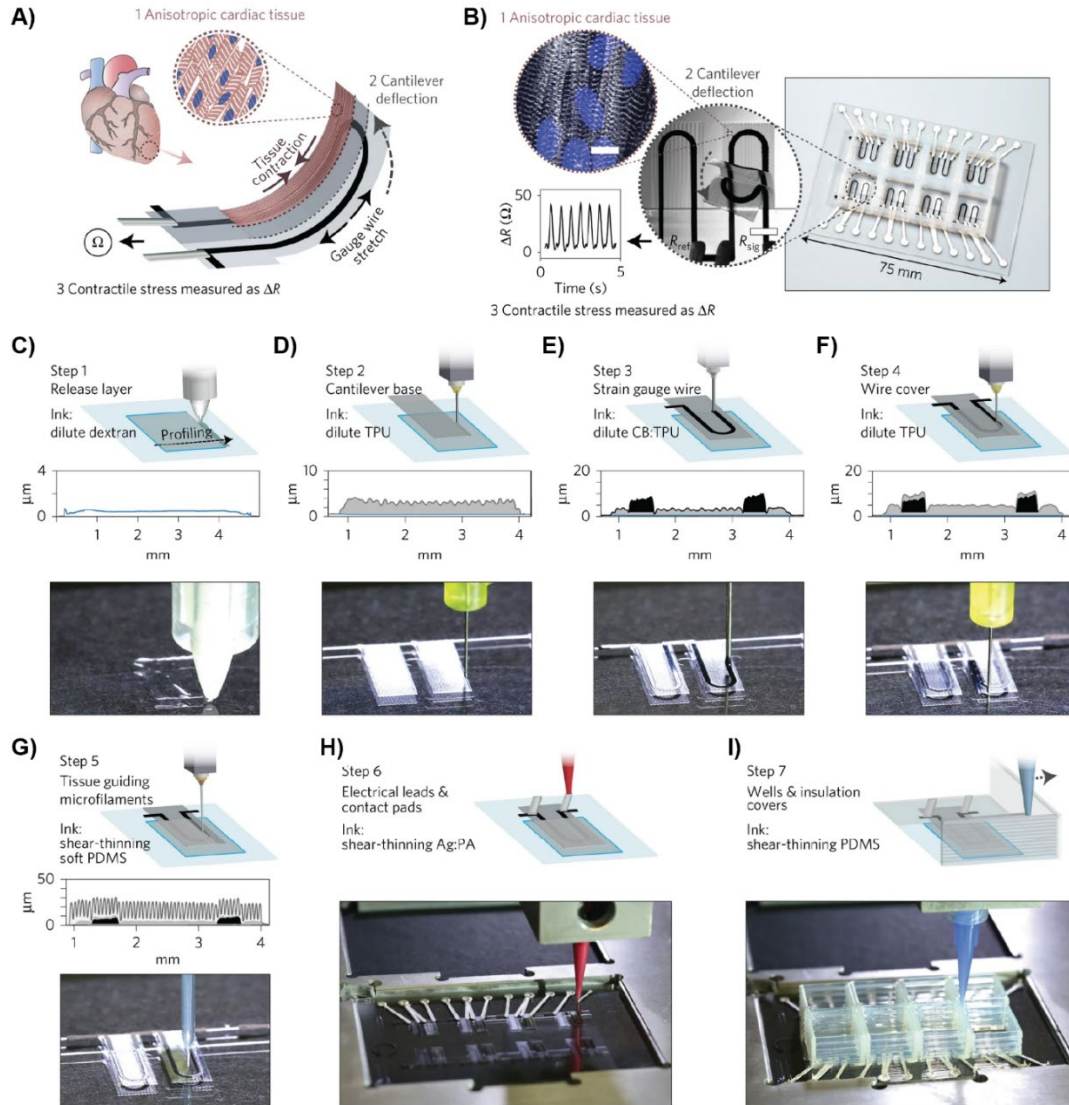


Figure 3.1: Instrumented heart-on-chip model via multi-material 3D printing. (A) Schematic view of device. Contraction of an anisotropic engineered cardiac tissue (1) deflects a cantilever substrate (2), thereby stretching a soft strain gauge embedded in the cantilever. This generates a resistance change proportional to the contractile stress of the tissue (3). (B) The fully printed final device. Insert 1: Confocal microscopy image of immunostained laminar NRVM cardiac tissue on the cantilever surface. Blue, DAPI nuclei stain. White, α -actinin. Scale bar, 10 μm . Insert 2: Still images of a cantilever deflecting upon tissue contraction. Insert 3: Example resistance signal. (C-I) Automated printing of the device on a 2 inch $\times$ 3 inch glass slide substrate in seven sequential steps. For each step, a corresponding still image from the printing procedure is shown. For steps 1–5, a stylus profiling cross-sectional contour of the cantilever is also shown. (C) In print step 1, a 0.5- μm dextran thin-film sacrificial layer is printed. (D) In print step 2, a 3 μm TPU thin-film cantilever base is printed. (E) In print step 3, a 6.5- μm -thick CB:TPU strain sensor loop is added to the cantilever base. (F) In print step 4, a 1.5- μm TPU wire cover is added. (G) In print step 5, 20- μm -tall, 60- μm -wide PDMS microfilaments are printed in slightly overlapping lines. The filaments constitute the top part of the cantilever and guide cardiomyocytes to form anisotropic laminar tissues. (H) In print step 6, electrical leads and contact are added using a high-conductivity Ag:PA ink. (I) In print step 7, covers to insulate exposed wires and wells to contain cells and media are printed using PDMS, PLA or ABS

3.2 EXPERIMENTAL

3.2.1 Materials System

Six inks were used to print the devices fabricated in this work. A water-soluble dextran layer enables selective release of the cantilevers from the substrate. A soft thermoplastic polyurethane ink (TPU), deposited as a thin film, insulates conductive features with limited vertical build-up. A carbon black doped TPU (CB:TPU) ink acts as a piezoresistive strain sensor. A soft polydimethylsiloxane (PDMS) ink enables precise micron-scale patterning of 3D tissue alignment features without significantly increasing the bending stiffness. A more rigid PDMS enables creation of structural liquid handling features, and a highly conductive silver polyamide (Ag:PA) ink electrically connects sensors without significantly contributing to the overall resistive load.

Release Layer:

10 g ml⁻¹ dextran (Sigma-Aldrich) was dissolved in 75:25 v:v, water : isopropanol. The ink was prepared by magnetic stirring in a closed container at 300 RPM until fully dissolved. The ink was then transferred to a pressure sensitive pen using a pipet.

Elastomeric Insulating Layer:

Thermoplastic Polyurethane (TPU) 15 wt% Elastollan 35A (BASF) dissolved in 4:1 v:v tetrahydrofuran:dimethylformamide solvent blend. The ink was prepared by magnetic stirring in a closed glass container at 300 RPM with a 1 inch stir bar until fully dissolved. Ink was loaded into a 3 cc EFD syringe barrel using a transfer pipette and left in the printing orientation for at least 30 minutes to allow bubbles to rise.

Piezoresistive Layer:

15 wt% Elastollan 35A TPU + 5 wt% carbon black (Vulcan XC72R, Cabot) dissolved in 4:1 v:v tetrahydrofuran : dimethylformamide. The ink was prepared by first dissolving the polymer by

magnetic stirring in a closed glass container at 300 RPM until fully dissolved, followed by addition of carbon black, and an additional 3 hours of stirring at 300 RPM. Ink was loaded into a 3 cc EFD syringe barrel using a transfer pipette and left in the printing orientation for at least 30 minutes to allow bubbles to rise.

Electrically Conductive Interconnects:

50 g silver flakes (99.95% purity, APS 5-8 μm ; Inframat Advanced Materials) was mixed with 5.2 g of 30 wt% Versamid 973 solution (BASF) dissolved in pentanol with an additional 2.72 g of pentanol added. The ink was prepared by combining all additives in a FlackTek Max 60 cup and mixing using a FlackTek SpeedMixer at 2350 RPM for 2 min. The ink was then loaded into a 10 cc EFD syringe barrel and centrifuged at 650 x g for 1 min to remove bubbles.

Soft Elastomeric Tissue Patterning Layer:

SE1700 (Dow-Corning) polydimethyl siloxane (PDMS) with 1:25 curative base ratio w:w was applied for cantilever covers, micro-pins and micro-wells. The ink was prepared by combining all additives in a FlackTek Max 60 cup and mixing using a FlackTek SpeedMixer at 2350 RPM for 2 min. The ink was then loaded into a 10 cc EFD syringe barrel with a spatula and centrifuged at 650 g for 1 min to remove bubbles.

Structural Elastomeric Layer:

SE1700 PDMS (Dow-Corning), with 1:10 curative:base weight ratio, mixed 1:5 wt:wt with Sylgard 184 1:10 curative:base weight ratio (Dow-Corning) is used for wells and covers, or as gasket adhesive below PLA or ABS wells and covers. The ink was prepared by combining all additives in a FlackTek Max 60 cup and mixing using a FlackTek SpeedMixer at 2350 RPM for 2 min. The ink was then loaded into a 10 cc EFD syringe barrel with a spatula and centrifuged at 650 g for 1 min to remove bubbles.

3.2.2 Multi-material direct ink writing (DIW)

Printing was carried out using a three-axis motion-controlled stage (Aerotech) with four independent z-axes. Prior to printing, a custom automation system was used to determine the substrate topology and relative x–y–z nozzle positions using an integrated laser profilometer, three CCD micrometers (Keyence), and custom machined fixtures. G-code generation and custom automation scripts were programmed using open-sourced Python libraries (Mecode). Extrusion was carried out using EFD syringes, dispense tips, and a digital electro-pneumatic regulator (Ultimus V High Precision Dispenser, EFD). Dispense tip diameters: TPU ink: 100 μm , CB:TPU ink: 200 μm , Ag:PA ink: 250 μm , Soft PDMS ink: 30 μm , Rigid PDMS ink: 410 μm . For dextran ink, a refillable contact-pressure sensitive pen (0.7 mm tip, Montana) served as the deposition nozzle.

3.2.3 Cardiomyocyte seeding on printed device

Prior to cell seeding, the printed devices were sterilized by ultraviolet–ozone exposure for 8 min. Subsequently, wells were incubated with a 50 $\mu\text{g ml}^{-1}$ solution of fibronectin (BD Biosciences) in PBS for 1 h. Fibronectin solution was aspirated and wells seeded with either primary NRVMs at a seeding density of 140 k cm^{-2} in 10% FBS in media 199 (Life Technologies) or hiPS-CMs (Cor4U, Axiogenesis) at 220 k cm^{-2} in designated Commercial Cor4U media (Axiogenesis). Cor4U cells were tested for mycoplasma contamination by the supplier prior to shipment. Authentication was achieved with puromycin-mediated positive selection, as described in further detail in the original publication supplementary information [118]. For the thicker tissue version, NRVMs were seeded at 1 M cm^{-2} adding cold BD Matrigel (BD Biosciences) to final concentration 0.45–0.6 mg ml^{-1} , thus below the gelling concentration. NRVMs were acquired from Sprague Dawley rats ($n \geq 10$ l, per harvest), applying procedures approved by the Harvard University Animal Care and Use

Committee, described in detail in the original publication [118]. hiPS-CMs were thawed, pre-plated and seeded following guidelines from supplier, as detailed in the Supplementary Information [118]. Cell media was changed at least every second day, applying 2% FBS in media 199 (Life Technologies) for NRVM culture, and designated Cor4U media for hiPS-CM culture.

3.2.4 Data acquisition

Data collection was performed using a custom-machined holder connecting the device to a Keithley Multichannel DMM 3706a (**Fig. 3.2**). Readouts were obtained as two-wire resistance recordings sampling at ≥ 60 Hz. A custom MATLAB (MathWorks) code was used for quantifying relative resistance changes upon tissue contraction, applying peak detection and comparison with local baseline. For electrically paced samples, a median filter (5 data points) was applied. Linear conversion constants between relative resistance change, cantilever curvature and stress generated by tissue, were established using the designated mechanical model.

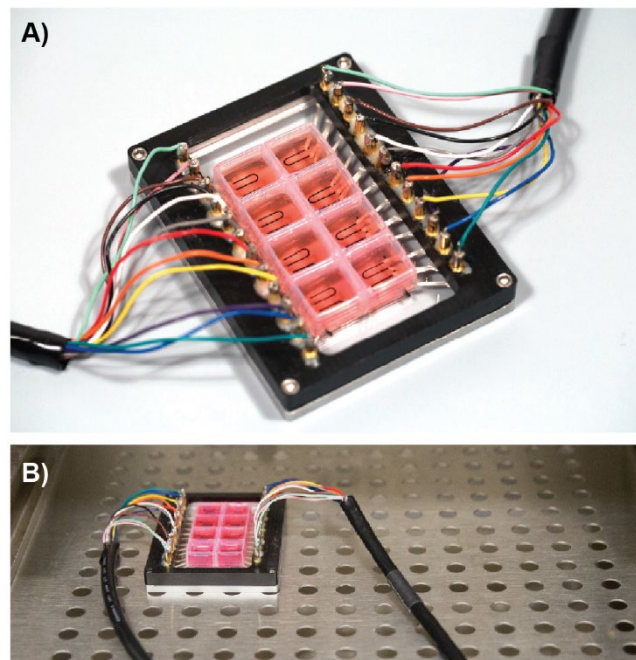


Figure 3.2: Multi-well recording setup. (A) Cell-seeded device in recording holder. (B) Setup inside cell incubator.

3.2.5 Immunostaining and morphological analysis

All immunocytochemistry procedures were conducted at room temperature. Samples were first fixed with 4% Paraformaldehyde/Phosphate Buffered Saline (PBS) (v/v) solution for 15 min and then permeabilized with 0.05% Triton-X/PBS (v/v) solution for 10 min. Subsequently, samples were incubated for 1 h with a monoclonal sarcomeric α -actinin (clone EA-53; Sigma-Aldrich) primary antibody, washed three times in PBS, and finally counterstained with Alexa Fluor 488-conjugated anti-mouse secondary antibody, Alexa Fluor 633-conjugated Phalloidin and DAPI (Invitrogen). Samples were imaged using confocal microscopy, acquiring projected z-stack images of the wavy laminar tissues. The alignment and overall spatial organization of α -actinin positive structures in the immune-stained digital images were evaluated with custom MATLAB (MathWorks) code, as previously described [119].

3.2.6 Optical mapping experiments

Action Potential propagation velocities for the engineered Neonatal Rat Ventricular Myocytes (NRVM) cardiac tissues were monitored using a modified tandem-lens microscope (Scimedia) equipped with a high-speed camera (MiCAM Ultima, Scimedia), a plan APO 1X objective, a collimator (Lumencor, Beaverton, OR) and a 200 mW Mercury lamp (X-Cite exacte, Lumen Dynamics). After four days culture in vitro, 10 mm $\times$ 10 mm engineered laminar NRVM tissues were incubated with a 4 μ M solution of a photovoltaic dye, RH237 (Invitrogen), for 5 min at 37 $^{\circ}$ C, and rinsed with Tyrode's solution prior to recording. Recordings were acquired at a frame rate of 200 Hz. Electrical point stimulation was applied to the corner of the tissue using two U-shaped platinum electrodes (Sigma-Aldrich) located 0.5–1 mm above the tissue, applying 1–2 Hz, 5–10 V pulses of 10 ms duration using a pulse generator (MyoPacer Cell Stimulator, IonOptix). Post-

processing of data was conducted with custom MATLAB (MathWorks) code, as previously described [120]. A spatial filter with 3×3 pixels was applied to improve the signal-to-noise ratio. Activation time was calculated as the average time to maximum upstroke slope of pulses when continuously paced at 2 Hz during a 5 s recording window.

3.2.7 Statistical analysis

For analysis of tissue sarcomere packing density (SPD), orientational order parameter (OOP) and sarcomeric length, one-way analyses of variance between the compositional groups were conducted using SigmaPlot (v12.0, Systat Software Inc.). All data sets passed Shapiro–Wilk normality tests and equal variance tests. For pairwise comparison, the Holm–Sidak method was applied. For all statistical analyses, p-values less than 0.05 were considered statistically significant. Sample sizes were chosen on the basis of previous studies applying muscular thin-film assays [119] [121] [120].

3.3 Results and Discussion

3.3.1 Device Design, Printing, and Characterization

To create this integrated device, six materials are patterned sequentially via direct ink writing multi-material 3D printing. To allow material integration at the microscale, the substrate topology and x–y–z positions of four individually addressable nozzles are first determined by an automated calibration process. After this calibration, the device is printed in a single continuous procedure (**Fig. 3.1C–I**). The stress generated by laminar cardiac tissues is limited to the range 1–15 kPa [110, 113]. Hence, to match this range, both the thickness and stiffness of each cantilever layer must be minimized. Towards this objective, we designed a series of highly dilute polymer-based inks. Their low solids content ensures patterning of thin individual layers (0.5–6.5 μm in

thickness). Additionally, by tuning the evaporation rate of the carrier solvent solution, the ink viscosity and corresponding wetting and spreading behavior is controlled to achieve the desired lateral dimensions (**Fig. 3.3**).

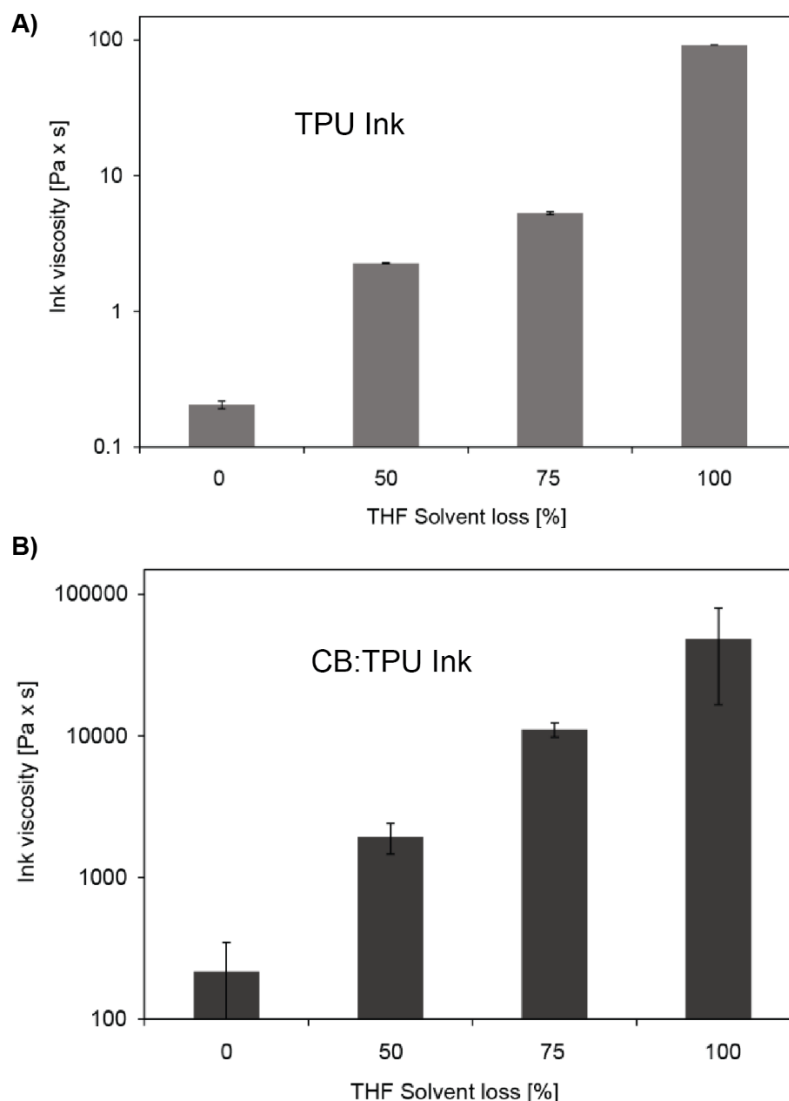


Figure 3.3: Apparent viscosity as a function of solvent loss of the insulating and piezoresistive TPU inks. (A) TPU ink viscosity increases upon THF solvent evaporation. Semi log plot of TPU ink viscosity as a function of THF solvent loss. The pristine ink contains a 1:4 ratio of DMF:THF (denoted as 0% solvent loss). Due to the substantial differences in solvent volatility, THF evaporates more quickly than DMF. Consequently, DMF fraction remains upon THF evaporation (pure DMF fraction denoted as 100% solvent loss). (n=3) error bars are st.dev. (B) CB:TPU ink viscosity increases upon THF solvent evaporation. Semi log plot of CB:TPU ink viscosity as a function of THF solvent loss. The pristine ink contains a 1:4 ratio of DMF:THF (denoted as 0% solvent loss). Due to the substantial differences in solvent volatility, THF evaporates more quickly than DMF. DMF fraction thus remains upon THF evaporation (pure DMF fraction denoted as 100% solvent loss). (n=3) error bars are st.dev.

Prior to patterning each inks, 0.5 μm dextran films are printed to serve as biocompatible water-soluble release layer, that allows the final cantilevers to detach from the substrate and deflect freely in programmed positions (**Fig. 3.1C**). Next, using dilute thermoplastic polyurethane (TPU) inks, 3- μm -thick cantilever bases, 6.5- μm -thick strain gauge wires and 1.5- μm -thick wire covers are printed in steps 2–4, respectively (**Fig. 3.1D-F**). The cantilever base and wire covers are printed using an unfilled insulating TPU ink, whereas the strain gauge wires are printed using a TPU ink filled with 25 wt% carbon black nanoparticles (CB:TPU). The printed TPU-based features exhibit elastic mechanical properties with a Young's modulus of 1.6 MPa (**Fig. 3.4**), whereas CB:TPU features readily cure to form an elastic piezo-resistive material with a Young's modulus of 8.8 MPa and resistivity of 1.19 $\Omega\cdot\text{cm}$ (**Figs. 3.4, 3.5, 3.6**).

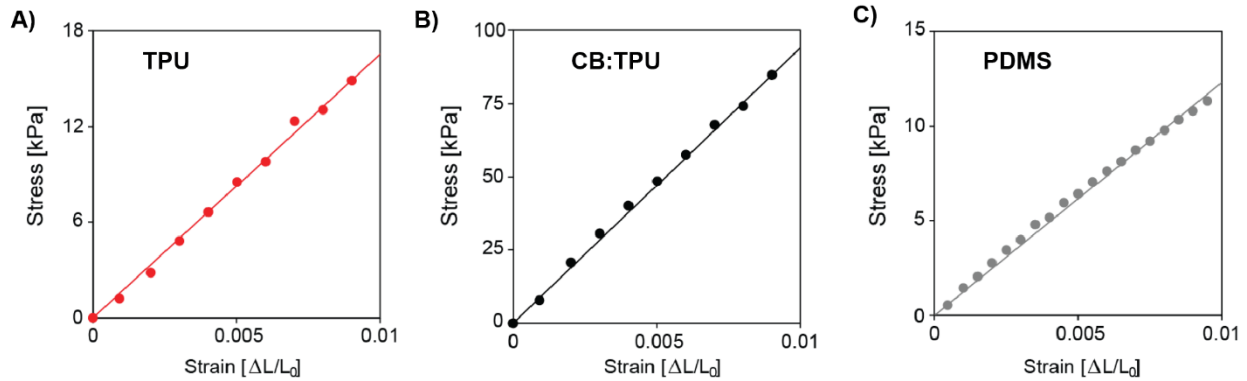


Figure 3.4: Stiffness of printed and cured features of cantilever. Representative stress-strain curves for cured tensile specimens made from the: (A) TPU ink, (B) CB:TPU ink, and (C) soft PDMS ink

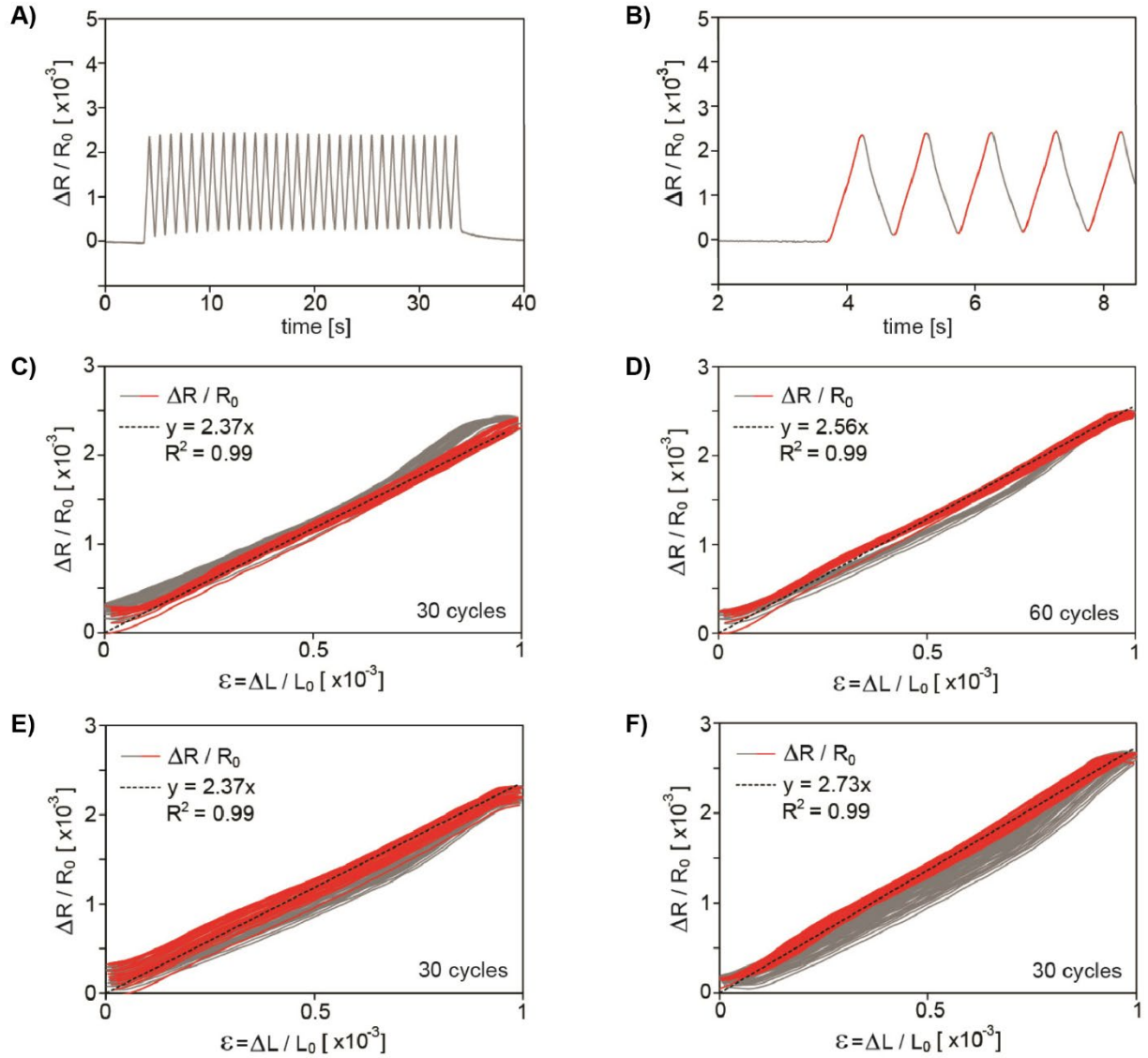


Figure 3.5: Determining gauge factor for CB:TPU strain sensor at 0.1% strain. (A-B) Relative change in CB:TPU resistance upon triangular cyclic straining to 0.1% at 1 Hz. (C-F) Relative resistance change vs. applied strain for 4 independent dog-bone samples. Dotted line indicates linear fit to part of strain cycles with increasing strain. CB:TPU gauges displayed limited hysteresis and conserved linearity during repeated strains. Average gauge factor is 2.51 ± 0.09 .

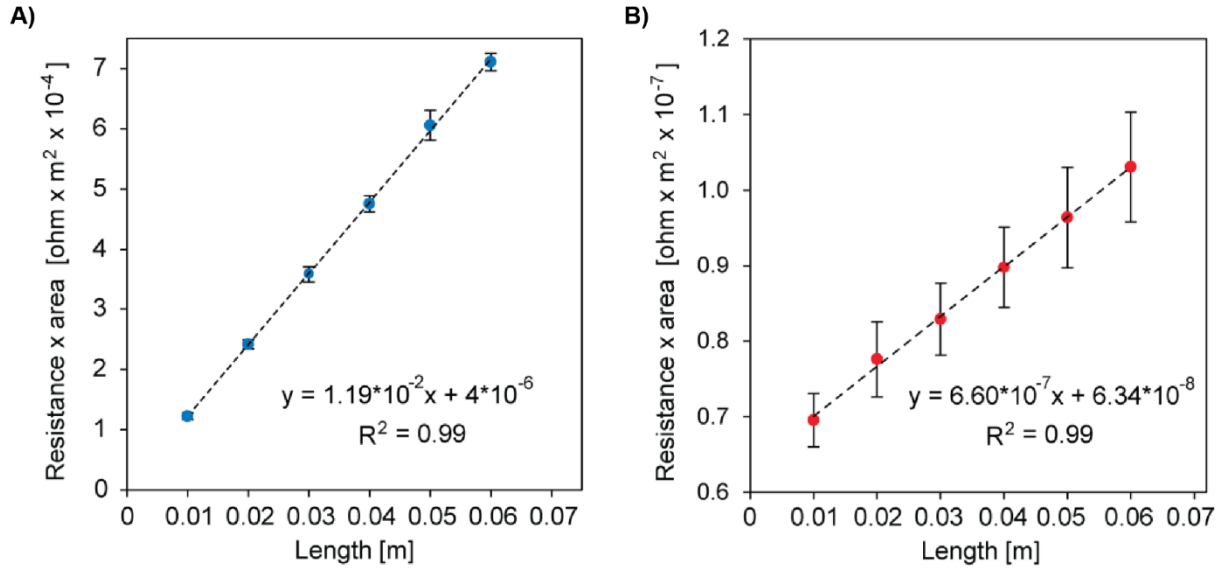


Figure 3.6: Electrical resistivity of printed features. (A) The electrical resistance of CB:TPU wires of varying length, (n=5) error bars are st.dev. Dotted line is linear fit to data. Slope of fitted line indicates electrical resistivity of $1.19 \, \Omega \cdot \text{cm}$, equivalent to a conductivity of $0.841 \, \text{S/cm}$ (B) The electrical resistance of Ag:PA wires of varying length, (n=4) error bars are st. dev. Dotted line is linear fit to data. Slope of fitted line indicates resistivity of $6.60 \cdot 10^{-5} \, \Omega \cdot \text{cm}$, equivalent to a conductivity of $1.52 \cdot 10^4 \, \text{S/cm}$.

Several alternative fillers were also investigated, including metals particles [39] and carbon nanotubes [122]. However, we found that carbon black imparts the best combination of ideal ink rheology, low stiffness, and low sensor hysteresis.

To accurately measure the stress exerted by the physio-mimetic laminar cardiac tissues, the embedded strain gauges within each cantilever must produce a reliable and detectable signal. We therefore evaluated the electro-mechanical properties of CB:TPU in a series of uniaxial strain tests (**Figs. 3.7 and 3.8**). At strains ranging from 0.0125% to 0.1%, the sensor creates a pronounced and measurable signal, and rapidly returns to its baseline resistance with minimal hysteresis (**Fig. 3.7A**). At 1% strain, the sensor displays substantial electro-mechanical hysteresis, requiring more than 10 seconds to recover to its baseline resistance following a strain event (**Fig. 3.7B**).

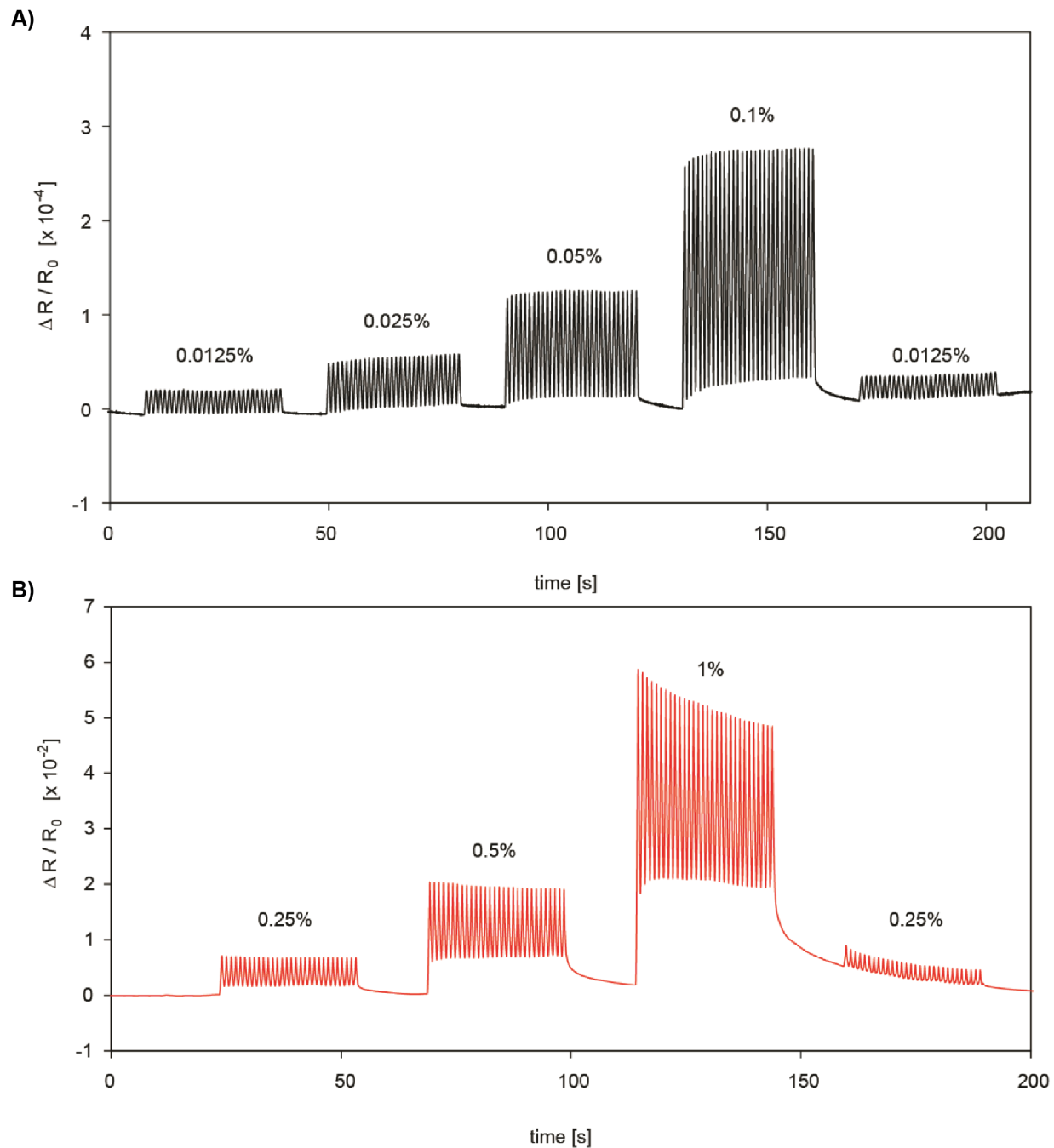


Figure 3.7: Strain-dependent electrical resistance for CB:TPU strain sensors. (A) Up to 0.1% strain, fast return to baseline and linear strain-resistance relationship is observed. (B) At 1% strain, slow baseline return and significant increase from linear strain-resistance relationship is observed.

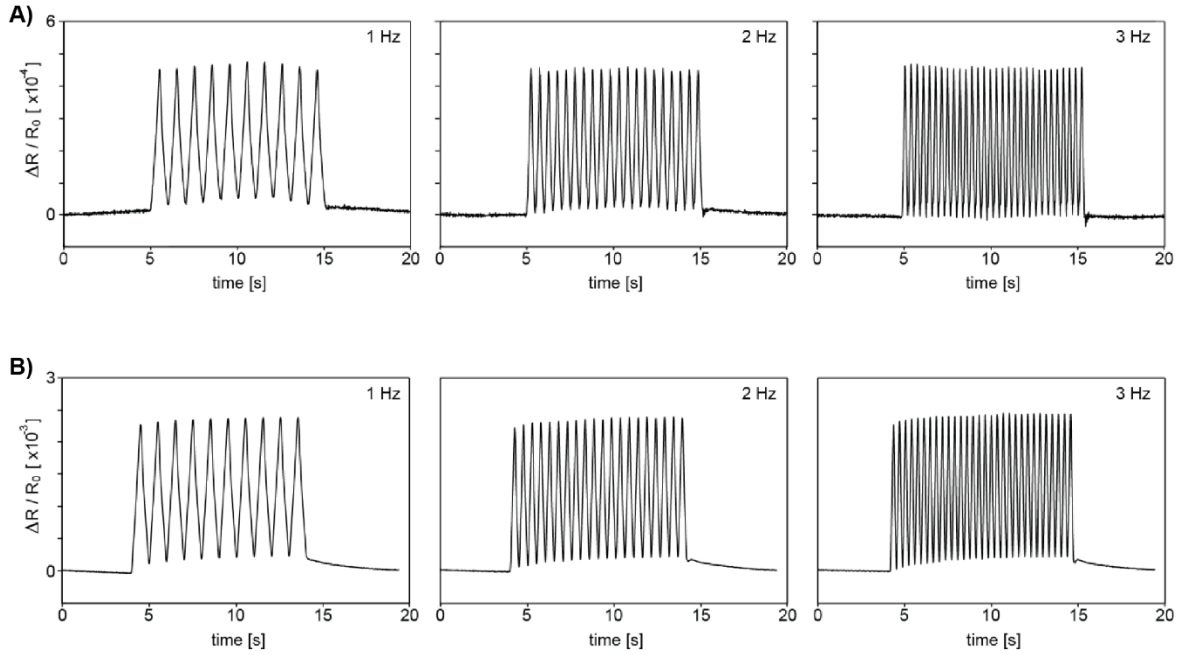


Figure 3.8: CB:TPU strain sensors tested at frequencies 1-3 Hz. (A) Left to Right: 0.02% strain exerted at 1, 2 and 3 Hz, (B) Left to right: 0.1% strain exerted at 1, 2 and 3 Hz. In these strain regimes relevant for the final device, negligible influence of the strain-rate (frequency) was observed on the sensor signal.

To mimic the strains exerted by tissue contraction, 1–3 Hz triangular strains of 0.1% were applied to CB:TPU gauges. In this strain range, the sensors exhibited a linear strain–resistance relationship with limited hysteresis and a corresponding average gauge factor of 2.51 ± 0.09 (**Fig. 3.5 and 3.8**).

The remainder of the microphysiological device is printed using concentrated viscoelastic inks optimized for deposition of self-supporting structures (Fig. 3.9). Using a viscous polydimethylsiloxane (PDMS) ink (Young's modulus of 1.28 MPa, see Fig. 3.4), ~60-μm-wide filaments are patterned on top of each cantilever (Fig. 3.1G). These comprise the majority of the cantilever thickness and serve as direct support below the physio-mimetic laminar cardiac tissue. Next, electrical leads and contact pads are printed using a high-conductivity, silver particle-filled, polyamide (Ag:PA) ink (Fig. 3.1H). Upon drying, the printed wires exhibit an electrical resistivity

of $6.6 \times 10^{-5} \Omega \cdot \text{cm}$ (Fig. 3.6B), which ensures that the primary electrical resistance of the final device arises from the embedded CB:TPU strain gauges.

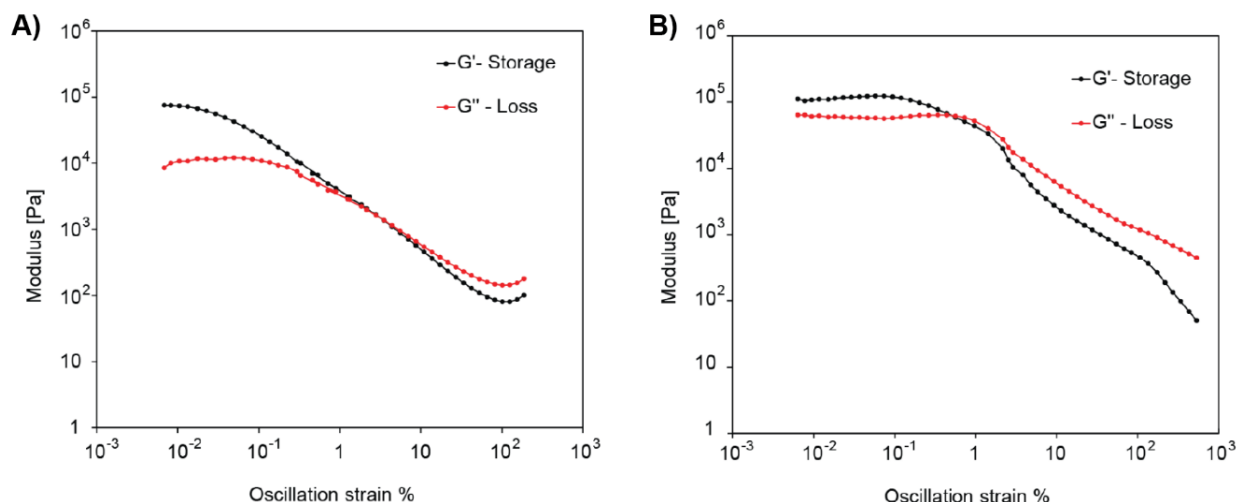


Figure 3.9: Viscoelastic ink rheology. (A) Ag:PA ink rheology. Log-log plot of the Ag:PA ink storage and loss moduli vs. oscillation strain %. At low strains/stresses, the storage modulus exceeds the loss modulus, indicating that the ink is behaving like a non-flowing solid. As the amplitude of strain increases, the ink exceeds its yield stress, and the loss modulus overtakes the storage modulus, indicating that the ink is behaving like a liquid that flows under high shear stresses. (B) Soft PDMS ink rheology. Log-log plot of the soft PDMS ink storage and loss moduli vs. oscillation strain %. At low strains/stresses, the storage modulus exceeds the loss modulus, indicating that the ink is behaving like a non-flowing solid. As the amplitude of strain increases, the ink exceeds its yield stress, and the loss modulus overtakes the storage modulus, indicating that the ink is behaving like a liquid that flows under high shear stresses.

Finally, the wire leads are covered with an insulation layer, and eight individually addressable wells are printed using either a PDMS ink or biocompatible rigid thermoplastic polymers such as polylactic acid (PLA) or acrylonitrile butadiene styrene (ABS). The rigid polymers can be preferable for drug study applications, as they are less prone to bulk absorption of hydrophobic drugs than PDMS [123] (**Fig. 3.1I**). After printing, the devices are cured at 100°C for 2 hours and subsequently seeded with cardiomyocytes, which self-assemble into laminar tissues mimicking the structure of the native heart.

3.3.2 Microfilament-guided tissue self-assembly

The musculature of the heart is composed of highly organized, structurally and electrically anisotropic layers [124]. To recapitulate this architecture in vitro, we printed a range of grooved microstructures by varying the spacing between curved $\sim 20\ \mu\text{m} \times 60\ \mu\text{m}$ (height $\times$ width) filaments and assessed their ability to guide the self-assembly of anisotropic laminar NRVM tissues (**Fig. 3.10**). We evaluated the degree of tissue structural anisotropy using immunofluorescent imaging of sarcomeric α -actinin and quantification of the sarcomere orientational order parameter (OOP) (**Fig. 3.10A–F**) [119]. All substrates showed an OOP > 0.2 , indicative of nonrandom sarcomere alignment. The highest OOP ~ 0.5 was observed for a $60\ \mu\text{m}$ filament spacing. Similarly, a $60\ \mu\text{m}$ filament spacing gave rise to the highest degree of electrophysiological anisotropy in the laminar NRVM tissues (**Fig. 3.10G–I**). For this spacing, action potential propagation was 2.7 times faster parallel to the grooves compared to the transverse direction.

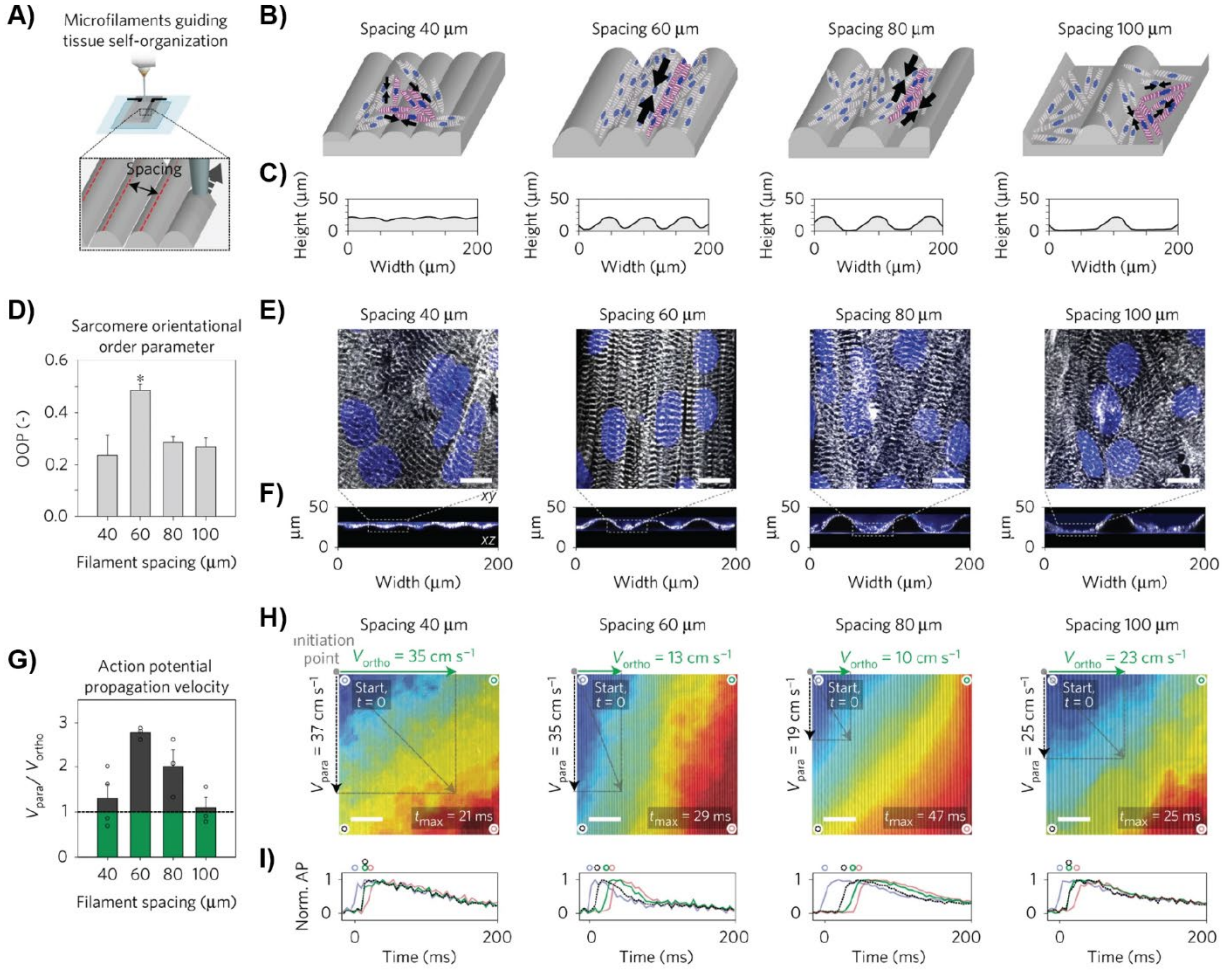


Figure 3.10: PDMS microfilament driven tissue alignment and morphological analysis. (A) Spacing of soft PDMS microfilaments. (B) Sketch of microfilaments guiding self-assembly of engineered cardiac tissue. (C) Stylus profilometer contours of substrates with filaments printed at 40, 60, 80 and 100 μm spacing. (D) Sarcomere OOP of laminar NRVM tissues developed on substrates with 40 ($n = 9$), 60 ($n = 13$), 80 ($n = 8$) and 100 μm ($n = 10$) filament spacing. Error bars are standard error of the mean (s.e.m.), *, $P < 0.05$. e,f, Representative confocal images from OOP data set z-projection (E) and x -z line scan (F). Blue, DAPI nuclei stain. White, α -actinin. Scale bars, 10 μm . (G) Ratio between action potential (AP) propagation speed parallel and orthogonal to the grooves for laminar NRVM tissue developed on substrates with 40, 60, 80 and 100 μm filament spacing, ($n \geq 3$). Individual data points included (circles). Error bars are s.e.m. (H) Representative activation time heat maps for AP data set, overlaid with wide-field microscope image of the samples as guide to the eye. Scale bars, 0.8 mm. Activation times normalized to maximum observed activation (t_{max} , red), to account for tissue source variation. 2 Hz electrical point stimulation is applied in top-left corner of samples. Mean observed propagation speed parallel (V_{para}) and orthogonal (V_{ortho}) to grooves is shown as vectors. (I) Normalized AP traces at four corners of activation map samples. Blue, at AP initiation corner. Red, at t_{max} -corner. Black, corner parallel to grooves. Green, corner orthogonal to grooves.

These data are in agreement with the longitudinal to transverse velocity ratio of 2.1 observed in the native ventricle [124]. Also, these anisotropic laminar tissues gave rise to

unidirectional and concerted cantilever deflection and exhibited the highest contractile stresses in the final devices. Collectively, these results demonstrate that our printing technique can be employed to engineer laminar cardiac tissues with a range of ordered architectures. Notably, the OOP and electrophysiology data closely matched values obtained using semi-manual micro-contact printing and molding techniques [112, 120, 121].

In order to accurately convert resistance signals measured in the final printed devices to stresses generated by the laminar cardiac tissues, we established an electromechanical model of the cantilevers based on a multilayer version of Stoney's equation (**Figs. 3.11E,F and 3.12**). The mechanical model relies on the dimensions and Young's moduli of each layer of the cantilever as well as the CB:TPU gauge factor. The model provides linear conversion factors between the relative changes in gauge resistance, changes in cantilever radius of curvature and, in turn, the longitudinal stresses generated by the laminar cardiac tissues. Applying these conversion factors, we obtained tissue twitch stress (σ), the differences between the systolic and diastolic stress, in the range of 7–15 kPa for laminar NRVM tissues, akin to prior reports [108, 112]. Further details of the mechanical model may be found in the original publication [118]. To further verify the model, we compared the sensor readout with stress values concurrently obtained through optical tracking of cantilever deflection and obtained highly similar stress values (**Figs. 3.11 G,H and 3.12 & 3.13**).

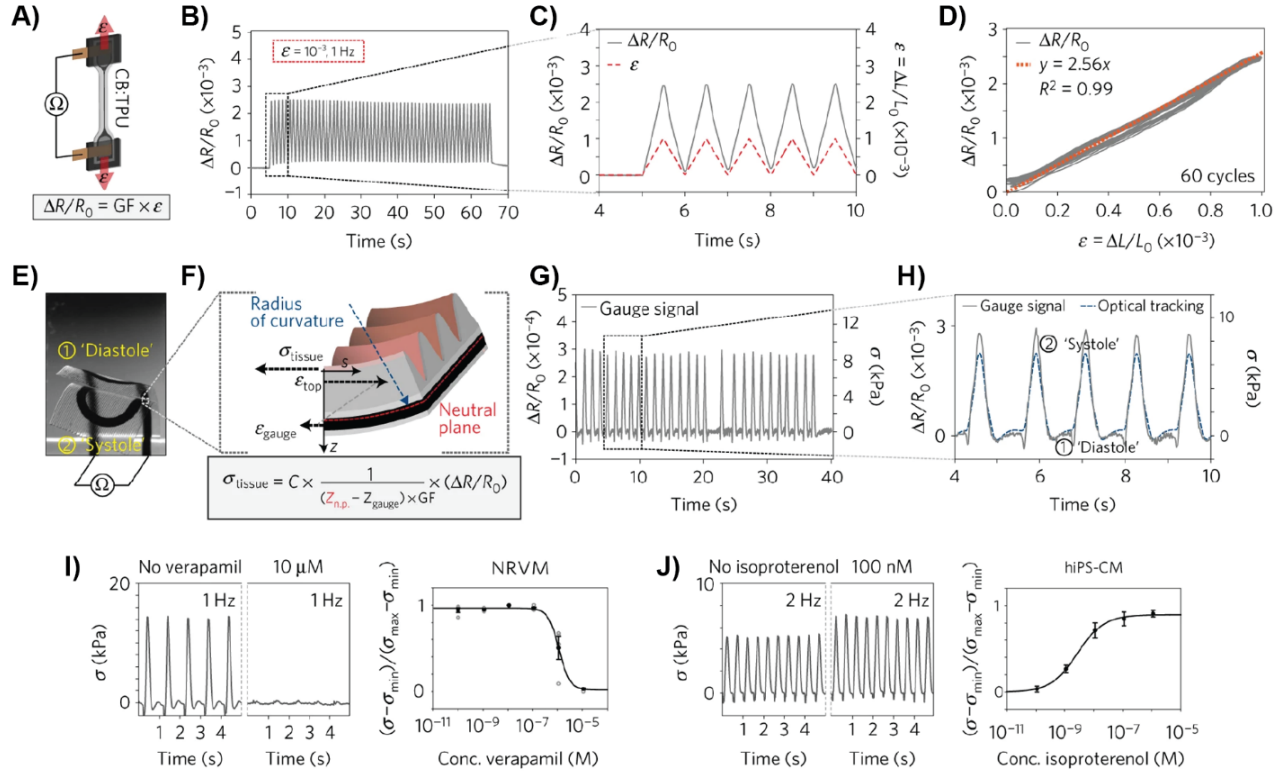


Figure 3.11 Converting sensor gauge signal to tissue twitch stress (A) Sketch of Instron test set-up for determining CB:TPU gauge factor (GF). (B-D), Relative change in CB:TPU resistance upon triangular cyclic straining to 0.1% at 1 Hz. In **c** the dark grey line is the observed relative resistance change and the red dotted line is the strain applied. (D), Relative resistance change versus applied strain. Orange dotted line indicates a linear fit to part of the cycles with increasing strain, yielding a gauge factor of 2.56. (E), Wide-field microscope images of cantilever bending upon tissue contraction. Minimum deflection corresponds to cardiac diastole (1) and peak deflection corresponding to systole (2). (F), Sketch of the mechanical model used to convert change in gauge resistance to stress generated by the tissue, through a linear conversion factor C as described in SI of original publication. (G-H), Relative resistance changes (left axis) and corresponding calculated tissue twitch stress (right axis) recorded from spontaneously beating cantilever. The blue dotted line in (H) indicates stress determined independently by optical tracking of the cantilever radius of curvature. (I) Representative traces of twitch stress generated by a laminar NRVM tissue when tissue is exposed to verapamil and corresponding dose-response curve ($n = 4$). Error bars are s.e.m., stress normalized between maximal and minimal values, tissue paced at 1 Hz, apparent $EC_{50} 1.12 \times 10^{-6}$ M. Individual data points included (circles). (J) Representative traces of twitch stress generated by a laminar hiPS-CM tissue when exposed to isoproterenol and corresponding dose-response curve, ($n = 10$). Error bars are s.e.m., stress normalized between maximal and minimal values, tissue paced at 2 Hz, apparent $EC_{50} 2.74 \times 10^{-9}$ M.

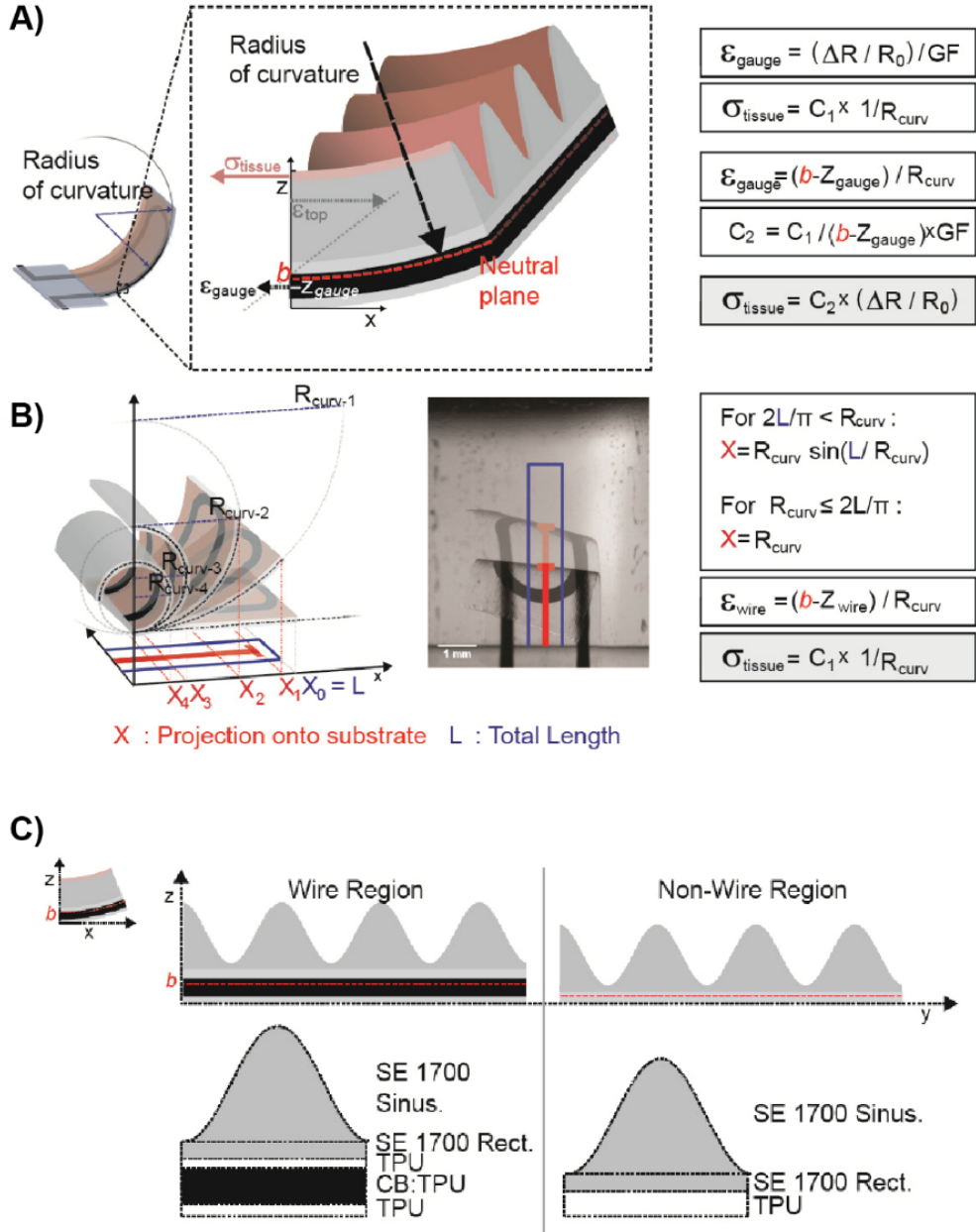


Figure 3.12: Electromechanical model of cantilever deflection. Converting electrical and optical readout to tissue stress using mechanical model based on a modified Stoney's equation. (A) A linear conversion factor can be established between relative change in resistance, radius of curvature and tissue stress, by establishing analytical mechanical model. (B) Optical tracking is used to measure cantilever curvature during the tests as an external independent validation of the mechanical model. (C) To establish a sufficiently descriptive mechanical model, we determined local neutral axis in the two distinct regions of the cantilever; the wire region and the non-wire region. The relative placement of layers and mechanical properties were derived from stylus profilometer data and Instron mechanical tests.

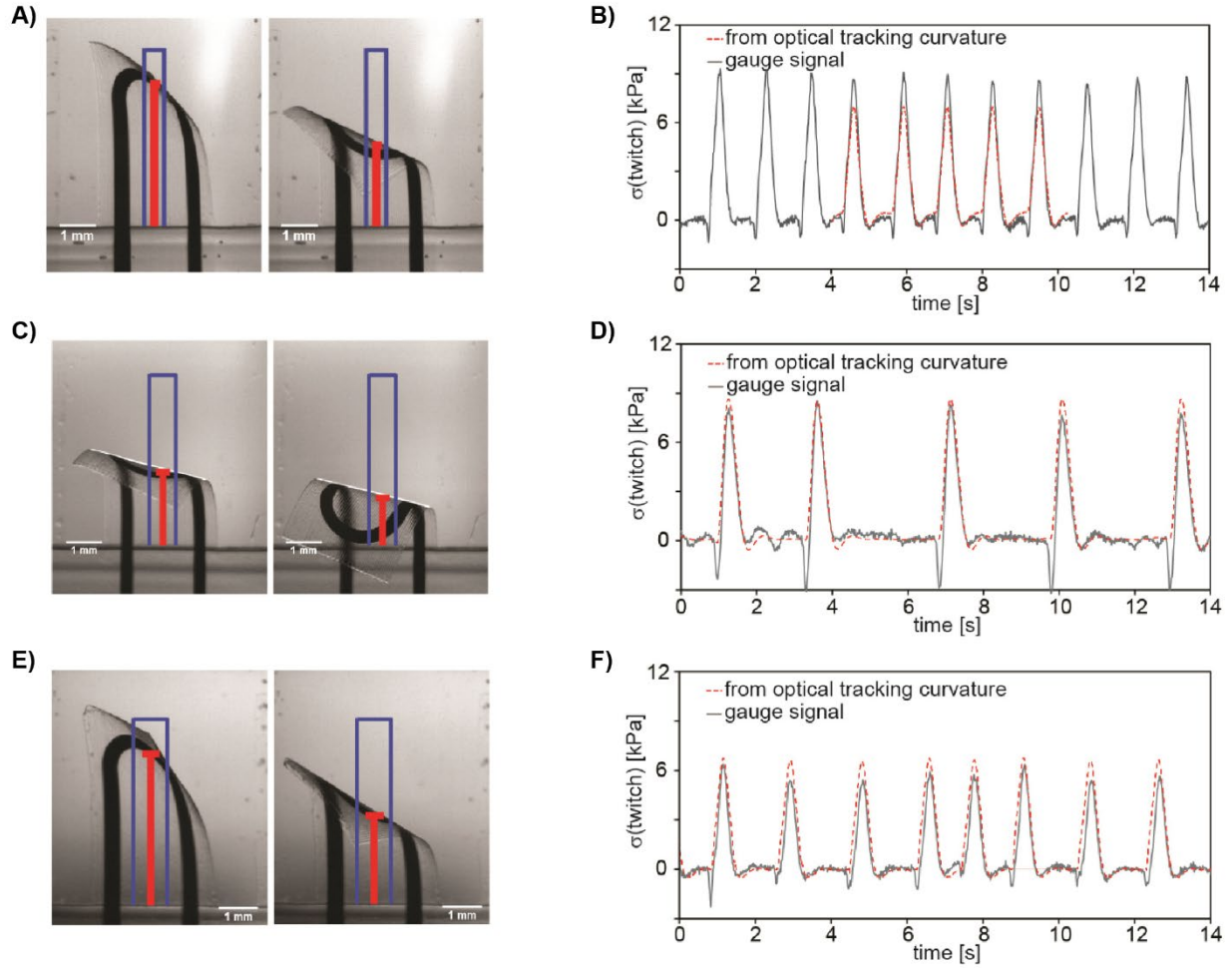


Figure 3.13: Comparing optical and electrical readout to verify mechanical model. To evaluate the robustness of the model, we performed synchronous optical tracking and electrical recordings of three independent cantilevers, seeded with NRVM anisotropic tissues. (A, C, E) optical tracking of cantilevers, Left: Diastole, Right: Systole (B, D, F) Comparison between stress calculated from optical tracking and synchronous gauge recordings. Variations are attributed to geometric variations in the curvature generated by the tissue and to variations in device printing from batch to batch.

We observed one discrepancy between the optical tracking and electrical readout: at the initiation of tissue contraction, a small decrease in gauge resistance is measured, prior to the increase caused by cantilever deflection. We attribute this decrease to a brief axial compression of the gauge wire occurring during initial tissue contraction, while cantilever deflection is counteracted by inertial and viscous forces. Notably, this observation does not influence tissue twitch stress values. Together, these results demonstrate that the CB:TPU strain gauges embedded

in our fully printed platform provide reliable readouts of tissue contractile stress. Following validation of sensor functionality, we demonstrated potential use cases through cumulative drug-dose studies using the L-type calcium channel blocker verapamil and the β -adrenergic agonist isoproterenol, as well as through long-term monitoring of contractile development in laminar hiPSC-CM tissues over 28 days (**Fig 3.11 I,J**). Full details of these studies can be found in the original publication [118].

3.4 CONCLUSION

Through multi-material 3D printing of a series of customized intrinsically stretchable electronic and elastomeric inks, we demonstrated the automated design and fabrication of instrumented cardiac microphysiological devices. We validated the functionality of our design by comparing the output to established optical tracking methodologies. The integrated sensors drastically simplify data acquisition and long-term functional studies of human tissue models *in vitro*. Leveraging the ability to track the temporal development in tissue mechanics will enable new insights into tissue morphogenesis, pathogenesis, and drug-induced structural and functional remodeling. Our digital manufacturing approach is versatile, allowing for fabrication of a range of instrumented microphysiological devices. Notably, our approach facilitates rapid customization to match device geometries, mechanical and biochemical properties to a specific diseased state or a unique patient-derived cell source. Our programmable microfabrication approach opens new avenues for in vitro tissue engineering, toxicology and drug screening research.

3.5 CONTRIBUTIONS

J.U.L., T.A.B., J.A.L. and K.K.P. designed the study. J.U.L. and T.A.B. designed the device. T.A.B. coded the 3D-print procedure and automation. J.U.L., T.A.B., A.K. and A.D.V. developed and characterized the printable materials. J.U.L., A.D.V. and T.A.B., optimized and printed devices. P.H.C. performed NRVM harvesting and prepared culturing media. J.U.L., M.Y. and A.P.N. performed NRVM culture, drug-dose experiments, and data analysis. M.Y. and J.U.L. conducted hiPS-CM culture, experiments and data analysis. F.S.P. and J.U.L. performed tissue staining, confocal imaging, and OOP analysis. S.-J.P. and J.U.L. conducted optical mapping experiments and analysis. H.Y. and J.J.V. developed the mechanical model of the device. J.U.L., T.A.B., J.A.L. and K.K.P. prepared illustrations and wrote the manuscript. F.S.P. and A.D.V. contributed to writing the manuscript.

CHAPTER 4

HYBRID 3D PRINTING OF SOFT ELECTRONICS

This chapter has been adapted from the following manuscript:

A. D. Valentine, T. A. Busbee, J. W. Boley, J. R. Raney, A. Chortos, A. Kotikian, J. D. Berrigan, M. F. Durstock, J. A. Lewis, “Hybrid 3D Printing of Soft Electronics”. *Advanced Materials* 29, 1703817 (2017)

4.1 INTRODUCTION

The emerging field of soft electronics is driven by the growing interest in wearable electronics [48, 62, 122, 125-135], robotics [136-138], and biomedical devices [139, 140]. The two prevailing approaches to fabricating soft stretchable electronics employ conceptually different motifs. One approach uses high-performance electronic materials in unconventional geometries to achieve thin, bendable, and stretchable designs [21, 22]. In this approach, conventional microfabrication methods are combined with approaches, such as transfer printing, to create stretchable battery arrays [13], ultralightweight electronic foils [141], solar cells [24], and multiplexed biosensing electrode arrays [25]. The other approach is to fully print soft materials and components to create devices in stretchable motifs, utilizing conductive composites [31, 32, 34-39, 122, 142-146], liquid metals [52, 54, 55, 147], and ionic liquids [59, 60, 148, 149].

Several printing methods have been introduced for electronic device fabrication due to their programmability, scalability, and low barrier-to-entry [150-157]. For example, inkjet printing enables the fabrication of high-performance flexible transistors, although a combination of multistep subtractive and additive processes is required [153, 154]. More recently, 3D electronics composed of flexible conductors and matrix materials have been fabricated by fused filament fabrication [151, 152]. However, in these initial embodiments, several manual assembly steps were needed to achieve the desired device functionality. Finally, direct ink writing is a versatile

approach, which has been used to create electrically small antennas [155], soft sensors [48, 62, 156], quantum dot light-emitting-diodes (QD-LEDs) [157], and cardiac organ-on-chip devices with electronic readout [118]. However, to unlock the full potential of programmable fabrication for high-performance soft electronics in arbitrary form factors, new printable highly conductive stretchable elastomers are needed, along with a manufacturing process that can seamlessly integrate rigid electrical components and integrated circuits.

Here, we report a new method, known as hybrid 3D printing, for producing soft electronics. Specifically, this method combines direct ink writing (DIW) with automated pick-and-place (P+P) of surface mount electronic components within a single integrated manufacturing platform (**Fig. 4.1**). A highly stretchable insulating matrix ink based on thermoplastic polyurethane (TPU) (**Fig. 4.1a**) and a stretchable conductive electrode ink based on silver-filled thermoplastic polyurethane (Ag-TPU) were formulated (**Fig. 4.1b**). These inks can be co-patterned in specific layouts, including soft sensing arrays (**Fig. 4.1c**). Passive and active rigid electrical components are then integrated to fabricate deformable circuits utilizing a digitally controllable vacuum pick P+P tip affixed to the same robotic gantry used for ink deposition. Finally, stretchable conductive traces are printed to create electrical interconnects between the P+P components (**Fig. 4.1e**). A representative motif is the flexible LED array shown in **Figure 4.1f**.

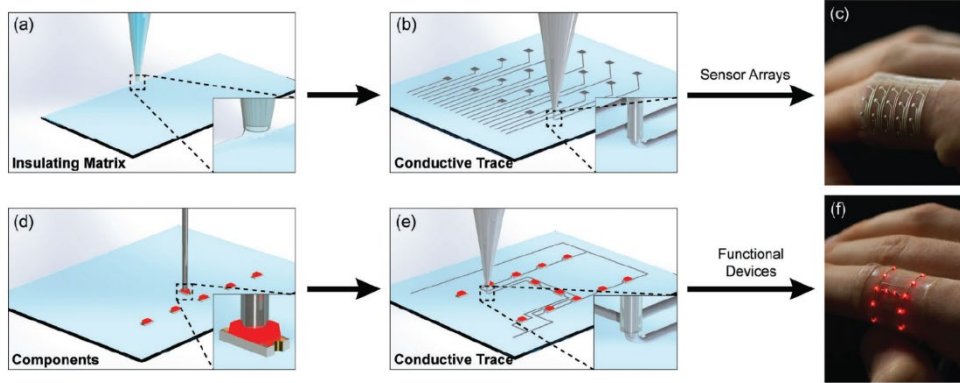


Figure 4.1: Hybrid 3D printing platform for soft electronics. Schematic images of a) direct ink writing of a TPU matrix for the device body and b) conductive Ag-TPU traces for the sensing elements. c) Image of a representative example of soft sensor array. Schematic images of d) pick-and-place (P+P) of components using vacuum nozzle onto target positions and e) direct writing of conductive Ag-TPU traces to interconnect the surface mounted LEDs placed in the form of a soft, stretchable “H” LED array. f) Image of a functional LED array wrapped around a human finger.

4.2 EXPERIMENTAL

4.2.1 Materials System

The insulating ink was formulated by dissolving 35 wt% thermoplastic polyurethane (TPU; Elastollan Soft 35A, $\rho = 1.18 \text{ g/cm}^3$) in a co-solvent mixture of N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) (Sigma-Aldrich) at a 1:4 volume ratio (DMF:THF). The mixture was magnetically stirred at 300 RPM in a closed container for 12 hours or until it was fully dissolved. The conductive ink was prepared by incorporating 36 vol% silver flakes (99.95% purity, APS 2–5 μm ; Inframat Advanced Materials, $\rho = 10.49 \text{ g/cm}^3$) into a portion of the insulating ink. 7 grams of the dissolved TPU solution and 11.72 grams of silver flakes were added to a FlackTek Max 20 cup. The mixture was homogenized in a FlackTek SpeedMixer planetary centrifugal mixer at 2350 RPM for a total of 30 minutes. This was carried out in three ten-minute cycles, with ten-minute rest periods between cycles to prevent heat buildup.

Both the pure TPU (insulating) and Ag-TPU (conductive) inks were loaded into 3 cc Nordson EFD syringes, centrifuged at 3000 RPM for 2 minutes to remove entrapped air, and prepared for direct ink writing.

4.2.2 Rheology Measurements

The rheological properties of both TPU and AgTPU inks were characterized under ambient conditions using a controlled stress rheometer (AR 2000ex, TA Instruments) equipped with a 40 mm tapered cone plate geometry (2.005° , 56 μm truncation gap). The conductive ink was remixed using a FlackTek Speedmixer for 5 min at 2350 rpm prior to rheological characterization. A solvent trap was used to limit evaporation during these measurements. Viscometry measurements were carried out over shear rates from 0.001 to 100 s^{-1} , while oscillatory measurements were carried out at a frequency of 1 Hz within the stress range of 0.01–10 000 Pa.

4.2.3 Hybrid 3D Printing

DIW 3D Printing was carried out with a three-axis motion-controlled stage (Aerotech) equipped with four independent z-axes that enable up to four inks to be co-printed. Print paths were generated using the open-source Python library (MeCode). Pneumatic-driven extrusion of inks was controlled with a digital electro-pneumatic regulator (Ultimus V High Precision Dispenser, EFD). 410 and 200 μm tapered dispense tips (EFD) were used for insulating TPU matrix and conductive Ag-TPU inks, respectively. Insulating base layers were cured at 80 $^\circ\text{C}$ for 2 h prior to conductive ink deposition. Finished devices were cured at 80 $^\circ\text{C}$ for an additional 2 h prior to testing. Automated pick-and-place (P+P) of all surface mount electrical components was carried out by mounting an empty 3 cc syringe, outfitted with a 250 μm non-tapered stainless steel nozzle, onto one of the 4 z-axes of the robotic gantry and digitally toggling the vacuum function (18 mm H_2O) on a digital pneumatic regulator (Ultimus V High Precision Dispenser, EFD). Prior to the

hybrid printing operation, surface mount components were placed into 0.7 mm-deep cavities in a precision-machined fixture rigidly mounted to the gantry base. Each cavity was sized to the component's bounding box plus a 25 μm offset. To pick a component, the empty syringe tip was positioned within 50 μm of the top surface, the vacuum was activated to lift the part, and the tip was moved upward vertically by 10 mm prior to moving to its target location. The tip was then lowered onto the soft substrate and the vacuum was turned off to release the component in the desired position. This sequence was repeated for each component.

4.2.4 Conductivity Measurements

To measure electrical conductivity, Ag-TPU samples were printed into single layer thin rectangular films (2 cm $\times$ 0.3 cm). After curing at 80 $^{\circ}\text{C}$ for 2 h, sample thicknesses were measured using a stylus profilometer. Electrical resistance measurements were acquired using a four-point resistance probe (RM3544, Hioki). The Levenberg–Marquardt method was used to obtain the power-law fit used to determine parameters such as the critical volume fraction at the percolation threshold.

4.2.5 Electromechanical Characterization

Printed Ag-TPU samples were mounted in tension clamps on a uniaxial tensile tester (Instron Model 5566). Clamps for a four-point resistance probe (RM3544, Hioki) were attached to the conductive traces, within the gauge length, so that electrical resistance could be measured simultaneously with mechanical loading. Multi-strain tensile testing was conducted at 0.3 mm s^{-1} and fixed-strain cyclic tensile testing at 1.0 mm s^{-1} .

4.2.6 Capacitive Pressure Sensor Measurement

Capacitive pressure sensor performance was evaluated by mounting printed sensors to rigid acrylic fixture on a compression testing apparatus, then applying fixed loads using a compression testing

machine (Model 5566, Instron). Capacitances were measured using an LCR (inductance, capacitance, resistance) meter (Model 880, B&K Precision).

4.2.7 LED Performance Under Strain Characterization

Linear tensile specimens were fabricated by first depositing a single layer of insulating ink (1 cm $\times$ 70 cm) and curing it at 80 °C for 1 hour. A small droplet of insulating ink was then deposited at the center of the rectangular base, onto which a 0603 surface-mount LED (LITE-ON, Super Red) was placed using a pick-and-place method. Linear Ag-TPU traces were subsequently printed on both sides of the LED, each extending 25 mm from the LED interconnect toward either end of the specimen (Fig. 4.2).

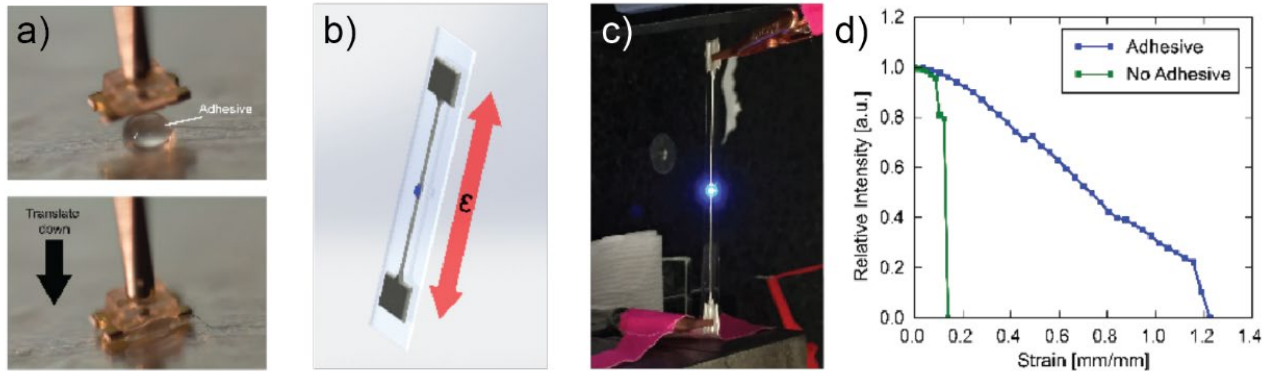


Figure 4.2: Performance of a rigid LED integrated into a stretchable device. (a) Images of TPU adhesive droplet before placement (top) and after placement (bottom) of surface mount electronic component. (b-c) Schematic illustration and corresponding image of AgTPU/LED specimen during tensile testing and (d) Plot of relative intensity of surface mount LED during tensile testing of AgTPU/LED specimens fabricated with and without printed TPU adhesive droplets.

After curing the assembled specimen at 80 °C for 1 hour, uniaxial tensile testing was performed at a strain rate of 1 mm/s using a universal testing machine (Instron Model 5566). The current–voltage (I–V) response of the LED was measured in real time using a source meter (Keithley 2400) connected via separate clamps placed within the testing gauge length. A custom MATLAB script was used to continuously acquire I–V data during mechanical testing.

4.2.8 Plantar Capacitive Sensor Array

The insulating TPU ink used for this demonstration was formulated identically to the matrix ink, with the addition of 2 wt% carbon black, relative to the polymer content of the base layer (Vulcan XC72R, Cabot), to improve visual contrast without introducing electrical conductivity between the printed electrodes. Capacitive pressure sensors were fabricated by sequentially printing alternating layers of Ag-TPU and insulating TPU onto the substrate. The bottom Ag-TPU electrode ($\sim 40\ \mu\text{m}$ thick) was printed first, followed by a dielectric TPU layer ($\sim 160\ \mu\text{m}$ thick), and then the top Ag-TPU electrode ($\sim 40\ \mu\text{m}$ thick). An additional TPU encapsulation layer ($\sim 150\ \mu\text{m}$ thick) was printed over each capacitive element and cured at $80\ ^\circ\text{C}$ for 2 hours.

To improve pressure uniformity across the sensor array during testing, a soft silicone pad with embedded rigid acrylic inserts was placed between the foot and the sensor array. After individual calibration of each sensor, pressure data were computed based on the total area associated with the array, accounting for inter-sensor spacing.

4.3 RESULTS AND DISCUSSION

4.3.1 Ink Design

To create soft electronics via hybrid 3D printing, we first developed matrix and conductive inks based on a thermoplastic polyurethane (TPU) that is both biocompatible and highly stretchable. To produce the conductive electrode ink, we added silver flakes ($\approx 2\text{-}5\ \mu\text{m}$ lateral dimension) to the pure TPU ink. The Ag-TPU ink flows readily through fine nozzles due to its strong shear thinning behavior and retains its filamentary form upon exiting the nozzle due to its relatively high storage modulus ($G' \approx 10^4\ \text{Pa}$) and shear yield stress ($\tau_y \approx 20\ \text{Pa}$) (**Figs. 4.3 a-c**). Upon printing and drying, conductive electrodes with trace widths down to $100\ \mu\text{m}$ diameter can be achieved that contain a percolating network of silver flakes (**Fig. 4.3d**). By contrast, the pure TPU ink

behaves as a Newtonian fluid with an apparent viscosity of $\approx 40 \text{ Pa}\cdot\text{s}$, no yield stress, and a storage modulus ($G' \approx 10^3 \text{ Pa}$) an order of magnitude lower than that of the conductive ink. As a result, it readily wets and spreads upon exiting the nozzle to form a cohesive soft substrate (**Fig. 4.3c**). Because they contain the same solvent, a robust interface develops between the Ag-TPU and pure TPU inks during printing (**Fig. 4.4**), yielding soft electronic devices that do not exhibit delamination or cracking during or after stretching. This is a crucial feature of these inks, since delamination of printed electrodes from the underlying polymer matrix is a common mode of failure in soft electronics [39, 158].

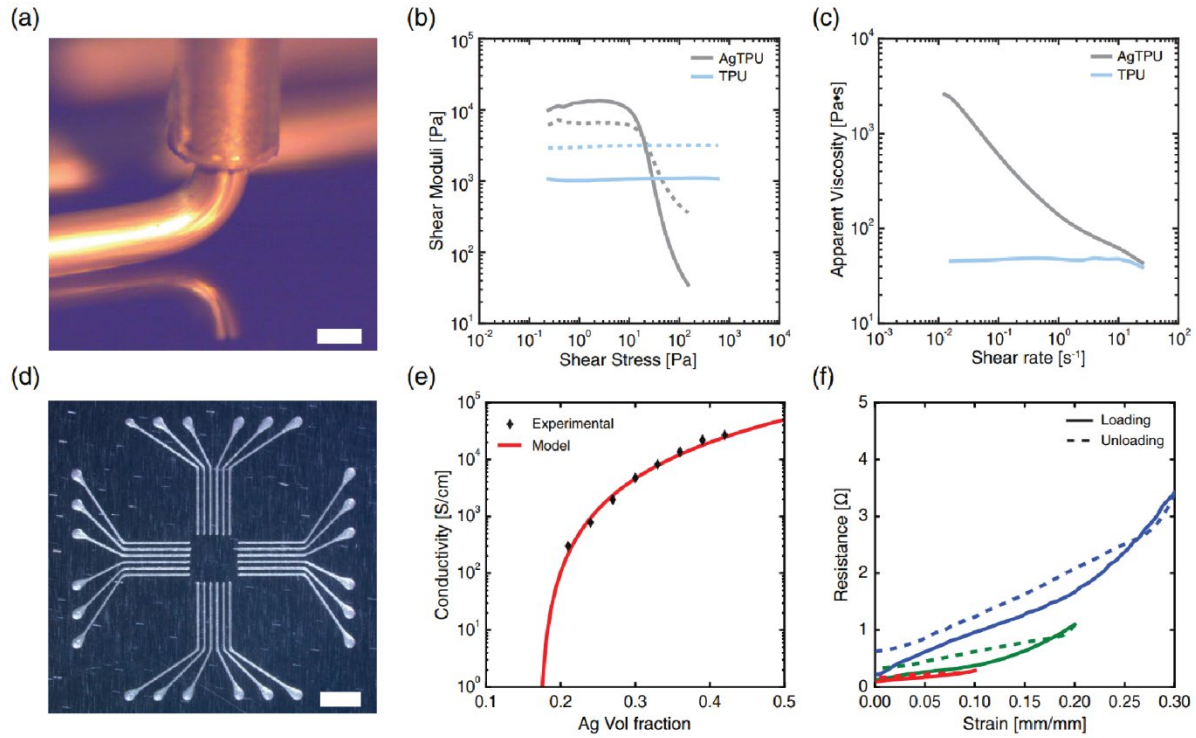


Figure 4.3: Printability, rheology, and electrical performance of the Ag-TPU ink. a) Image of direct writing of Ag-TPU ink through a $200 \mu\text{m}$ nozzle (scale bar $200 \mu\text{m}$). b) Shear moduli as a function of shear stress, comparing storage modulus G' (solid line) and loss modulus G'' (dashed line) and c) apparent viscosity as a function of shear rate for the TPU and Ag-TPU inks. d) Direct writing of Ag-TPU electrodes in a 24-pad wiring scheme with electrode widths of $100 \mu\text{m}$ (scale bar = 2 mm). e) Electrical conductivity of Ag-TPU composite as a function of silver flake content. The red line represents the best fit of a power-law model to the experimental data (black), as described by the relationship in Eq. 4.1. f) Electrical resistance of Ag-TPU during single strain cycles of 10%, 20%, and 30% (red, green, and blue, respectively).

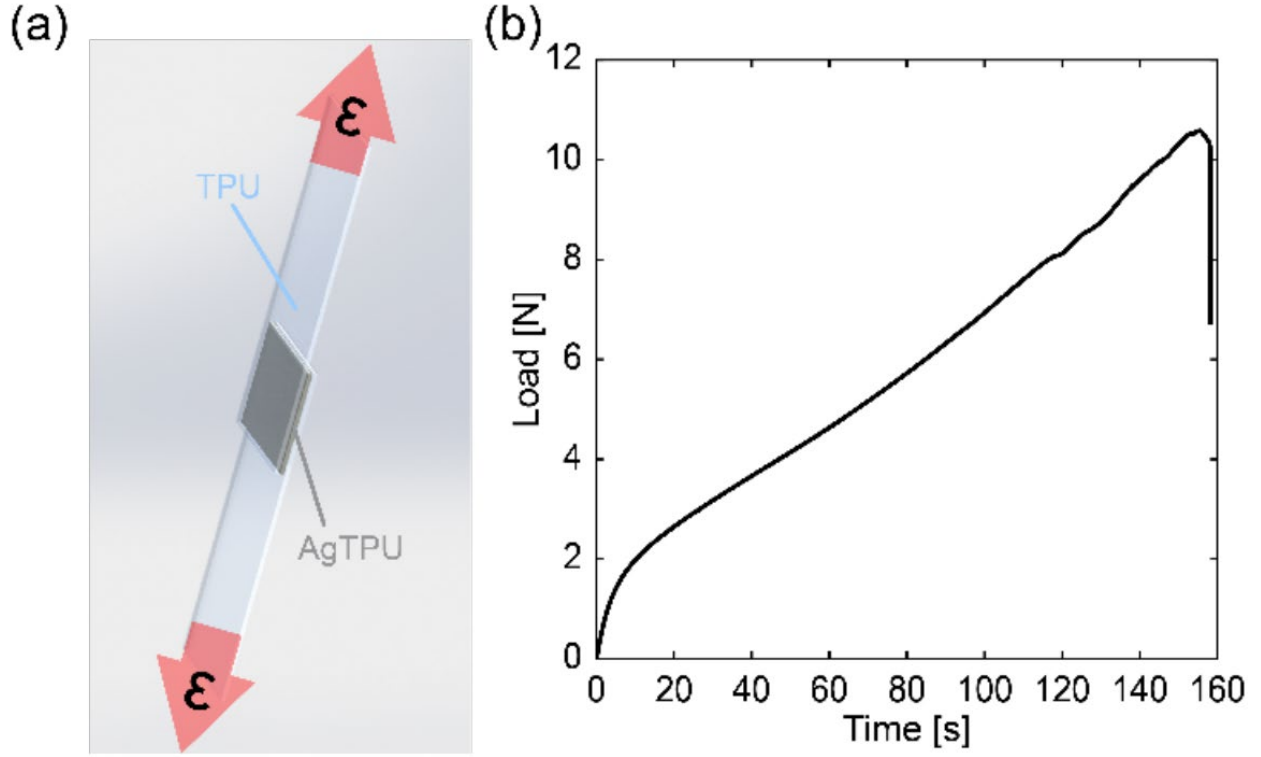


Figure 4.4: Mechanical testing of Ag-TPU-TPU interface. (a) Schematic illustration of the lap shear specimen and (b) load during axial stretching of printed sample, demonstrating a max load of >10N.

The conductivity of Ag-TPU as a function of the volume fraction of silver flake is shown in **Figure 4.3e**, along with the respective power-law theory for a percolating network [42] given by

$$\sigma = \sigma_0 (V_f - V_c)^S \quad (4.1)$$

where σ is the conductivity of the Ag-TPU composite, σ_0 is the bulk conductivity of silver, V_f is the volumetric fraction of silver flake in the ink (in dried form), V_c is the critical volume fraction at percolation (in dried form), and S is the power law exponent. Our experimental data are in good agreement with predicted behavior, yielding values of $V_c = 0.171 \pm 0.01$ and $s = 2.56 \pm 0.11$ (**Fig. 4.3e**). Due to their anisotropic nature, shear-induced alignment of silver flakes within the AgTPU ink is expected during printing, which gives rise to a modest conductivity enhancement (**Fig 4.5**)

[159, 160]. From these data, we chose to work with AgTPU inks composed of 36 vol% Ag, which exhibit an initial conductivity above 10^4 S cm^{-1} .

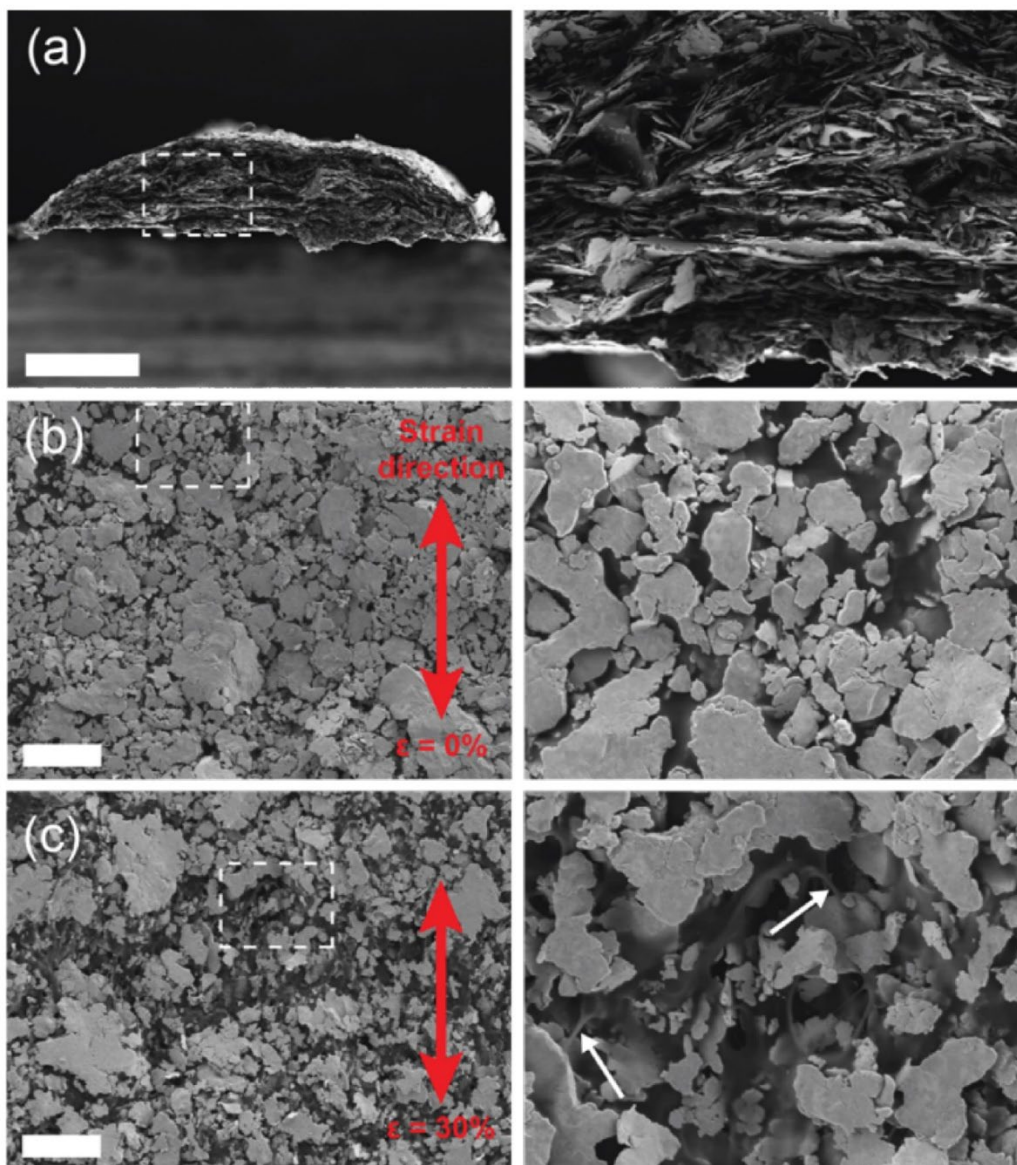


Figure 4.5 Conductive silver flake distribution in printed electrodes: (a) SEM image of Ag-TPU filament (cross-sectional view) showing orientation of silver flakes (Scale bar 50μm). (b) SEM image of Ag-TPU filament (top surface) (scale bar = 50 μm) under 0% strain and (c) 30% strain. Arrows highlight polymer fibrils under tension. (Scale bars = 10 μm) Images on the righthand side represent insets of dashed line regions in images on the lefthand side.

4.3.2 Electro-Mechanical Characterization of Leads and Strain Sensors

Using an electromechanical testing apparatus, we characterized the electrical properties of Ag-TPU in situ during mechanical stretching. Ag-TPU maintains an overall low resistance ($<4\ \Omega$) through loading and unloading up to 30% strain (**Fig. 4.3f**). These distinctive unloading curves are likely a result of the well-known mechanical hysteresis of thermoplastic polyurethanes [161]. Further examination of an Ag-TPU specimen before and during stretching reveals permanent distortion of the silver flake network and stretching of the polymer matrix itself (**Figs. 4.5 b,c**). When strained up to $\approx 200\%$, the electrical conductivity of the printed Ag-TPU electrodes decreases to a value of $0.1\ \text{S cm}^{-1}$ (**Fig. 4.6b**). At a higher strain of approximately 240%, the electrodes undergo electrical failure due to a complete disruption of the percolative silver flake-polymer network. Triangular cyclic testing at 5% strain for 1000 cycles was used to investigate the electrical performance of the printed Ag-TPU features over extended stretching (**Fig. 4.6b**). Given their high initial conductivity, low change in resistance, and long-term cyclic stability, our Ag-TPU inks yield mechanically robust, stretchable conductors.

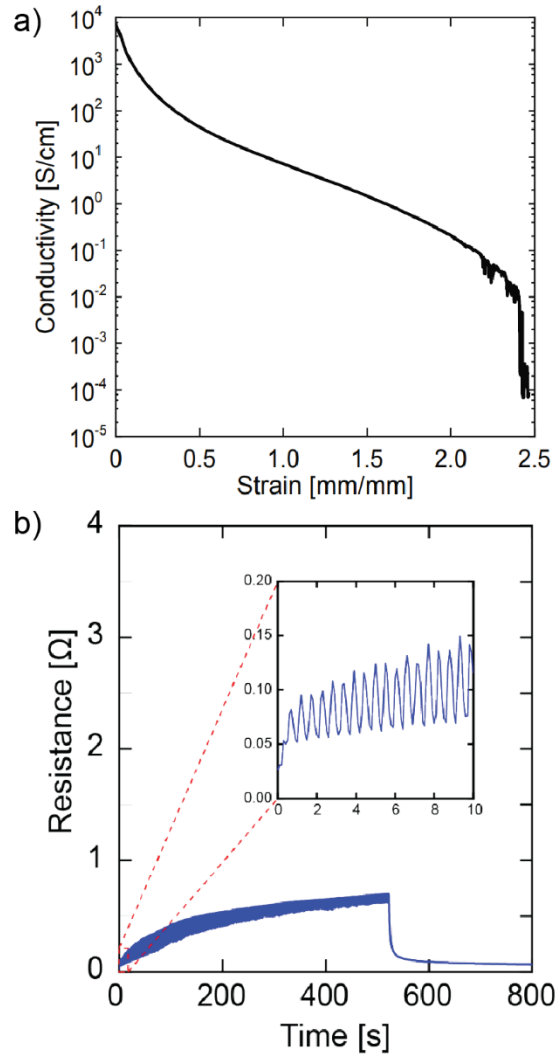


Figure 4.6: Electromechanical characterization of printed electrodes. a) Electrical conductivity as a function of strain for a printed AgTPU sample subjected to tensile testing at a rate of 0.3 mm/sec, which exhibits electrical failure at ~240% strain and (b) electrical resistance of printed AgTPU film undergoing triangular cyclic strain cycle tests (1000 cycles, 5% strain, 1.72 Hz). [The inset highlights first 20 cycles.]

To further investigate the performance of Ag-TPU, we fabricated the strain sensor shown in **Figure 4.7ai**. Notably, the printed Ag-TPU electrodes exhibit a low electrical resistance coupled with a high normalized change in resistance ($\Delta R/R_0$) (**Fig. 4.7aii**). When this device is subjected to a triangular strain cycle, it exhibits a linear, repeatable electrical response. A key figure of merit for evaluating strain sensor performance is the gauge factor ($GF = (\Delta R/R_0)/\epsilon$), where $\Delta R/R_0$ denotes

the relative resistance change and ϵ denotes applied strain. By plotting these values, a GF of ≈ 13.3 is observed for the printed AgTPU electrodes (**Fig. 4.7a**iii), which is comparable to many other particle-laden composites used for strain sensors [46, 162, 163].

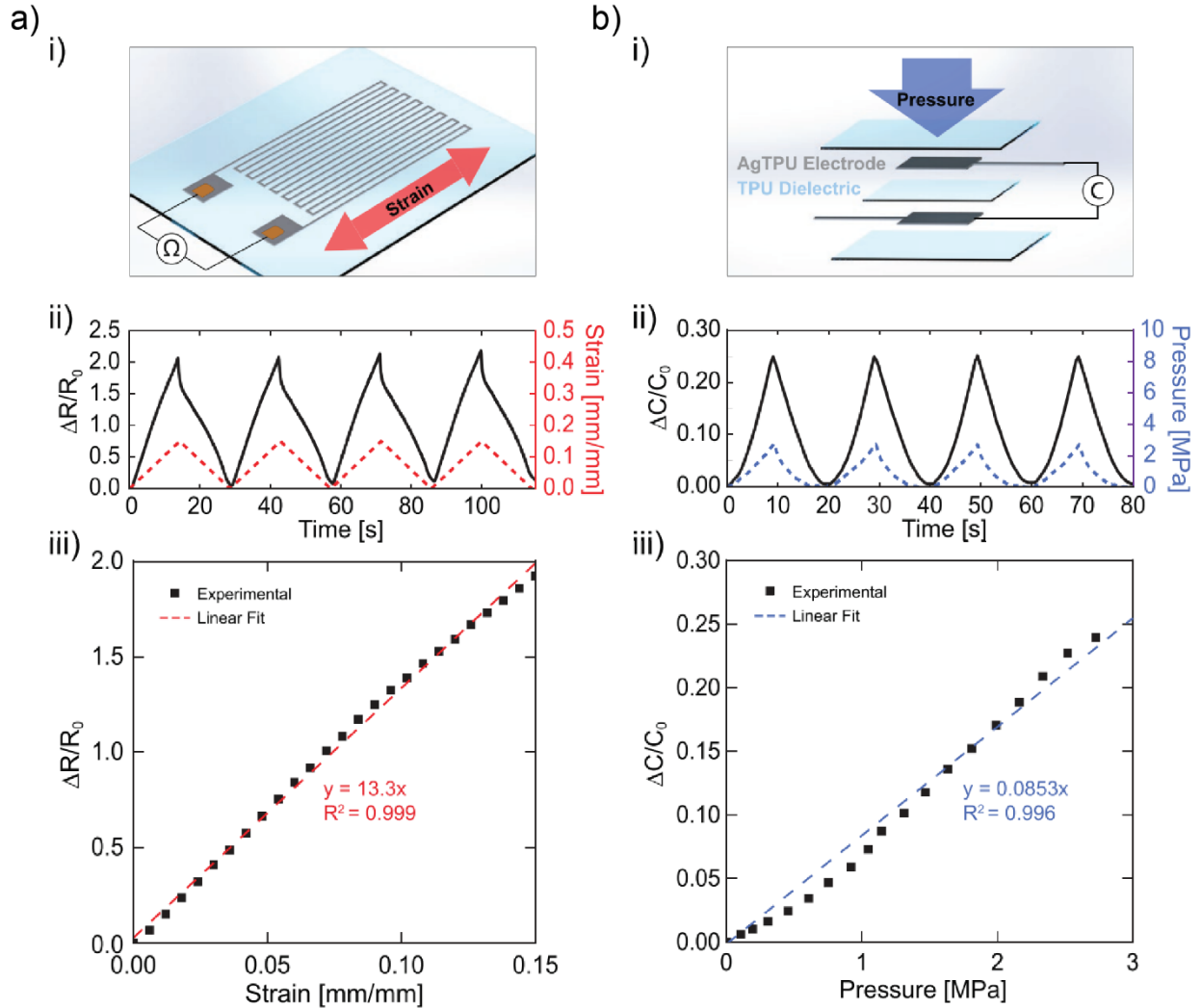


Figure 4.7: Working principle and electromechanical performance of printed sensors. a) Strain sensor device and performance: i) device scheme, ii) plot of $\Delta R/R_0$ over time during a triangular strain cycle, and iii) plot of $\Delta R/R_0$ versus strain. b) Capacitive pressure sensor and performance: i) device scheme, ii) plot of $\Delta C/C_0$ over time during a triangular strain cycle, and iii) plot of $\Delta C/C_0$ versus pressure.

4.3.3 Variable Capacitance Sensor

Next, we printed a parallel-plate capacitive sensor composed of matrix and conductive materials in a multilayered architecture. The pure TPU matrix serves as an insulating layer with a dielectric constant of 9.1 and a low elastic modulus of $E \approx 2.3$ MPa. The parallel-plate capacitive sensor uses the pure TPU as a deformable dielectric layer surrounded above and below by highly conductive Ag-TPU electrodes (**Fig. 4.7b_i**). A cross-sectional view of the multilayer printed sensor is shown in **Figure 4.8**.

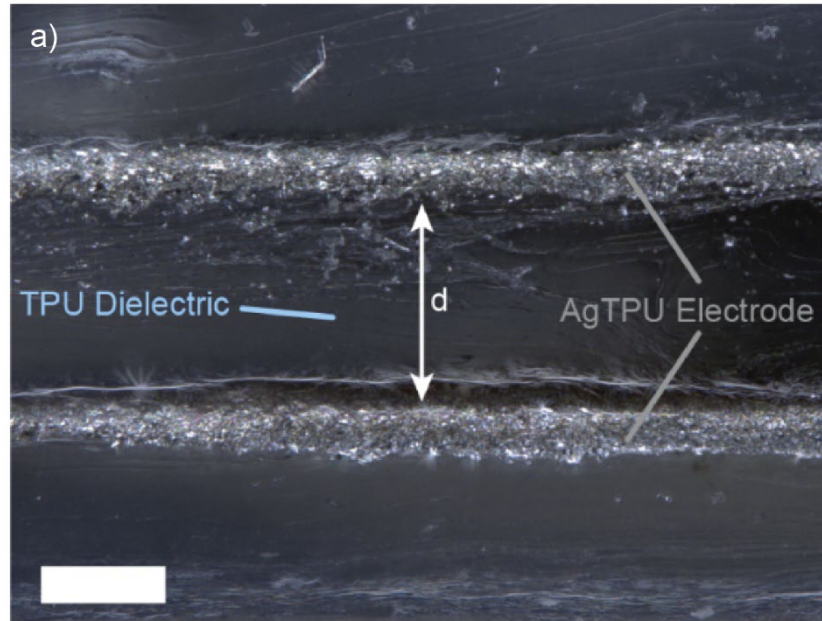


Figure 4.8: Cross-section image of parallel-plate capacitive sensor, showing AgTPU electrodes and TPU dielectric layer. (Scale bar = 100 μm)

Upon applying an external pressure, the insulating layer thickness (d) between the two printed electrodes is reduced, leading to a measurable increase in capacitance. **Figure 4.7b_{ii}** shows the capacitive sensor response to multiple cycles of applied pressure, highlighting its consistent performance. In this device, the normalized change in capacitance, $\Delta C/C_0$, depends linearly on pressure (**Fig. 4.7b_{iii}**) up to 3 MPa.

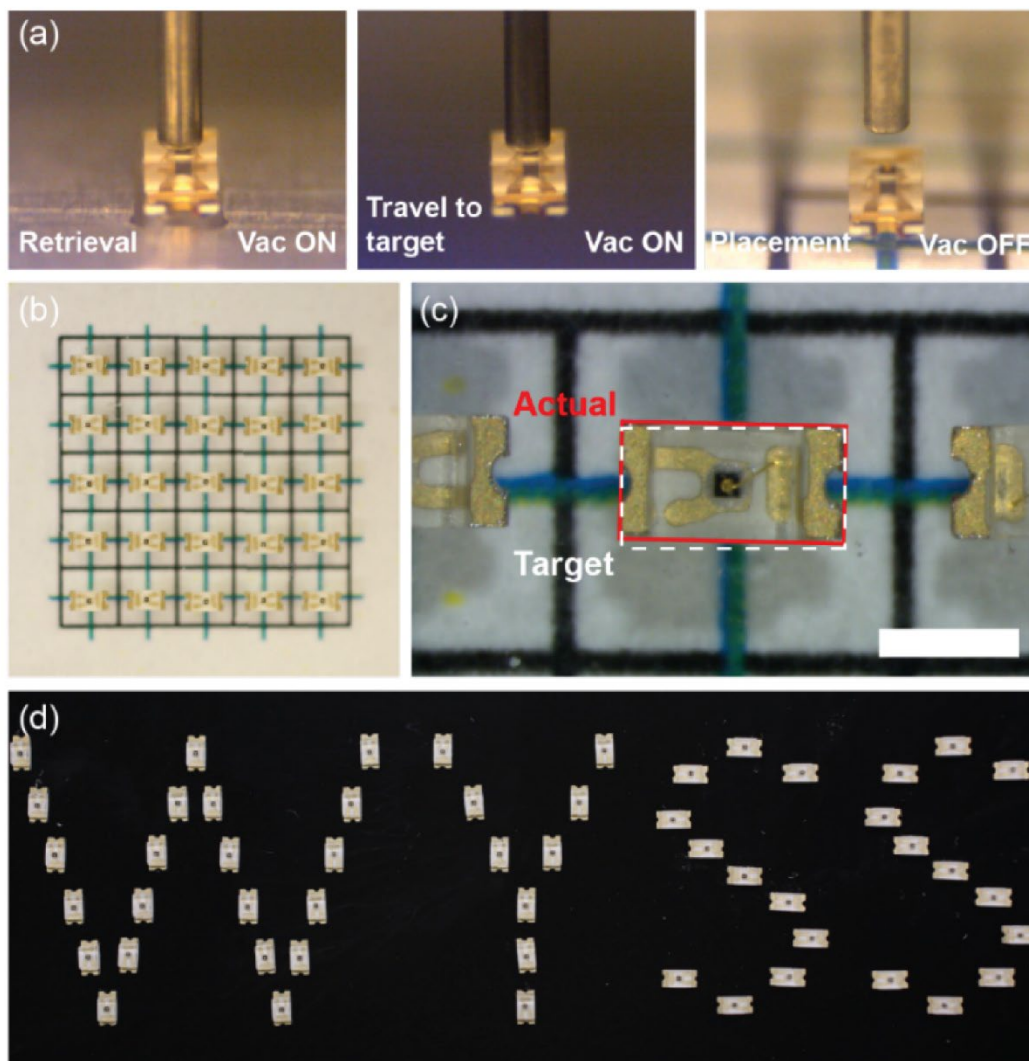


Figure 4.9: Automated pick-and-place of surface mount LEDs. (a) Images of pick-and-place (P+P) process, including retrieval of surface mount electrical component from stock (left), travel to target (middle), and placement on TPU substrate (right). (b) Placement of surface mount light emitting diodes (LEDs) onto grid patterns for accuracy measurements. (c) Representative view of one component's final position, which compares its target location (white) with its actual location (red). (Scale bar = 1mm). (d) Demonstration of pick-and-place of 52 LEDs into a programmed pattern via hybrid 3D printing.

4.3.4 Pick and Place Process and Component Integration

To assess the accuracy of the automated P+P process, surface mount LEDs are placed from a fixture onto a grid for optical measurements (**Fig. 4.9a–c**). By comparing the target position to the actual position, we determined a positional error $136 \mu\text{m} \pm 62$ ($\approx 10\%$ of their overall dimensions)

and rotational error of $1.45^\circ \pm 1.05$ ($n = 27$). This method is reliable, allowing 52 components to be placed in a single step (**Fig. 4.9d**). **Figure 4.10a** illustrates P+P of five distinct components, with lateral dimensions ranging from $0.8 \text{ mm} \times 1.6 \text{ mm}$ (LED) to $9 \text{ mm} \times 9 \text{ mm}$ (microprocessor). By programming the target locations of 16 different components interconnected by printed electrodes in a customized layout, we can manufacture complex microcontroller devices, such as the representative microcontroller device shown in **Figure 4.10b**.

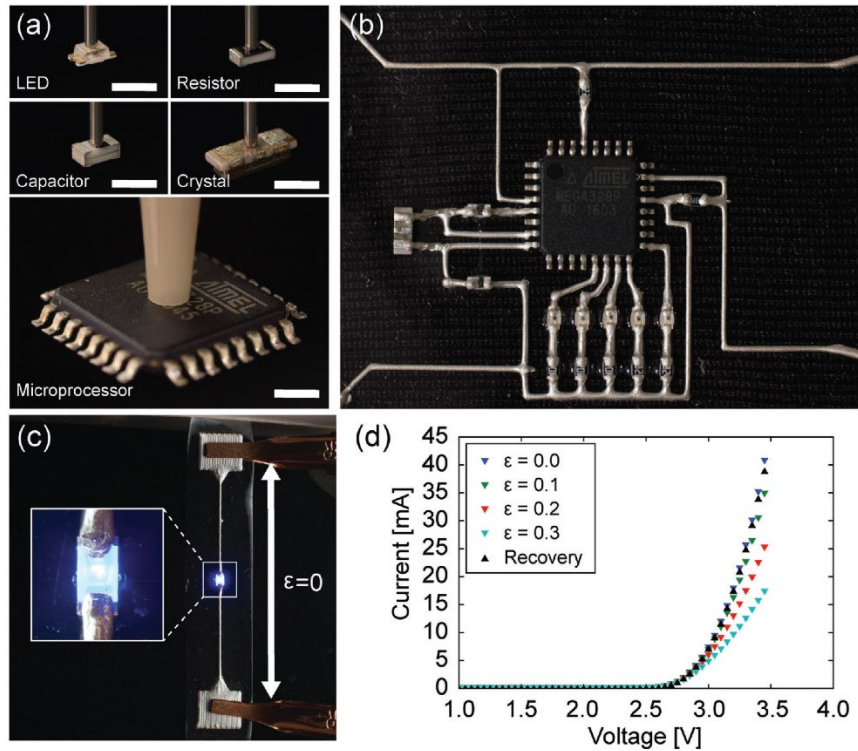


Figure 4.10: Hybrid 3D printing of a stretchable electronic device. a) Images of pick-and-place of surface mount electrical components, including LED, resistor, capacitor, crystal oscillator, and microprocessor chip (scale bar = 2 mm). b) Image of microcontroller circuit fabricated by hybrid 3D printing, in which surface mount electrical components are interconnected with printed AgTPU electrodes onto an underlying TPU matrix. c) Image of hybrid 3D printed LED device; the inset shows interface of surface mount LED with the AgTPU electrodes. d) Current-voltage characteristics of LED device at 0%, 10%, 20%, 30% strains and upon releasing from strain (recovered state).

These surface mount electrical components are composed of rigid materials that are orders of magnitude stiffer than the TPU printed matrix and Ag-TPU conductive electrodes. When these

components are adhered to printed electrodes alone, delamination at the component/Ag-TPU interface occurs at very low strains ($\epsilon = 0.14$) as shown in **Figure 4.2d**. This observation arises due to poor bonding between the surface mount component and the printed Ag-TPU electrode. When stretched, stress concentration is localized at the component-electrode interface leading to delamination. To enhance bonding, small droplets of TPU are directly printed beneath each component body (**Fig. 4.2a**) to create an adhesive region of increased thickness that distributes the applied stress across the entire component/TPU matrix interface. This important modification led to nearly an order of magnitude higher strain to failure ($\epsilon = 1.22$) as shown in **Figure 4.2d**. A representative device composed of 12 LEDs is now able to bend to a radius of curvature of 2.8 mm (**Fig. 4.11**) without experiencing any loss of functionality, i.e., significant reduction in LED intensity or mechanical failure.

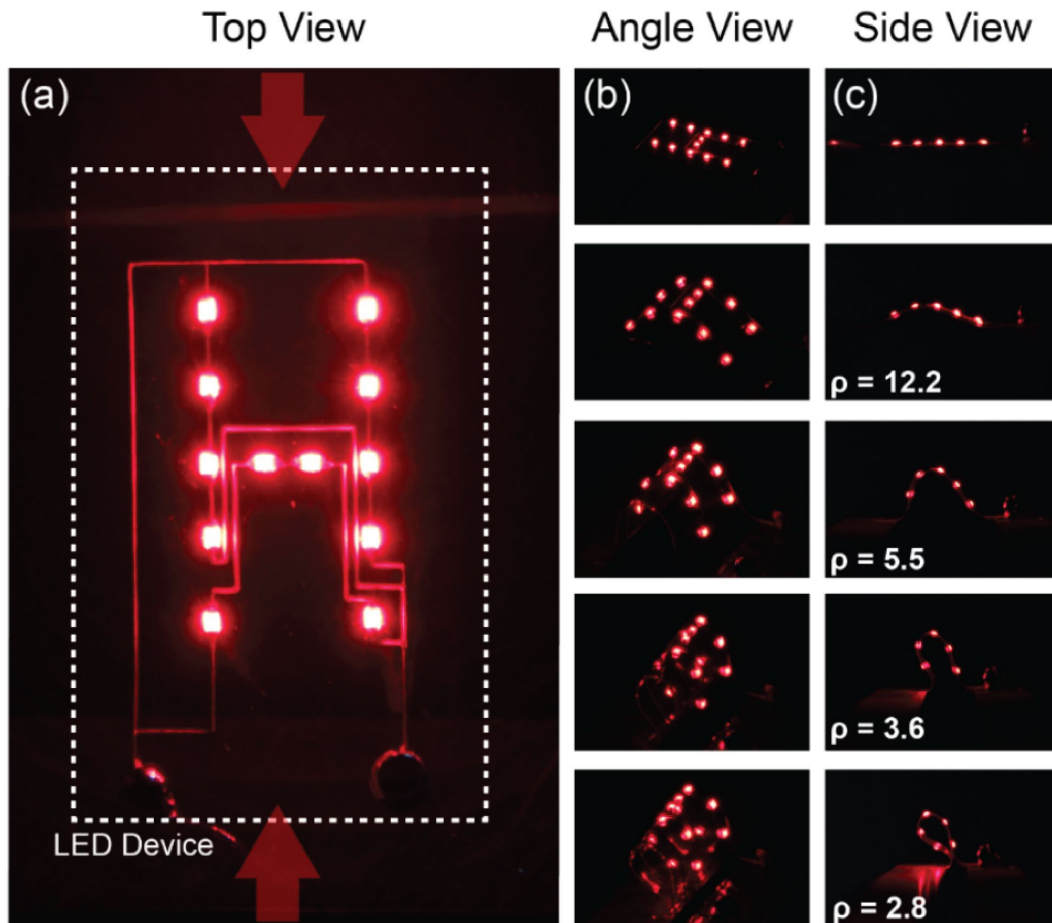


Figure 4.11: Images of functioning LED device produced by hybrid 3D printing, during bending. (a) top, (b) angled, and (c) side views of the H-device as a function of increasing bending radii of curvature (ρ) in mm. (top-flat to bottom-highest bending)

Component integration is further characterized by fabricating a model architecture using our hybrid 3D printing method (**Fig. 4.10c**). Specifically, we print an insulating matrix (TPU), P+P an LED component, and then print conductive interconnects (Ag-TPU). Current–voltage responses of this model device are acquired at various strains. The resulting current decreases with different values of strain ($\epsilon = 0.3$). However, the current–voltage characteristics seem to completely recover after the specimen is returned to its original length (**Fig. 4.10d**), which further illustrates our ability to reliably incorporate conventional electrical components into soft, stretchable devices in a robust manner.

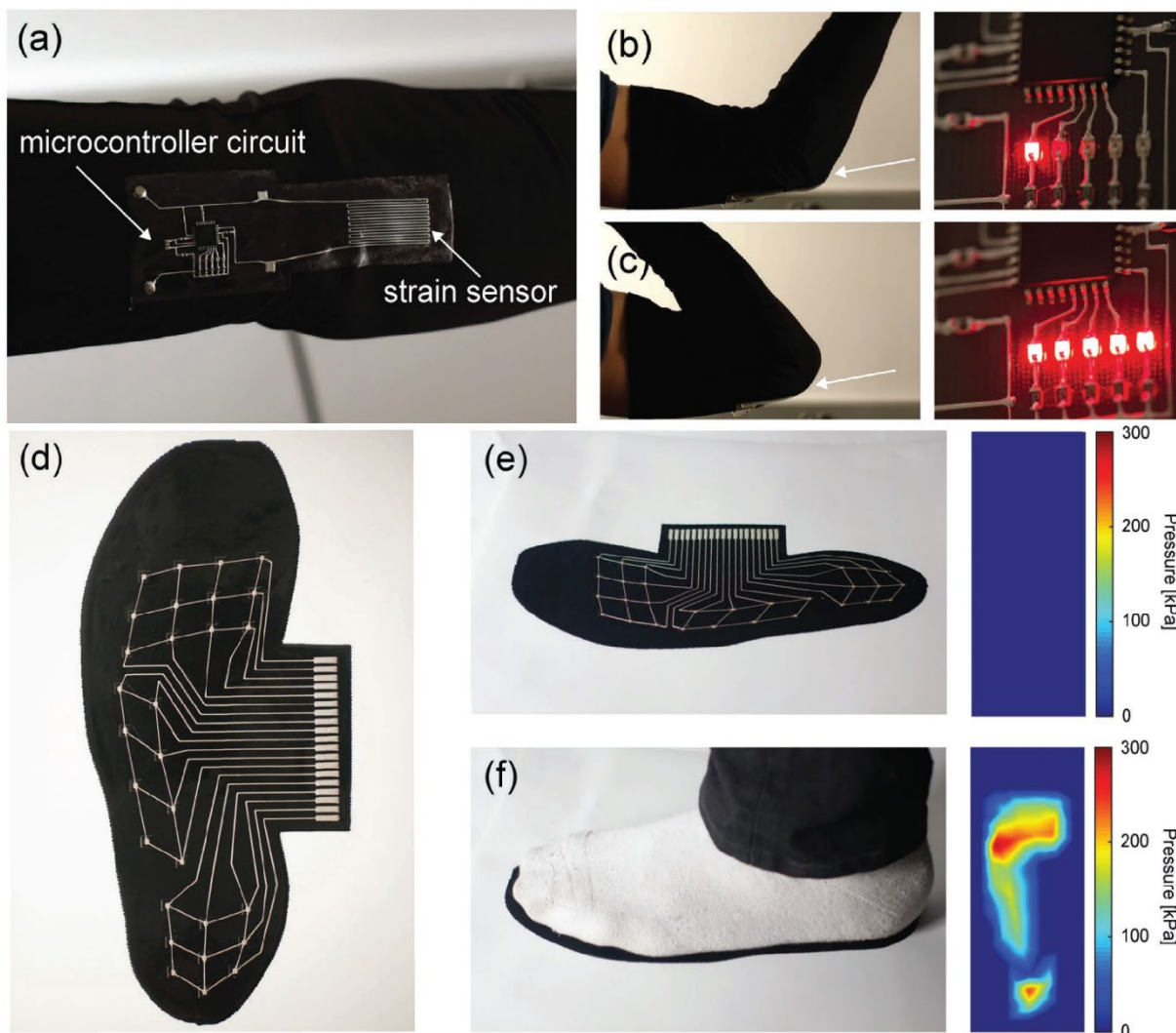


Figure 4.12: Wearable soft electronics fabricated by hybrid 3D printing. a) image of textile-mounted printed strain sensor and microcontroller circuit. b,c) Images of real-time function of the wearable strain device (identified with arrows) at modest and maximum joint bending, respectively, along with the corresponding LED readout. d) Image of plantar sensor array. e) Illustration of sensor array readout in the absence of applied pressure and f) upon the application of pressure by a human foot.

4.3.5 Printed Soft Electronics

To fully demonstrate our hybrid 3D printing platform, we created a complex microcontroller device coupled with a strain sensor and a large-area soft sensor array. The wearable electronic system is fabricated by co-printing both the TPU matrix and Ag-TPU electrodes along with P+P of a microcontroller chip and LEDs (**Figure 4.12a**). The printed strain sensor is positioned

posterior to the elbow joint and serves to provide strain data input to the microcontroller that corresponds to various joint angles. The microcontroller circuit is designed using an ATMEGA328 chip (Atmel) to read the sensor data and output the readout to five indicator LEDs (**Fig. 4.12b,c**). A custom-programmed script is loaded onto the chip prior to assembly, which can be further modified to carry out other functions. This textile-mounted soft electronic system functions in real time, providing the user with visual feedback corresponding to the extent of joint bending (**Fig. 4.12b,c**).

As a final embodiment, we created a sensor array composed of 29 capacitive sensors in the custom shape of a person's left foot (**Fig. 4.12d**). A carbon black-doped TPU is used as the bottom layer insulating matrix to enhance the visualization of the printed Ag-TPU electrodes. This plantar sensor array is designed with a multiplexed wire scheme to minimize the number of external connections. Using this layout, only 19 connections are needed rather than 58 (i.e., 2 electrodes for each of the 29 sensors). In the absence of applied pressure (**Fig. 4.12e**) the sensors do not experience any deformation and, hence, no change in capacitance. During walking, the sensor array is deformed (**Fig. 4.12f**) and the relative capacitance of each sensor is measured, resulting in a unique plantar pressure profile (all sensors are calibrated prior to testing). Given the soft, flexible form factor of the plantar sensor array, it could be readily integrated into the insole of a shoe and used to read out pressure profiles.

4.4 CONCLUSION

In summary, we report a new hybrid method for manufacturing high-performance soft electronics that combines direct ink writing with automated pick-and-place of surface mount electrical components. By developing novel insulating and conductive inks, functional strain and pressure sensors were fabricated and characterized. This hybrid method enables surface mount electrical

components of arbitrary shapes and sizes to be readily integrated into printed soft wearable circuits. Importantly, the broad set of printable materials (e.g., ceramics, polymers, metals) and devices (e.g., antennas, batteries, waveguides) previously developed for DIW offers a unique opportunity to expand the functionality of 3D printed structures via this hybrid manufacturing platform.

4.5 CONTRIBUTIONS

T.A.B, A.D.V., and A.K. formulated and optimized the Ag-TPU and TPU inks. A.D.V., T.A.B. J.W.B, J.R.R., A.C, A.K., J.D.B, and M.F.D. tested ink properties, and contributed to device and sample design and fabrication. A.D.V. and J.A.L prepared the manuscript.

CHAPTER 5

DROPLET-BASED VISCOELASTIC INK PRINTING OF HYBRID STRETCHABLE ELECTRONICS WITH SPATIALLY PROGRAMMABLE MECHANICS

This chapter has been adapted from the following manuscript:

Busbee, T.A., Rininger, R.W., and Lewis, J.A., “Droplet-based Viscoelastic Ink Printing of Hybrid Stretchable Electronics with Spatially Programmable Mechanics.” *Advanced Materials* (to be submitted).

5.1 INTRODUCTION

Human bodies are inherently compliant, yet most conventional electronic devices are rigid. There is growing interest in seamlessly integrating electronic devices with human physiology to manage communication, biometric data, and clinical therapies [164-166]. The field of stretchable electronics addresses this fundamental mismatch by developing electronic systems with mechanical properties closely matched to human tissues [167]. The fabrication of personalized, conformable, and dynamically responsive electronic devices requires manufacturing methods capable of both customization, due to the inherent variability in human anatomy, and the unique mechanical demands of wearable devices [168].

Existing fabrication strategies for stretchable electronics can generally be classified into two categories. The first category employs rigid electronic materials, such as metals and semiconductors, configured into geometrically engineered structures (e.g., serpentine or mesh patterns) to achieve stretchability [7, 169, 170]. The second category utilizes inherently soft materials, including conductive polymer composites [39, 171], liquid metals [52, 55], and ionic conductors [59, 62], to fabricate fully compliant devices [8, 70, 172]. Both methods typically rely

on microfabrication and transfer printing techniques, restricting customization potential [8, 169, 173]. Historically, research efforts in stretchable electronics have primarily emphasized the development of novel materials [52], sensors [48, 62], electrical components [18] or the optimization of geometric designs for individual functional elements, such as electrical interconnects [174]. In contrast, comprehensive, scalable digital fabrication methods for assembling these components into customizable, robust, and multifunctional electronic systems have received comparatively less attention.

Current additive manufacturing technologies remain incapable of producing high-density integrated circuits and microprocessors, thus necessitating hybrid approaches that integrate rigid, lithographically fabricated electronic components with printed, stretchable conductive matrices [167]. Chapter 4 described a promising hybrid method employing direct ink writing for patterning stretchable conductors and elastomeric insulators with integrated robotic pick-and-place systems for precise placement of rigid electronic components [171]. However, the integration of rigid components into compliant substrates induces mechanical stress concentrations at rigid-soft interfaces, jeopardizing device reliability [9, 18, 175]. Biological systems such as the ligament-to-bone interface offer inspiration by naturally incorporating gradient stiffness transitions to effectively distribute mechanical loads [14-16]. Gradient stiffness regions have been demonstrated to mitigate stresses at rigid-soft interfaces in stretchable electronic devices [30] and digital approaches, like the use of voxelated graded stiffness elastomers created via UV inkjet printing, have also shown excellent interface protection effectiveness for isolated deformation events, but have limited intrinsic material durability under repeated cyclic deformations [176, 177].

Despite the potential advantages offered by digital fabrication for stretchable electronics, significant challenges remain in material compatibility and throughput. Inkjet-based techniques,

though advantageous due to their digital programmability, parallelization potential, and multi-material capabilities, face severe viscosity limitations (typically $<60 \text{ mPa}\cdot\text{s}$) and require submicron particle sizes [88-90]. These restrictions hinder the formulation of printable materials capable of meeting the demanding dynamic mechanical and electrical performance criteria essential for stretchable electronics. Conversely, extrusion-based techniques, including fused filament fabrication and direct ink writing, accommodate a wider range of material viscosities, but their reliance on precise mechanical nozzle translation limits their throughput and design flexibility [93, 101]. Recent efforts have focused on generating multi-material, multinozzle arrays to achieve higher throughput, yet, to date, these printheads lack independent nozzle control [94, 178].

In this chapter, we introduce droplet-based viscoelastic ink printing (DVIP), a novel drop-on-demand technique that merges the scalability and digital precision of inkjet printing with the capability to deposit highly viscoelastic inks (**Fig. 5.1**). DVIP employs heated, mechanically actuated microvalves with $100\text{-}300 \text{ }\mu\text{m}$ orifice diameters to eject pressurized, UV-curable elastomeric inks with viscosities exceeding $60,000 \text{ mPa}\cdot\text{s}$. DVIP therefore expands the range of printable ink viscosities by more than three orders of magnitude over conventional inkjet printing. Our custom, open-source electronics platform interprets bitmap-based instructions to facilitate simultaneous, multi-material droplet-based printing of complex patterns from image-based designs. We systematically characterize the droplet formation, jetting stability, and curing behavior of a newly formulated class of 100% solids thiol-ene elastomeric inks specifically tailored for stretchable electronics. These materials exhibit elongation exceeding 300% with elastic moduli that are continuously tunable across three orders of magnitude, while maintaining mechanical integrity under repeated dynamic loading, thus substantially outperforming previously reported jettable elastomers. Using DVIP, we demonstrate the precise co-printing of elastomeric materials

with spatially architected mechanics, the integration of printed stretchable liquid metal interconnects, and the implementation of robotic rigid component placement to produce hybrid stretchable electronic devices, both with and without zonally graded interfaces for embedded rigid electronic component interface protection. We show that these hybrid devices based on zonal strain relief exhibit dramatically improved dynamic electrical performance and mechanical robustness than their monolithic counterparts. This versatile approach is further highlighted by creating multi-layer 3D stretchable electronics with embedded sensors and selectively encapsulated PCB modules.

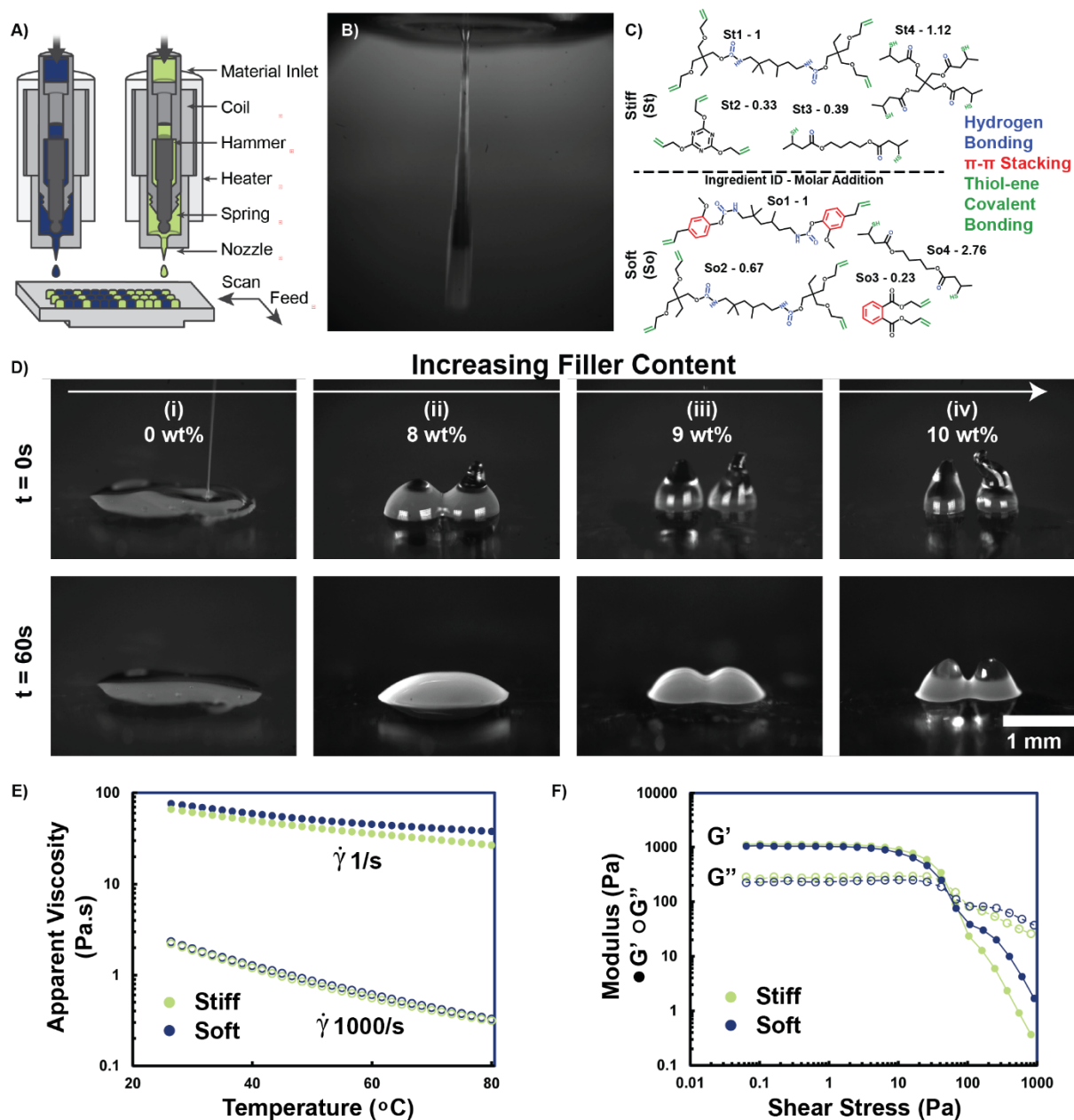


Figure 1. New printing method: droplet-based viscoelastic ink printing (DVIP). (A) A schematic illustration of the droplet-based viscoelastic ink printing (DVIP) system. (B) A high speed image of a representative viscoelastic ink after ejection from a microvalve-based nozzle. (C) The chemical structures of resins used to create stiff and soft thiol-ene elastomer inks. (D) High-speed camera images of printed droplets composed of soft viscoelastic ink with varying filler loading acquired $t=0$ sec (immediately upon droplet impact) and $t=60$ sec (after drop coalescence and relaxation). [The measured yield stress (τ_y) and storage modulus (G') of each ink shown: (i) $\tau_y = 0$ Pa and $G' = 0$ Pa, (ii) $\tau_y = 34.12$ Pa and $G' = 584$ Pa, (iii) $\tau_y = 51.6$ Pa and $G' = 1672$ Pa iv) $\tau_y = 65.5$ Pa and $G' = 1949$ Pa (E) Semi-log plots of apparent viscosity (measured at shear rates of 1/s and 1000/s) as a function of temperature for the soft and stiff elastomeric inks optimized for DVIP (8.5 wt% and 6.1 wt% fumed silica respectively). (F) Log-log plots of storage (G') and loss (G'') moduli as a function of shear stress (τ) for the soft and stiff optimized DVIP inks.

5.2 EXPERIMENTAL

5.2.1 Materials System

Three classes of ink were developed for digital printing hybrid stretchable electronics, each of which has the requisite viscoelastic rheological properties and shelf stability optimized for DVIP. To tailor the elastomeric ink properties, we first synthesized two customized allyl-functional urethane oligomers. The soft thiolene ink, which is used to produce elastomeric extensible regions within these devices, exhibits a low elastic modulus, high elongation at break, and high resilience. The stiff thiol-ene ink, which is used to pattern strain-relieving regions, has substantially higher elastic modulus and strength compared to soft thiol-ene ink. [Note: An alternative stiff (AS) thiolene ink was also created and characterized but was ultimately not used in device fabrication.] When both soft and stiff thiol-ene inks are zonally patterned, device deformation via stretching is primarily accommodated by the soft regions. A third ink, composed of an anhydrous eutectic-Gallium-Indium (eGaIn) emulsion, was also formulated to function as the stretchable electrical interconnects in the printed devices.

Allyl-Urethane Oligomer Synthesis: All reagents were used without further purification unless otherwise noted. The soft allyl functional urethane mixture (So1 and So2) was synthesized as follows. To a Flaktek Max 60 polypropylene mixing cup, 16.328 g of Trimethylolpropane diallyl ether (Perstop TMPDE-90), 18.780 g Eugenol (Sigma-Aldrich ReagentPlus 99%), and 20 g trimethylhexamethylene diisocyanate (Evonik Vestanat TMDI) were added. The top of the container was purged with dry nitrogen (Polytek PolyPurge) before being sealed tightly and mixed for 60 sec at 1000 RPM in a FlakTek 1200-500 VAC. The container was then placed in an oven at 70 °C for 1 h. After 1 h, the mixture was mixed for another 30 sec at 1000 rpm, then placed back in the oven at 70 °C for 14 h. The resulting mixture is stable at room temperature for > 1 month.

The stiff allyl functional urethane was made according to the same procedure, by adding 32.656 g of trimethylolpropane diallyl ether and 16 g of trimethylhexamethylene diisocyanate to a Max 60 cup.

Soft Thiolene Ink: First, a stabilizer and dye feedstock was made in a 20 mL glass scintillation vial. The soft feedstock was made by adding 3.46 g diallyl phthalate (sigma-aldrich 97%), 0.03675 g 4-Methoxyphenol MEHQ (Sigma-Aldrich ReagentPlus 99%), 0.1103 g Pentaerythritol tetrakis(3,5-di-tert butyl-4-hydroxyhydrocinnamate *irganox 1010* (Sigma-Aldrich 98%), and 0.396 g 2-Propenylphenol mixture of cis and trans (Sigma-Aldrich 98%). The vial was then sealed, and was lightly shaken with the bottom above a heat gun set to 450 °C for a period of about 30 seconds, or until all powders were fully dissolved and the liquid mixture was optically clear. This feedstock was then stored at room temperature for subsequent use in multiple batches.

To make the ink, the allyl-urethane oligomer synthesized previously (So1/So2) was reheated to 70 °C for 30 minutes to induce pourability. To a Flaktek Max 60 container, 16.018 g of 1,4-Bis (3-mercaptopbutyryloxy) butane (Karenz BD-1), 1.3109 g of the soft feedstock, 0.2711 g ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate *TPO-L* (DoubleBond Chemical), 0.3615 g 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane (ThermoScientific 92%), and 19 g of the soft allyl functional urethane oligomer (So1/So2) was added. The container was then sealed, and mixed at 1000 RPM for 1 minute in the speedmixer. Next, into the same container, 1.446 g of Aerosil R816 fumed silica (Evonik) and 1.627 g Ultrabond 5780 fumed silica (Cabot) was added. The container was sealed again, and mixed at 2000 RPM for 1 minute in the speedmixer. Next, the lid was replaced with a Max 60 lid with a 4 mm hole drilled in it, and then vacuum mixed with the vacuum set to 40 mbar for the following sequence: 1200 RPM – 60 s, 1600 RPM – 90 s, 2000 RPM – 140 s, 800 RPM – 10 s, 0 RPM – 2 s. Following mixing, the ink was immediately transferred to a 55

CC syringe cartridge with plunger (Nordson EFD), while it was still warm from mixing. The syringe was fitted with a 250 micron tapered nozzle (Nordson EFD), and the ink was extruded at 90 PSI into the back of 4x amber colored 10CC syringe barrels (Nordson EFD) to filter the ink. If the nozzle clogged, it was replaced with a new one to continue the filtering. Once completed, plungers were inserted into the 10-CC cartridges, which were then centrifuged at 3000 RPM for 1 min (Thermo Scientific Megafuge 8) to remove air. The resulting ink cartridges were stored at room temperature for up to 2 weeks prior to printing.

Stiff Thiolene Ink: This ink was made following the same procedure as the soft thiolene ink albeit with different raw materials. For the stiff stabilizer feedstock: 5.51 g 1,3,5- triallyl-1,3,5-triazinane, 2,4,6-trione (Ambeed 99.2%), 0.0958 g irganox 1010, 0.0319 g MEHQ, 0.3439 g Propenyl Phenol, 0.01916 g Oil-Glo Ultra SPI-OGYG-16 (Spectroline). For the ink: 16.665g Pentaerythritol tetrakis (3-mercaptopbutylate) (Karenz PE1), 3.179 g 1,4-Bis (3-mercaptopbutyryloxy) butane (Karenz BD-1), 2.481 g stiff masterbatch, 0.2971 g TPO-L (DoubleBond Chemical), 0.3961 g 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane (ThermoScientific 92%), 17.496 g of the stiff allyl functional oligomer (St1), 0.7923 g Aerosil R711 (Evonik), and 1.6243 g Ultrabond 5780 (Cabot).

Anhydrous eGaIn Emulsion: First a 4 wt% solution of hydroxypropyl cellulose (Sigma Aldrich MW: 100,000) was made by dissolving hydroxypropyl cellulose in propylene glycol propyl ether (Sigma Aldrich 98.5%). This was mixed for 1 min at 2000 RPM every 12 h until fully dissolved, clear, and homogenous. Eutectic gallium indium was made by adding 8.615 g Indium metal (Rotometals 99.99%) and 26.474 g Gallium metal (Rotometals 99.99%) to a 20 mL Scintillation vile. The vile was then flushed with Nitrogen, capped with a piece of aluminum foil, and placed in an oven at 165 °C for 16 hours to alloy. After removal from the oven and cooling, 0.695 g 4 wt% hydroxypropyl cellulose solution, 0.007 g Cabot XC-72R carbon black, and 1.291 g of

additional propylene glycol propyl ether were added to the scintillation vial. Next, the mixture was emulsified with a high speed microhomogenizer (VWR Model 200 - 5000 to 35,000 rpm) at 25% power for 4 min, while manually stirring the head around in all directions to maximize contact. At the end, a thick pourable grey liquid forms, which is poured into 2x capped 3cc syringe cartridges (Nordson EFD). Plungers were added to the syringes and allowed to settle upside down for 12 h before using. The homogenizer was then cleaned by homogenizing a water-based carbopol gel. Upon settling, the ink separates into 2 phases, a dense emulsified liquid metal phase at the bottom, and an excess solvent phase at the top. The syringes are connected to the valves in the same orientation, with the dense phase being used for printing, while the solvent phase acts as a solvent evaporation shield, enabling the ink to be stored on the printer for up to 1 month.

Alternative Stiff (AS)- Allyl-urethane oligomer formulation: The AS-allyl-urethane oligomer was synthesized using the same procedure as in the allyl-urethane synthesis section, but with the following formulation; 5 grams trimethylhexamethylene diisocyanate (Evonik Vestanat TMDI), 6.23 g 4,4'-Methylenebis(cyclohexyl isocyanate) *HMDI*, and 20.37 g Trimethylolpropane diallyl ether.

Alternative Stiff (AS) Elastomer Ink: First, an AS feedstock was prepared by combining 2.575 g diallyl phthalate, 0.537 g irganox 1010, 0.072 g 4-methoxyphenol *MEHQ*, 0.772 g 2-propenylphenol mixture of cis and trans. Then the ink was prepared by combining 20 g AS-allyl-urethane oligomer, 17.27 g pentaerythritol tetrakis (3-mercaptopbutylate) (Karenz PE1), 1.036 g AS feedstock, 0.574 g 1,3,5-triallyl-1,3,5-triazinane, 2,4,6-trione, 0.379 g 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane, 0.284 g TPO-L, 1.16 g Aerosil R816, 1.16 g Ultrabond 5780.

5.2.2 Rheology Measurements

Rheological properties of the thiol-ene and anhydrous eGaIn Emulsion inks were characterized using a TA instruments Discovery HR20 Rheometer with the liquid cooling and electric heating plate attachment. A 20 mm stainless steel parallel plate attachment with heatbreak was used with a 300 micron gap. Curves of apparent viscosity as a function of temperature were gathered at 1/s and 1000/s shear rates, ramping the temperature from 25 °C to 80 °C at a rate of 5 °C/min. Curves of storage and loss moduli as a function of oscillation stress were gathered with the same setup – 1 Hz frequency was used while ramping the stress from 0.01 Pa to 1000 Pa with 10 points measured per decade, with 3 s conditioning time and 5 s sampling time per point.

5.2.3 Droplet-Based Viscoelastic Ink Printer

The custom-built DVIP system used to digitally print samples and devices consisted of three primary elements. The printhead, which houses the microvalves, material reservoirs, pick and place system, and UV curing system, is mounted to a robotic gantry system capable of precise movement in 3 axes (X, Y, Z). The robotic gantry has an integrated controller that enables programmed movement via G-code and is configured to output 24 V signals that are synchronized with the machine's movement. Finally, the droplet raster image processing (dRIP) controller is a custom-designed microcontroller that synchronizes droplet deposition with the motion of the robotic gantry. Details on dRIP hardware design and operation are provided at github (<https://github.com/lewislab/drip-hardware>). It reads position signals from the gantry controller and image-based instructions from print files, then delivers current pulses to the printhead valves (via a custom cable harness) to precisely deposit droplets at the specified locations, enabling accurate digital printing of the intricate patterns defined by the input images. The dRIP firmware that executes this may be found on github (<https://github.com/lewislab/drip>).

The microvalves were purchased from Fritz Gyger AG. SMLD 300G H J0.3 T3 M M6x0.75 valves were used to print all elastomeric devices and for valve testing. SMLD 300G H J0.15 T2 M M6x0.75 valves were used to print the variable drop demonstration shown in **figure 5.2B**, and were also used for all anhydrous eGaIn emulsion printing. The heated single valve holders were also purchased from Gyger and then modified. The temperature sensor holder was removed, drilled out, and replaced with a Honeywell 100 ohm platinum RTD (Digi-key 480-4948-ND). The foil heaters were used as received. The temperature was controlled using an Omron E5DC–RX2DSM-000 controller for each valve. Anhydrous eGaIn emulsion was deposited at room temperature. Valve signals were generated using ZC1 valve controllers in edge control mode. The open time for each valve was controlled by serially programming each ZC1 controller according to the manufacturers instructions. The ZC1 controllers were triggered by a custom microcontroller (dRIP), which generated 24 V signals when a valve was to be fired (**Fig. 5.2**). An LED UV curing device was also mounted to the printhead for in situ curing (Phoseon FireEdge FE300 75x10AC385-5W), and we activated electronically using a relay in communication with the gantry controller. The valve nozzles were shielded from reflected UV light during curing using a steel plate, which was automatically picked up by magnets mounted on the printhead between layers. The plate was then removed by an automation script using a custom laser-cut arm (**Fig. 5.3**). The pick-and-place operation was performed using an empty 3-cc syringe cartridge fitted with a 16-gauge tapered tip (Nordson EFD), attached to a Nordson EFD Ultimus V pressure box. The pressure box was set to 0.1 psi in standby mode and 18” H₂O vacuum level in suction mode (**Fig. 5.4**). The gantry system was a Voxel8 AL-1 printer, which was modified by removing the printhead and all auxillary systems prior to installing the custom printhead. The controller (Delta Tau Power Brick) was configured to generate a togglable position synchronized output (24 V

square wave with 50% duty cycle every time the actuators moved 100 microns combined in the X and Y directions. The synchronization wave spacing was configurable using an M-code for adjustment to various resolutions. The custom microcontroller counts these pulses for spatiotemporal awareness and valve timing. Notably, the microcontroller is compatible with any gantry system that can output a 24V position synchronized output square wave.

The specific details of file preparation and gcode creation for device printing are provided on github (<https://github.com/travisbusbee/image-processor>). The H-shield was printed using a 400 $\mu\text{m} \times 400 \mu\text{m}$ grid size, with 300 μm opening microvalves. The printing parameters included an open time of 300 μs , an ink pressure of 65 psi, a valve temperature of 69 $^{\circ}\text{C}$, a scan rate of 50 mm/s, and a standoff distance of 6 mm. The stretchable electronic device and variable capacitance sensor were printed using an 800 $\mu\text{m} \times 800 \mu\text{m}$ grid size, with 300 μm opening microvalves. The opening times were 420 μs for the soft ink and 440 μs for the stiff ink. Both inks were printed at a pressure of 75 psi, with valve temperatures set to 71 $^{\circ}\text{C}$. Printing was performed at a scan rate of 50 mm/s. The printhead was moved upward by 0.5 mm in the Z-direction between each layer, starting with a standoff distance of 6 mm. A scan rate of 50 mm/s was used to ensure adequate residence time of the inks in the heated valve holder to reach the valve temperature. In future embodiments, a cartridge pre-heating attachment may be used to preheat the inks. In such cases, the valve settings will be capable of firing at rates up to 1 kHz, corresponding to scan speeds of up to 800 mm/s. UV curing after each layer was executed at a UV power of 100% from a standoff distance of 10 mm by scanning the UV lamp over the part twice at a rate of 2.5 mm/s. UV post curing was done by placing printed parts in a box illuminated with an omniscure UV lamp (through a waveguide) at a UVA+B intensity of 80 mW/cm² for a period of 10 min on the top and bottom surfaces sequentially. The parts were then thermally cured in a forced air oven at 120 $^{\circ}\text{C}$ for 1 h.

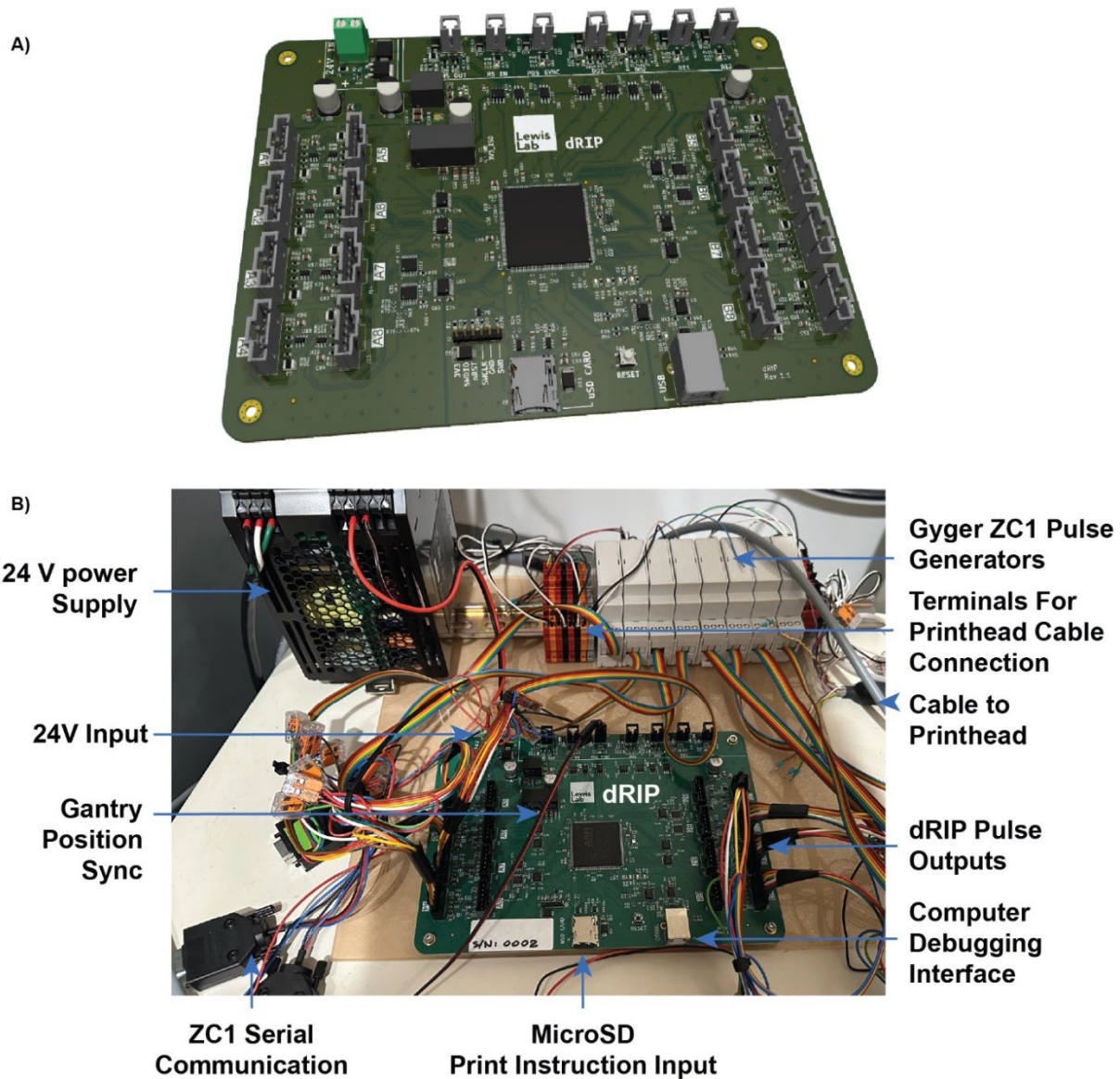


Figure 5.2. Droplet Raster Image Processing (dRIP) Microcontroller and Electrical Setup. (A) A rendering of the custom droplet Raster Image Processing (dRIP) control board that we created. (B) An image of the control board setup used in this research.

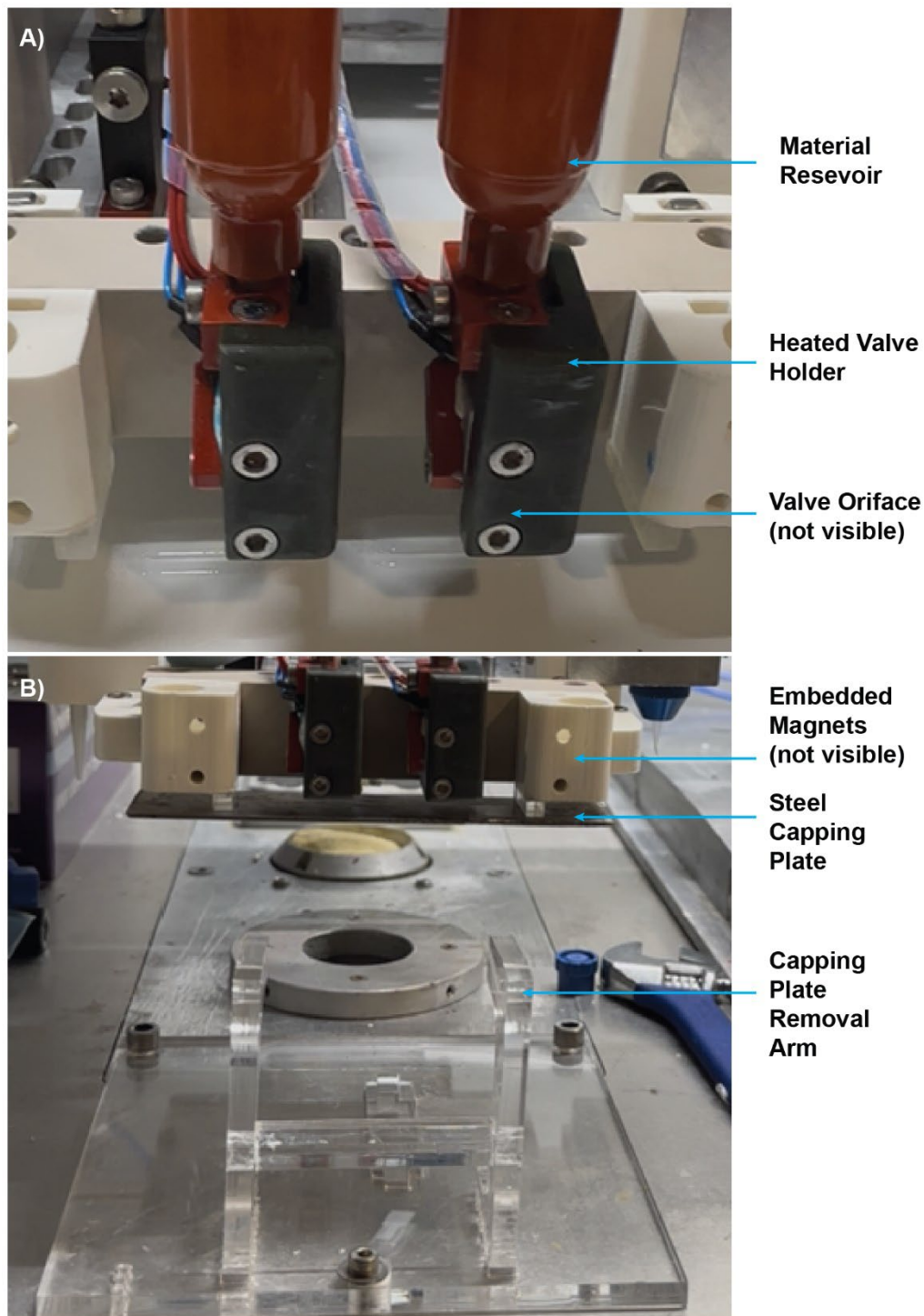


Figure 5.3. dRIP printhead and automatic UV shielding mechanism (A) A photo of the DVIP printhead with the UV shield removed, in the ready for printing state. (B) A photo of the DVIP printhead with the UV shield attached, positioned above laser cut arms used for the automatic capping process.

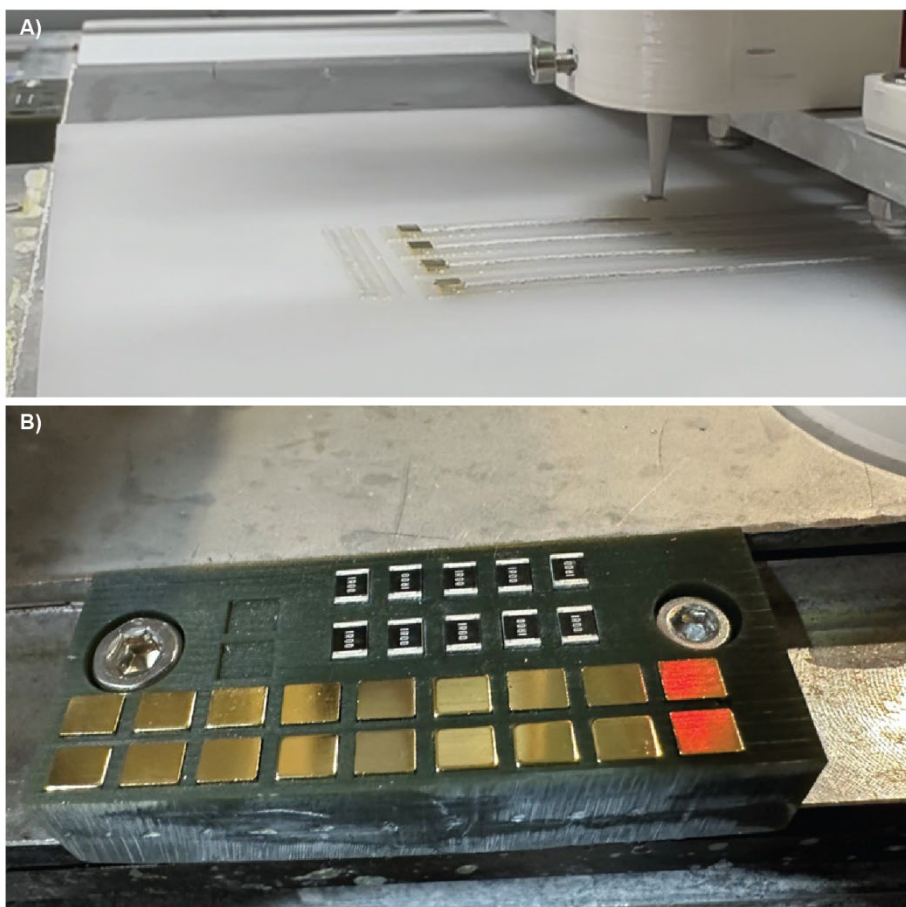


Figure 5.4. Robotic pick and place of electrical components and fixture (A) A photo of the vacuum pick and place process as a resistor is placed onto a stretchable electronic device. (B) A photo of the 3D printed fixture used to house and align the rigid components used in pick and place.

5.2.4 High Speed Imaging

High speed imaging was done using a Photron Fastcam Mini AX 200 fitted with a Proximity Infinitube FM-200 and 55mm/0.83x lens. The frame rate was 4000 fps, and illumination was done with a custom array of white LEDs.

5.2.5 Mechanical Testing

Mechanical testing was carried out on an Instron 68TM-10 frame equipped with a 1 kN load cell. Samples were tested at a strain rate of 60 mm/min.

5.2.6 Cyclic Electrical Testing

An Ender 3 3D printer was modified by removing the printhead and replacing it with a custom 3D printed electrical clamp system (**Fig. 5.5**). The clamps were fitted with a gold plated spring loaded pogo pin soldered to a braided wire. The wires were attached to a Hioki RM 3544-01 Resistance Meter with a 4-point probe attachment. The resistance was gathered by serial connection to a computer. The cyclic testing was performed by executing G-code on the modified Ender at a translational rate of 30 mm/s, with a strain of 25% followed by a return to 0% strain. The testing included 150 ms dwells at each strain maximum and minimum. The electrical resistance as a function of strain was captured using the same system at a strain rate of 1 mm/s.

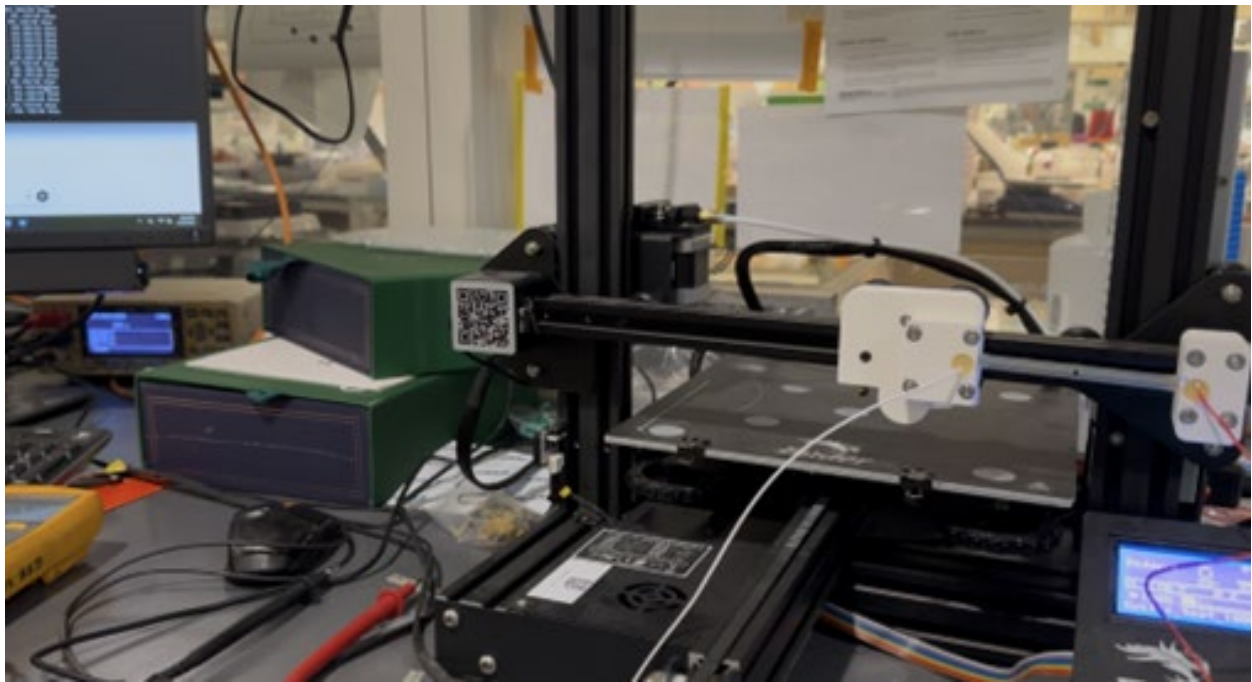


Figure 5.5. Cyclic Electrical Testing Setup A photo of the mechanical testing device used for cyclic electrical performance measurement.

5.2.7 Capacitance Testing

The measure capacitance as a function of time was captured with a GwIntek LCR-6020 device at the medium capture rate with averaging set to 4, with a frequency of 1 kHz and a voltage level of 1 V.

5.3 RESULTS AND DISCUSSION

5.3.1 Droplet-based viscoelastic ink printing (DVIP)

We built a customized, scalable DVIP system that employs electropneumatic microvalves housed in temperature-controlled ink reservoirs mounted to a 3-axis robotic gantry (**Fig. 5.1A**). In this initial embodiment, the DVIP printhead contains two microvalve-regulated ink reservoirs—each of which houses a different viscoelastic ink. Higher throughput can be achieved simply by adding additional microvalve/ink reservoirs to the printhead, akin to inkjet printing. During DVIP, elongated droplets form when each current-controlled microvalve is periodically opened to eject the pressurized fluid (ink) through a fine orifice (**Fig. 5.1B**). To enable DVIP, the ideal inks should exhibit viscoelasticity, with strong shear-thinning behavior and rapid yield stress recovery, as well as thermal stability and fast post-deposition curing. This combination of properties enables the precise deposition of nearly hemispherical, non-spreading droplets, allowing printed layer thicknesses of up to 0.5 mm in a single pass. To meet these criteria, we created UV-curable elastomeric inks using secondary thiol-ene chemistry with custom allyl-functional urethane oligomers and precisely tuned loading levels of fumed silica rheological modifiers (**Fig. 5.1C**).

To minimize the apparent viscosity of the oligomer blend, thereby establishing a reduced baseline for the high-shear apparent viscosity, we selected and synthesized oligomers with the lowest achievable molecular weights ($M_w < 650$). Additionally, we preferentially incorporated building blocks containing flexible ether linkages in the backbone. Achieving a resilient yet tough

elastomer—essential for stretchable electronics demanding high-cycle dynamic mechanical performance—requires three key elements: 1) sufficient molecular mobility within the polymer network 2) reversible interactions to dissipate deformation energy through dynamic bond breakage and reformation, and 3) covalent cross-links to ensure the polymer returns to its original geometry post-deformation [179-181]. To promote effective molecular mobility within the polymer network, we utilized thiol-ene chemistry due to its excellent compatibility with UV curing processes and its ability to efficiently convert low molecular weight oligomers into high molecular weight polymer chains with relatively uniform molecular weight distribution and network structure [182]. To incorporate dynamic bonds, we synthesized custom allyl-functionalized urethane oligomers, each containing two urethane groups per molecule, thereby introducing multiple hydrogen bonding sites into the polymer structure. Eugenol, a bio-derived and low-toxicity molecule with allyl functionality, was selected as an oligomer building block because its benzene ring enables additional reversible interactions through π - π stacking [183]. To incorporate covalent cross-linking, we synthesized a tetrafunctional allyl urethane oligomer by reacting trimethylolpropane diallyl ether with diisocyanates, creating molecules with four reactive functional groups composed of two difunctional segments separated by flexible diisocyanate spacers. This design ensures optimal spacing between cross-linked chains, enhancing the overall network mobility and dynamic mechanical performance [184]. Secondary thiol oligomers containing ether functionalities in their backbone were selected as the thiol-based curative. The secondary thiol groups exhibit reduced odor and moderated reactivity, enabling inks with extended high-temperature pot life and rapid UV curing (**Fig. 5.6 A-B**) [185].

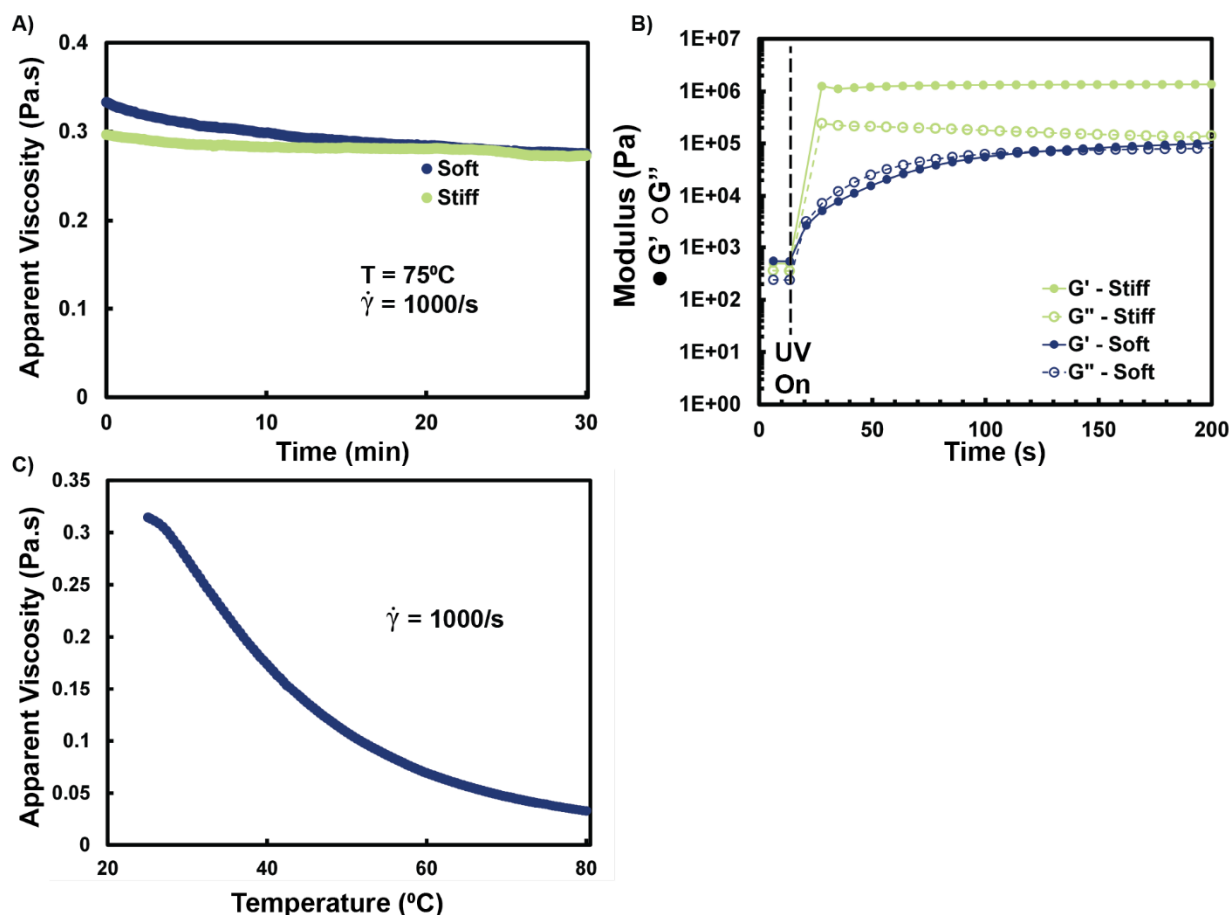


Figure 5.6. Thermal stability and UV curing of thiolene inks (A) A plot of apparent viscosity as a function of time of the optimized soft and stiff DVIP inks measured at a temperature of 75°C and a shear rate of $1000/\text{s}$ —showing the high temperature rheological stability of the inks. (B) A semi-log plot showing the storage (G') and loss (G'') moduli of the stiff and soft inks as a function of time before and during UV exposure. UV source was an Omnicure Series 2000 (Excelitas Technologies) delivered to the UV attachment of the TA HR-20 rheometer via waveguide with no filter. (C) A plot of apparent viscosity as a function of temperature ($^{\circ}\text{C}$) of the soft base resin without rheological modifiers at a shear rate of $1000/\text{s}$

To optimize the oligomeric (base formulation) ink rheology, we used fumed silica as a rheological modifier. We directly imaged the effects of filler loading on droplet shape and spreading upon impact on the underlying substrate using a high-speed camera (**Fig. 5.1D**). In the absence of fumed silica (0 wt% filler), the droplets immediately spread upon impact due to their low apparent viscosity (45 mPa·s and 310 mPa·s at 70°C and 25°C respectively – **Fig. 5.6C**). With increasing filler loading, the impinging droplets exhibit a conical shape upon impact at $t = 0$

s, which relaxes over short times ($t = 60$ s) driving the coalescence of adjacent droplets. The extent of droplet coalescence varies considerably over a narrow range of filler additions. At 8 wt% filler loading, two adjacent droplets, which are easily identifiable upon impact at $t = 0$ s, undergo sufficient wetting and spreading to drive their complete coalescence into a larger (single) droplet at $t = 60$ s. At 9 wt% and 10 wt% filler loading, the printed droplets retain their conical shapes over this period, while exhibiting increasingly less wetting, spreading, and coalescence. We find that a filler loading of 8.5 wt% fumed silica provides the optimal balance between droplet shape retention and coalescence. Next, we created a stiff elastomeric ink using a different set of oligomers and matched the ink rheology by adjusting its filler loading to 6.1 wt % fumed silica so that its viscoelastic properties matched that of the optimized soft elastomeric ink (**Fig. 5.1E-F**). Both filled inks possessed a low-shear apparent viscosity above 60,000 mPa·s at room temperature, which decreased significantly to a value of less than 400 mPa·s at higher shear rates and elevated temperatures (**Fig. 5.1E**) allowing efficient droplet formation and rapid shape recovery during DVIP. Their characteristic shear yield stress (t_y) values of 41 Pa and storage moduli (G') values of 1050 Pa are nearly identical (**Fig. 5.1F**), which allows the printed and coalesced droplets to retain a 3D shape.

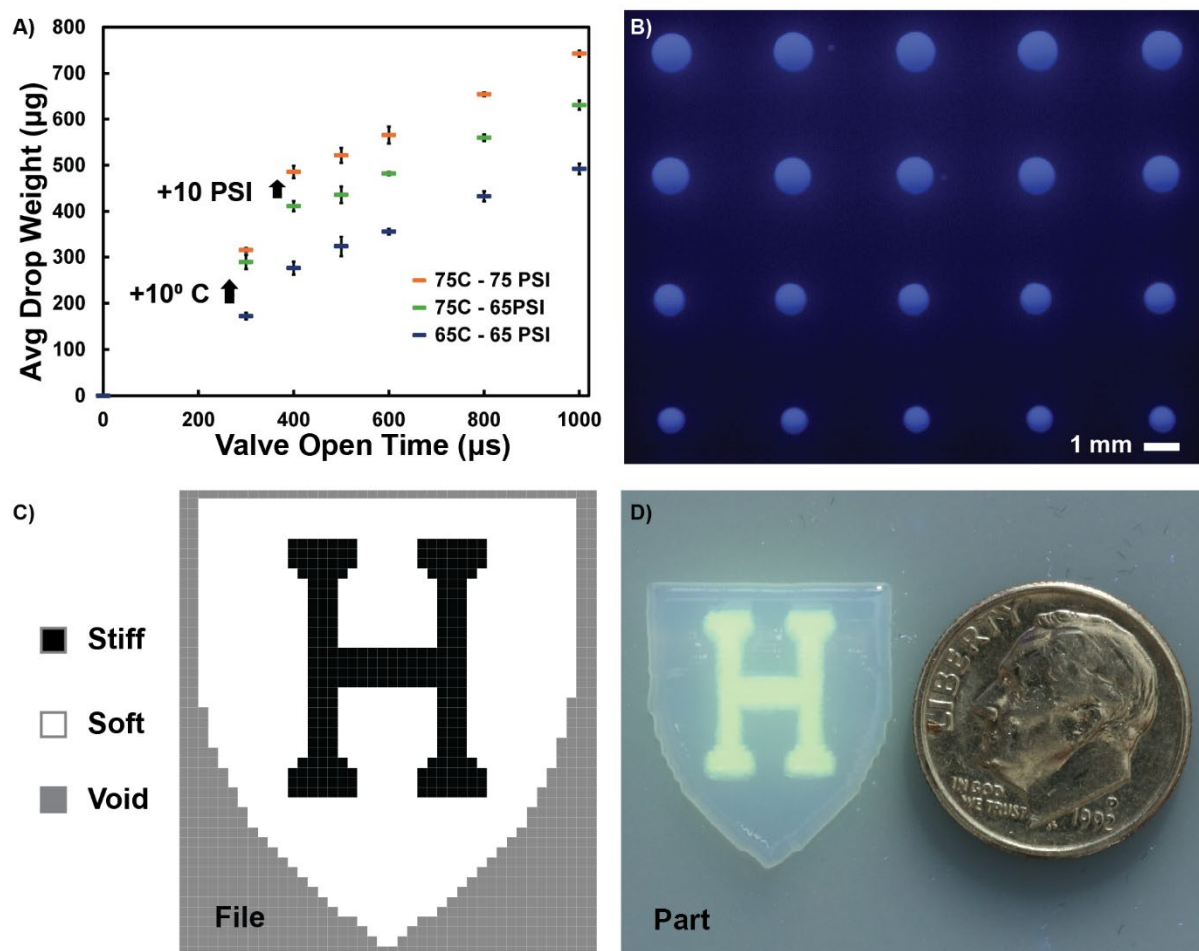


Figure 5.7. Thermal stability and UV curing of thiolene inks (A) A plot of apparent viscosity as a function of time of the optimized soft and stiff DVIP inks measured at a temperature of 75°C and a shear rate of 1000/s -- showing the high temperature rheological stability of the inks. (B) A semi-log plot showing the storage (G') and loss (G'') moduli of the stiff and soft inks as a function of time before and during UV exposure. UV source was an Omnicure Series 2000 (Excelitas Technologies) delivered to the UV attachment of the TA HR-20 rheometer via waveguide with no filter. (C) A plot of apparent viscosity as a function of temperature (°C) of the soft base resin without rheological modifiers at a shear rate of 1000/s

Using the optimized soft elastomeric ink, we then characterized the effects of microvalve temperature, pressure, and open time on average droplet weight and size based on 500 consecutive droplet ejections. First, we find that a minimum microvalve open time of 300 μ s is required for reliable ejection—above which the droplet weight increases linearly from 172 μ g to 492 μ g with open time (**Fig. 5.7A**). By increasing valve temperature and pressure at a given open time, one

can increase the drop weight by roughly 58% across the defined range tested without altering the printed drop shape. Because open time can be independently controlled for each microvalve, it is a powerful tuning parameter that can be used to alter the characteristic drop size “on-the-fly” thereby modulating local voxel sizes within each print, or to calibrate drop sizes within a multi-valve array (**Fig. 5.7B**). To demonstrate this capability, we printed an array of droplets of varying sizes from 650 μm to 1050 μm through a 150 μm orifice, where each row in the array corresponds to a different open time ranging in value from 300 μs (top row, **Fig. 5.7B**) to 1800 μs (bottom row, **Fig. 5.7B**), respectively. We assessed the accuracy and repeatability of droplet formation and positioning by printing 150 droplets using a 300 μm orifice onto a 15 $\times$ 10 grid with uniform target spacing in both the X (scan) and Y (feed) directions at a scan rate of 50 mm/s (**Fig. 5.8**). Microscopy coupled with image analysis revealed that the average droplet diameter is 1070 ± 34 μm . For droplets nominally printed with a center-to-center spacing of 2400 μm , the measured values achieved are 2479 ± 21 μm and 2470 ± 27 μm in the scan and feed directions, respectively.

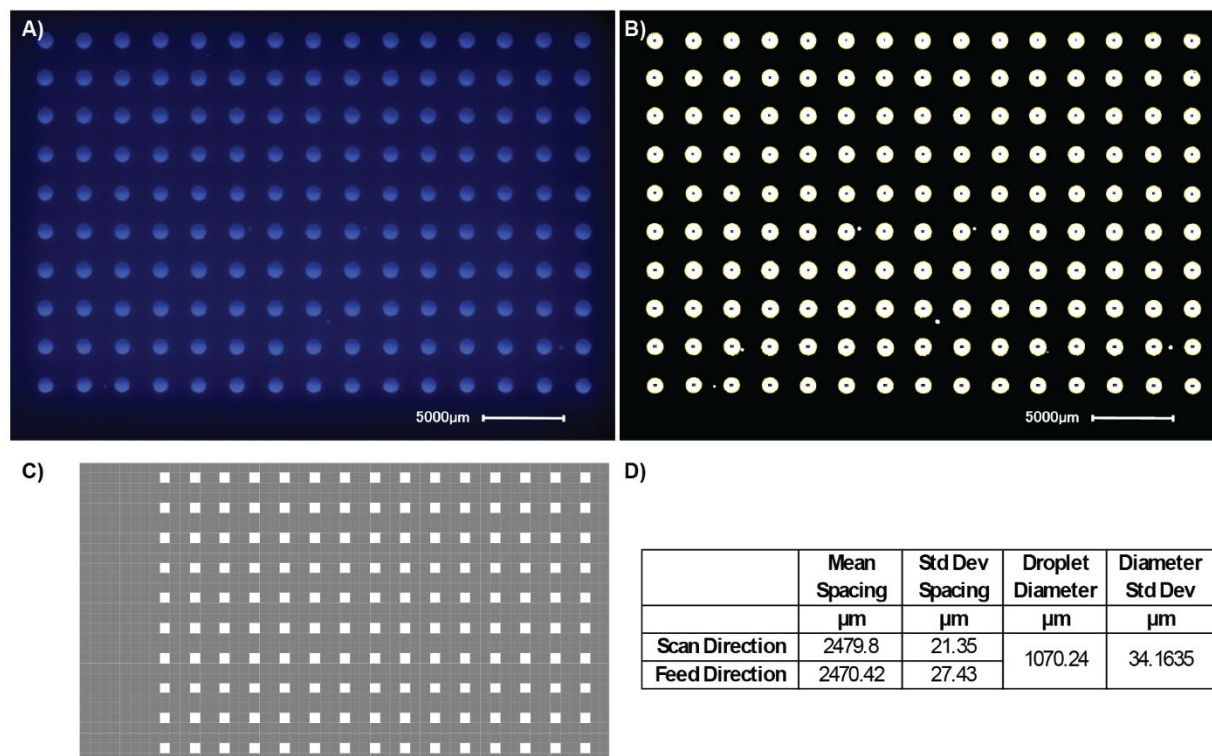


Figure 5.8. Thermal stability and UV curing of thiolene inks (A) A plot of apparent viscosity as a function of time of the optimized soft and stiff DVIP inks measured at a temperature of 75°C and a shear rate of 1000/s -- showing the high temperature rheological stability of the inks. (B) A semi-log plot showing the storage (G') and loss (G'') moduli of the stiff and soft inks as a function of time before and during UV exposure. UV source was an Omnicure Series 2000 (Excelitas Technologies) delivered to the UV attachment of the TA HR-20 rheometer via waveguide with no filter. (C) A plot of apparent viscosity as a function of temperature (°C) of the soft base resin without rheological modifiers at a shear rate of 1000/s

A primary advantage of DVIP is its inherent scalability via microvalve array parallelization, where droplet deposition rates scale linearly with the number of microvalves used. While our current demonstration is based on only two microvalves and corresponding ink reservoirs that operate simultaneously, we designed this DVIP system for future scalability. Specifically, the printing process is performed in raster mode with droplet placement aligned to a square grid, ensuring compatibility with both multi-valve arrays (spaced in the feed dimension) printing different parts of the image in parallel, and multiple ink channels (spaced in the scan dimension) printing different materials simultaneously within the same pass. By aligning valve spacing to pixel dimensions, complex multi-material geometries can be printed in parallel via

raster-based image processing at high volumetric deposition rates with minimal added system complexity. To demonstrate this architecture, we developed an open-source electronic control system that interprets bitmap instruction files (**Fig. 5.2**), synchronizes with robotic position signals, and triggers microvalve firing sequences for co-printing of stiff and soft elastomer droplets along a given scan path. The printhead then advances by one pixel length in the feed direction to print the next line. **Figures 5.7C-D** show a representative bitmap instruction file composed of a stiff elastomeric H (black) surrounded by a soft elastomeric shield (white) and a photo of the resulting multi-material print, respectively. Droplet sizes are carefully tuned by varying the print temperature, pressure, and open time to enable consistent co-printing of both inks onto a 400 μm grid. Since the DVIP system architecture adheres to array-compatible constraints, it can be readily scaled to N-nozzle configurations for parallel multi-material printing using the same control logic.

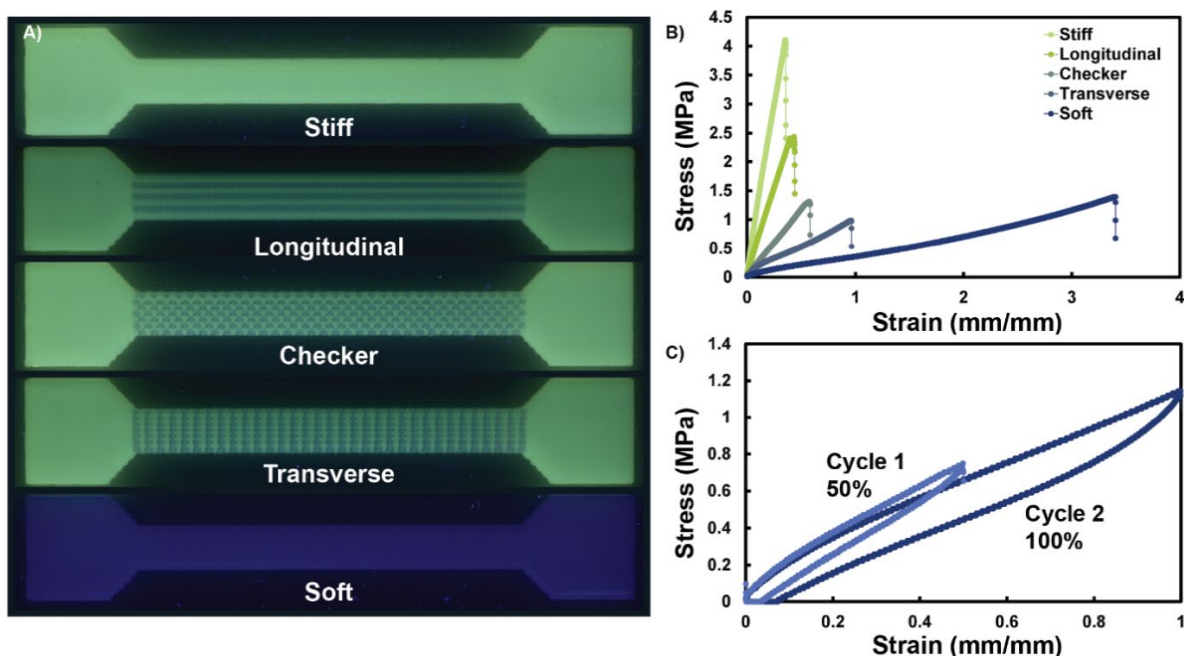


Figure 5.9. Programmable mechanics via DVIP. (A) Image of printed tensile bars (three layers in height) taken under UV light (long wavelength - 385 nm), which highlights localized compositional differences encoded by co-printing stiff-soft inks in different patterns. [Note: Both purely stiff and soft elastomeric tensile bars are printed as controls.] (B) The measured stress-strain response during uniaxial tensile testing of each printed tensile bar, which is measured at strain rate of 60 mm/s. (C) The measured stress-strain response of a fully soft tensile bar elongated to 50% strain, then 100% strain with a return to zero after each stretch.

5.3.2 Architected elastomers with zonal mechanics via DVIP

Multi-material printing of viscoelastic elastomeric inks affords significant design flexibility with minimal impact on DVIP throughput. As a simple demonstration, we co-printed architected elastomeric substrates in the form of three-layer tensile testing specimens, whose composition and geometry are defined by the input bitmap files. Control samples composed solely of soft or stiff elastomer are printed alongside three architected composites of varying patterns, namely longitudinal, checker, and transverse (**Fig. 5.9A**). A UV-fluorescent tracer added to the stiff ink allows one to directly visualize the voxelated soft and stiff regions under 385 nm UV illumination. Natural light photos of the same samples before and after mechanical testing are provided in **Figure 5.10B**. By varying their local composition and architecture, elastomeric substrates with tunable Young's modulus values ranging from ~700 kPa to >18 MPa are generated via DVIP (**Fig. 5.9B**). The soft elastomer exhibits an elongation at break exceeding 300%, which to our knowledge is the highest reported value for any bulk UV curable elastomer used in drop-on-demand inkjet printing. This exquisite combination of high extensibility and printability marks a significant advance for digitally printed stretchable materials. It is also possible to print even higher modulus and strength materials (modulus up to 600 MPa with strength up to 18 MPa) with an elongation at break exceeding 45% by further adjusting the resin composition (**Fig 5.11**). The architected substrates exhibit mechanical properties that lie between the pure controls – demonstrating that discrete material combinations can be spatially programmed to achieve a continuum of mechanical responses. The soft elastomer readily sustains strains up to 100% and returns to its original shape with minimal hysteresis, enabling the soft regions in our programmable composites to absorb applied strain with minimal energy loss for precise, repeatable deformation and recovery (**Fig. 5.9C**).

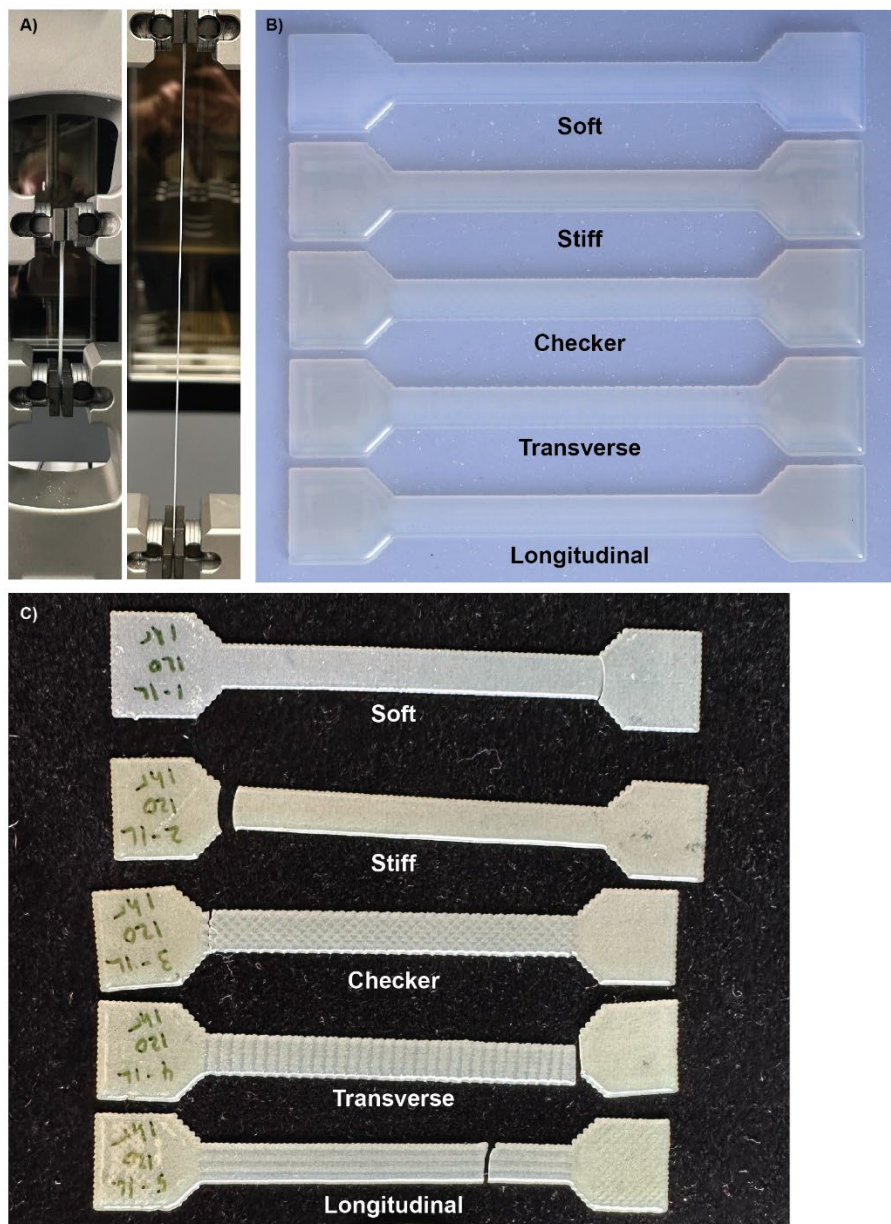


Figure 5.10. Mechanical properties of architected composites (A) A photo of a fully soft tensile specimen during tensile testing at 0% and 300% strain—highlighting the stretchability of the soft elastomer. (B) A photo of tensile samples under white light. (C) A photo of tensile samples after tensile test to break—highlighting the minimal permanent deformation of samples.

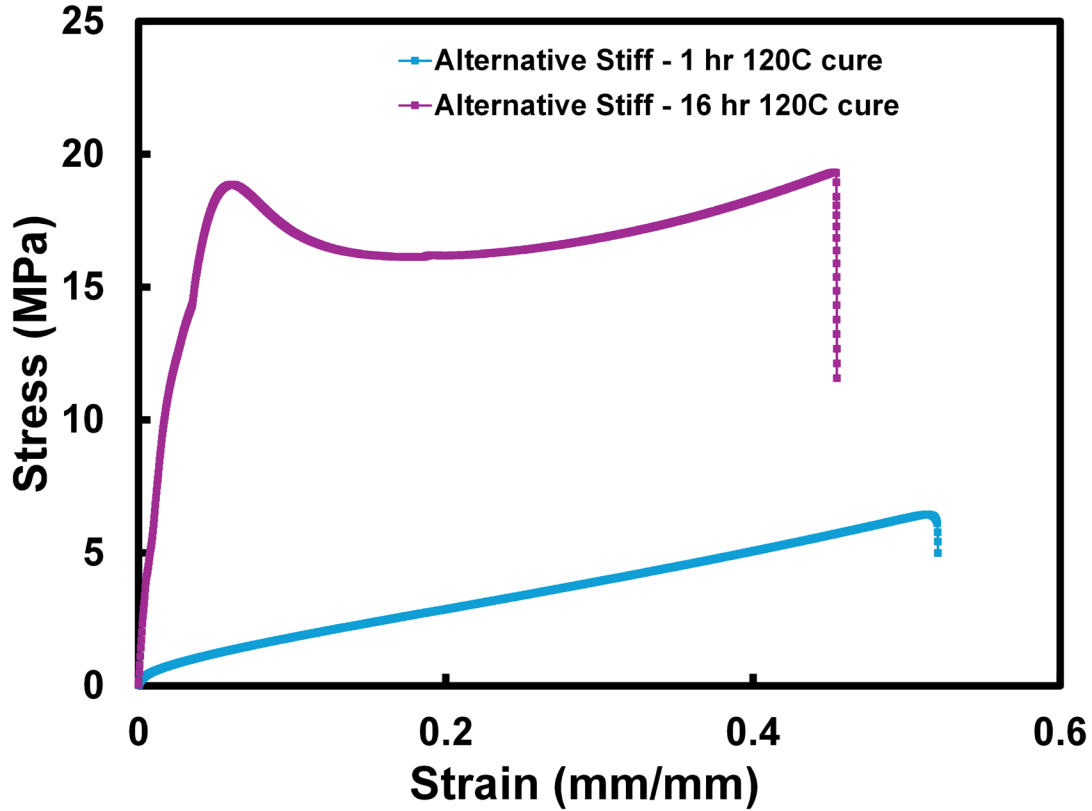


Figure 5.11. A plot of the tensile stress as a function of strain of the alternative stiff ink formulation after curing for 1 hr and 16 hrs at 120 °C. Mechanical testing was done according to procedure presented in the materials and methods section.

5.3.3 Stretchable Electronics via DVIP

We designed stretchable electronic test structures for uniaxial mechanical testing to characterize how zonally architected substrates affect dynamic electromechanical performance of stretchable electronic devices. The devices contain rigid surface-mount components interconnected with stretchable conductive ink within a printed elastomeric matrix with zonally architected mechanics. Eutectic gallium-indium (eGaIn) is an attractive candidate for a printable stretchable conductive ink due to its ability to undergo large strains without electrical hysteresis. However, eGaIn possesses a high surface tension and low viscosity making it difficult to digitally print [57]. Although liquid metal emulsions have emerged with better printability [52, 56], these aqueous-based inks often contain bubbles (defects) that form via gas evolution after high shear mixing. To

overcome these limitations, we created an anhydrous eGaIn emulsion using propylene glycol propyl ether as an evaporative solvent together with hydroxypropyl cellulose and carbon black, which serve as emulsifier and viscosifier, respectively (**Fig. 5.12A**). The resulting ink exhibits the desired shear thinning and viscoelastic behavior for DVIP (**Fig. 5.12B**). This ink is stable and printable via DVIP at room temperature for several weeks. Akin to other liquid metal emulsions, our ink requires mechanical activation to attain an average electrical conductivity of 2.69×10^5 S/m (**Fig. 5.13 A-C**). Mechanical activation is achieved either by compressing the printed elastomer top layer or by stretching to modest strains of 20-40% (**Fig. 5.13C**). To demonstrate the utility of zonally architected substrates, we fabricated two stretchable electronic devices—one with zonal strain relief surrounding each embedded component and the other without relief around the $1 \text{ } \Omega$ resistor. **Figure 5.12 C-D** shows a schematic and corresponding image of the devices under long wave 385 nm UV light. While the fluorescent imaging shows the zonal reinforcement, the structure appears nearly homogeneous under natural light (**Fig. 5.14A**). Rigid surface mount components were placed into digitally defined cavities using a robotically integrated vacuum pick-and-place tool (mounted on the printhead) to pick components from a 3D printed component fixture (mounted to the build surface) (**Fig. 5.4**), using the methods previously described [171]. The surface-mount contact pads at both ends of the device were encapsulated, leaving small exposed portions on top. This design creates robust electrical contacts that seal the liquid metal inside the composite elastomeric structure while providing an exposed surface for external interfacing. The anhydrous eGaIn emulsion was deposited in a separate step using a third microvalve mounted on the same z-axis of the robotic gantry, prior to component placement. In most cases, the conductive ink is already activated during the process of removal from the silicone build surface. Images of isolated traces printed with the anhydrous eGaIn emulsion are shown in **Figure 5.13A**.

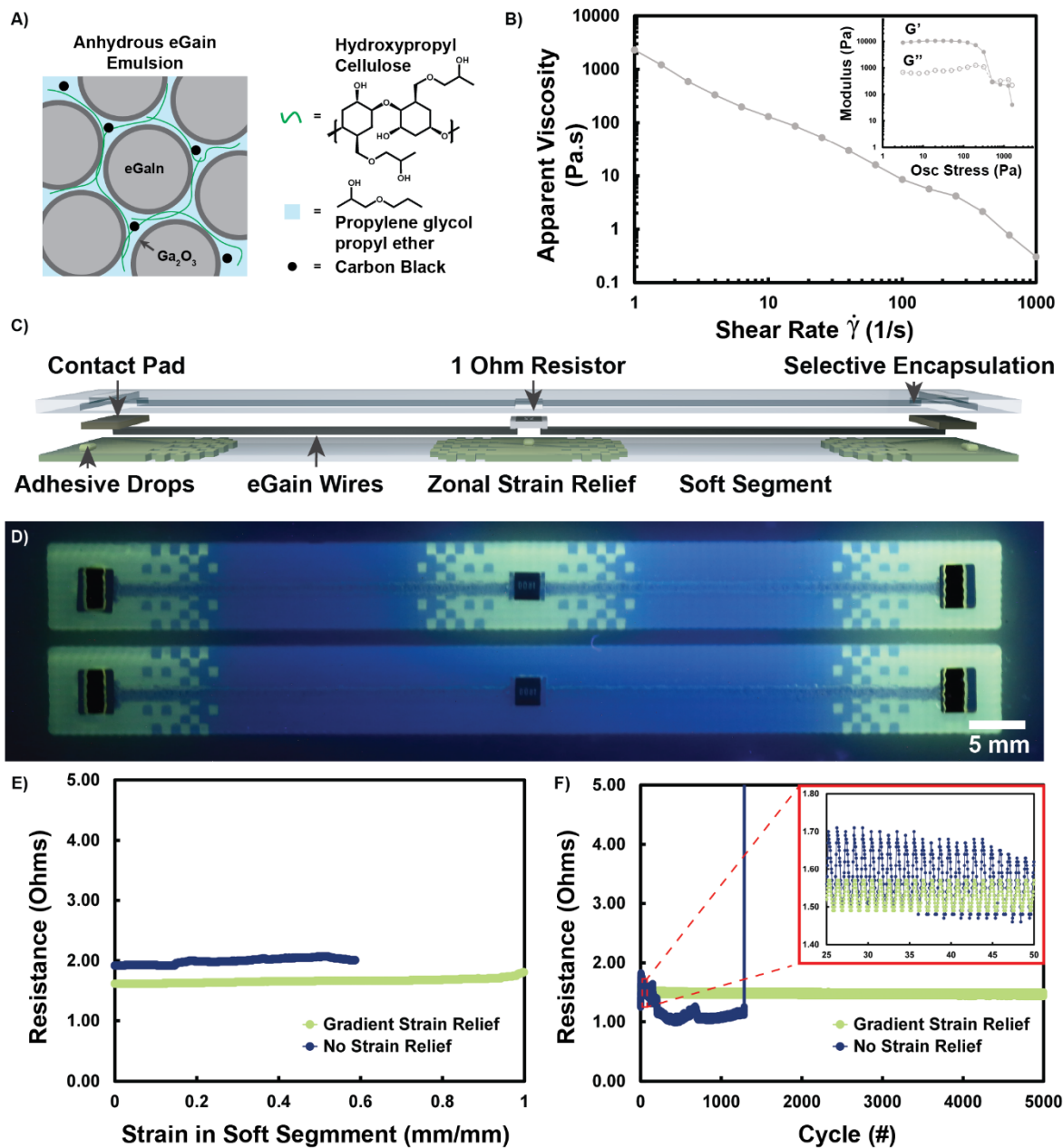


Figure 5.12. Stretchable electronics via DVIP and their dynamic electrical performance (A) A schematic showing the core components of the anhydrous liquid metal emulsion ink (B) A log-log plot of the apparent viscosity as a function of shear rate of the anhydrous liquid metal emulsion measured at 25 °C showing its highly shear thinning behavior (B-inset) A log-log plot of storage (G') and loss (G'') moduli as a function of shear stress (τ) of the anhydrous liquid metal emulsion measured at 25 °C (C) An illustrative exploded view schematic of the multi-layer stretchable electronic device and its embedded components (D) A photo under long-wave (385 nm) UV light of the strain relieved device (top) and non-strain relieved device (bottom). (E) A plot of the resistance (Ω) as a function of strain in the soft segment of the stretchable electronic device, with and without strain relief, as it is elongated at a strain rate of 1 mm/s to a soft segment strain of 1. (F) A plot of resistance (Ω) as a function of stretch cycle number (#) of the stretchable electronic device as it is repeatedly elongated to 25% overall strain at a strain rate of 30 mm/s. (F-inset) A zoomed in view of cycles 25-50 of the same plot.

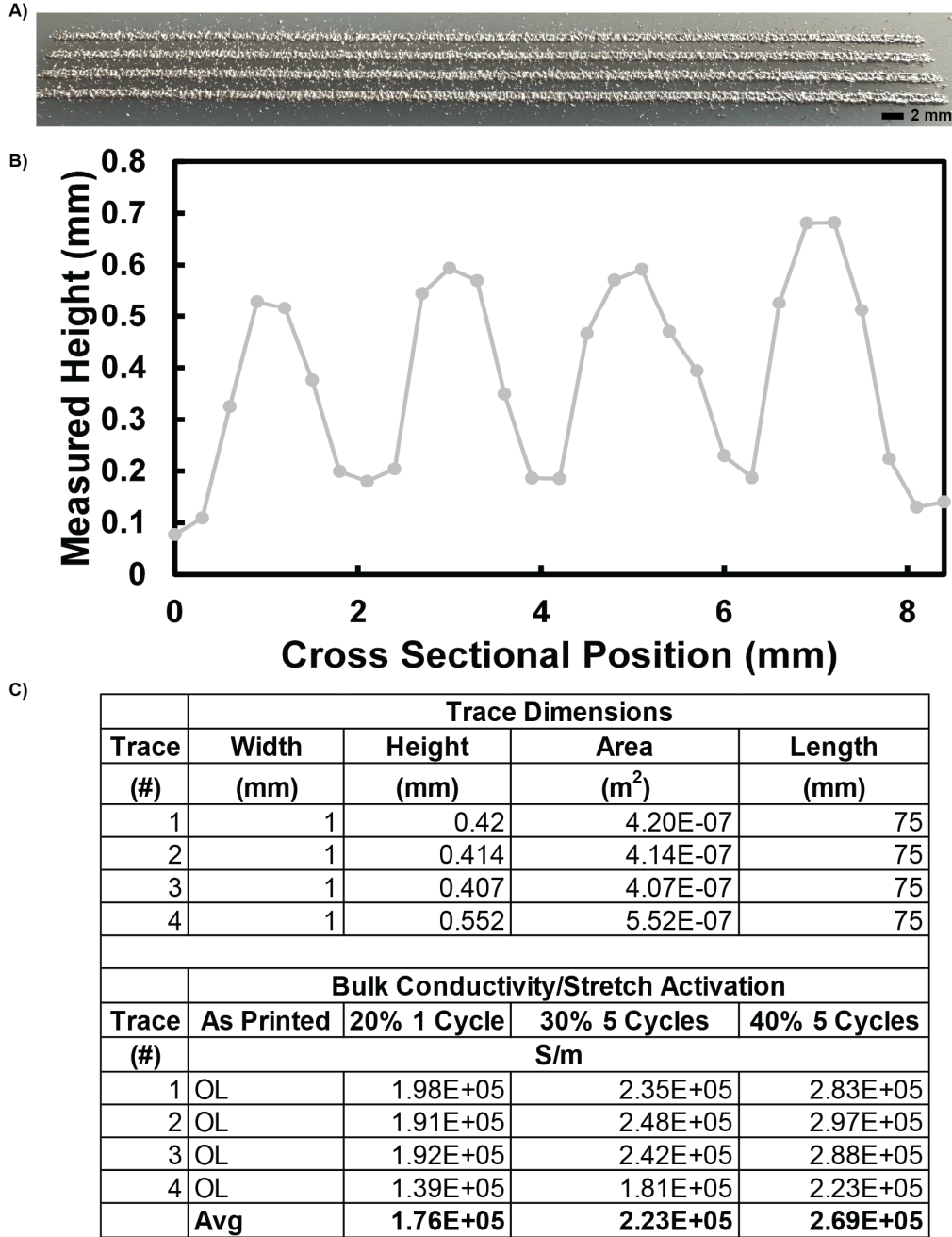


Figure 5.13. Anhydrous eGaIn Traces via DVIP, and their electrical conductivity as a result of various activation conditions (A) A photo of 4 traces of anhydrous eGaIn emulsion deposited via DVIP. Each trace consists of 2 directly overlapping passes with the following settings: Scan speed 15 mm/s, droplet spacing 300 μm , Ink reservoir pressure = 55 PSI, $T = 23^\circ\text{C}$, Open time = 300 μs . A 150 μm opening microvalve was used. (B) A plot of measured height (mm) as a function of the cross-sectional position (mm) across all 4 traces, collected with a laser line scanner (Keyence LJ-V7300). The plot shows the approximate cross-sectional geometry. (C) A table showing the measured dimensions of each trace, and the measured conductivity of each trace following 4 different activation conditions. Condition 1: No mechanical activation. Condition 2: 1 cycle of stretching to 20% strain. Condition 3: 5 repeated cycles of stretching to 30% strain. Condition 4: 5 repeated cycles of stretching to 40% strain.

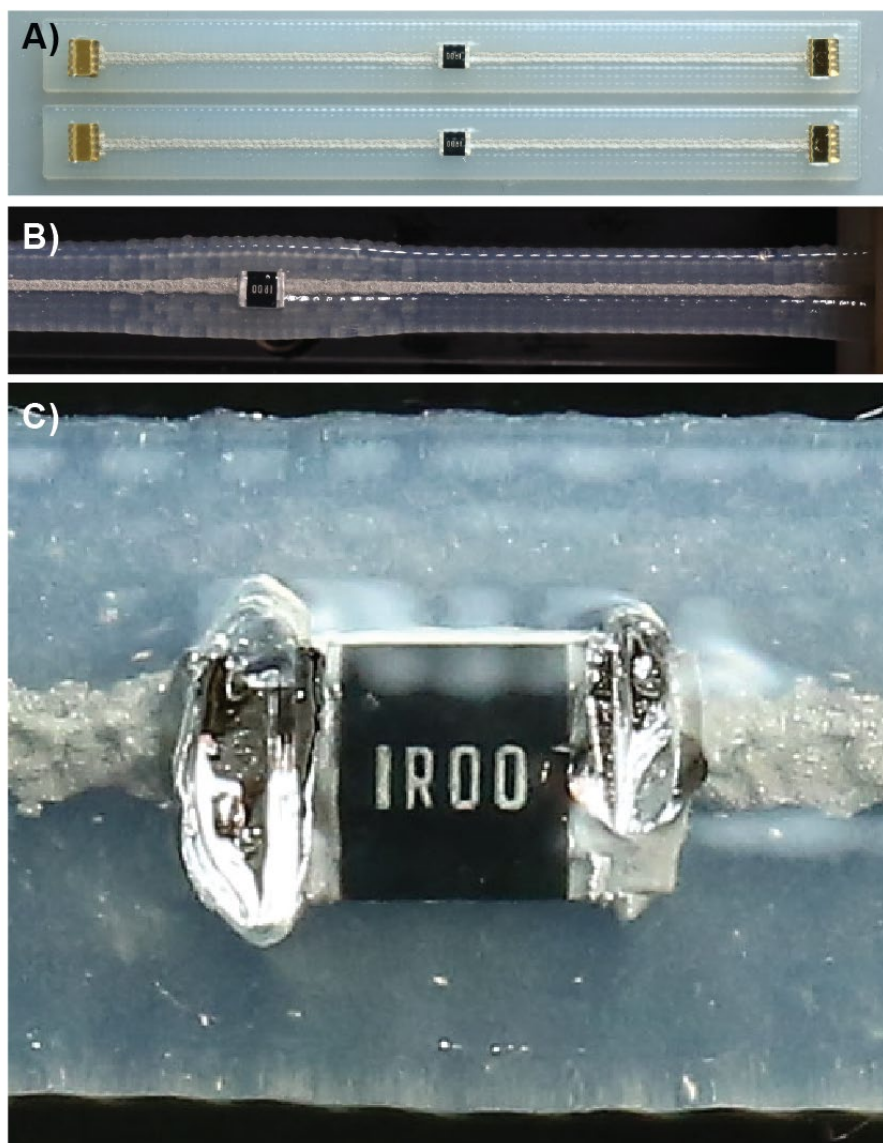


Figure 5.14. Stretchable electronic devices with and without zonal strain relief and their behavior under strain (A) A photo of the zonally strain relieved (top) and non-strain-relieved device (bottom) under natural light, demonstrating the homogeneity of the multi-material droplet integration. (B) A photo of the strain relieved device during cyclic stretch testing, highlighting the capability of the zonal reinforcement to isolate strain to the stretch zone. (C) A photo of the failure region of the non-strain relieved device. The device mechanically fails at the interface of the rigid component and the soft elastomer.

After fabrication and thermal curing, the devices were subjected to 5,000 cycles of 25% overall tensile strain and a single cycle of 100% soft segment strain to evaluate durability. Devices with zonal strain relief outperformed those without in all tests. **Figure 5.14B** shows a strain-relieved device during stretch, where deformation localizes in the soft segment while the region

around rigid components remain largely undeformed. **Figure 5.14C** illustrates failure in the non-relieved device, showing mechanical degradation that initiates at the rigid–soft interface, and eventually propagates across the device. **Figure 5.12E** shows the high-strain performance: the strain-relieved device tolerated 100% soft-segment strain with $<0.25\ \Omega$ resistance change and endured 5,000 cycles at 25% strain with negligible baseline drift and a repeatable resistance amplitude of $0.1\ \Omega$ (**Fig. 5.12F**). In contrast, the non-relieved device failed mechanically at 60% strain and exhibited significant drift after only 50 strain cycles, with full mechanical failure after 1,300 strain cycles. Thus, zonally architected strain reliefs led to a 100 fold increase in electromechanical fatigue life. In both tests, the failure of the device without zonal strain relief initiated at the interface between rigid resistor corners and the surrounding soft polymer, due to stress concentrations.

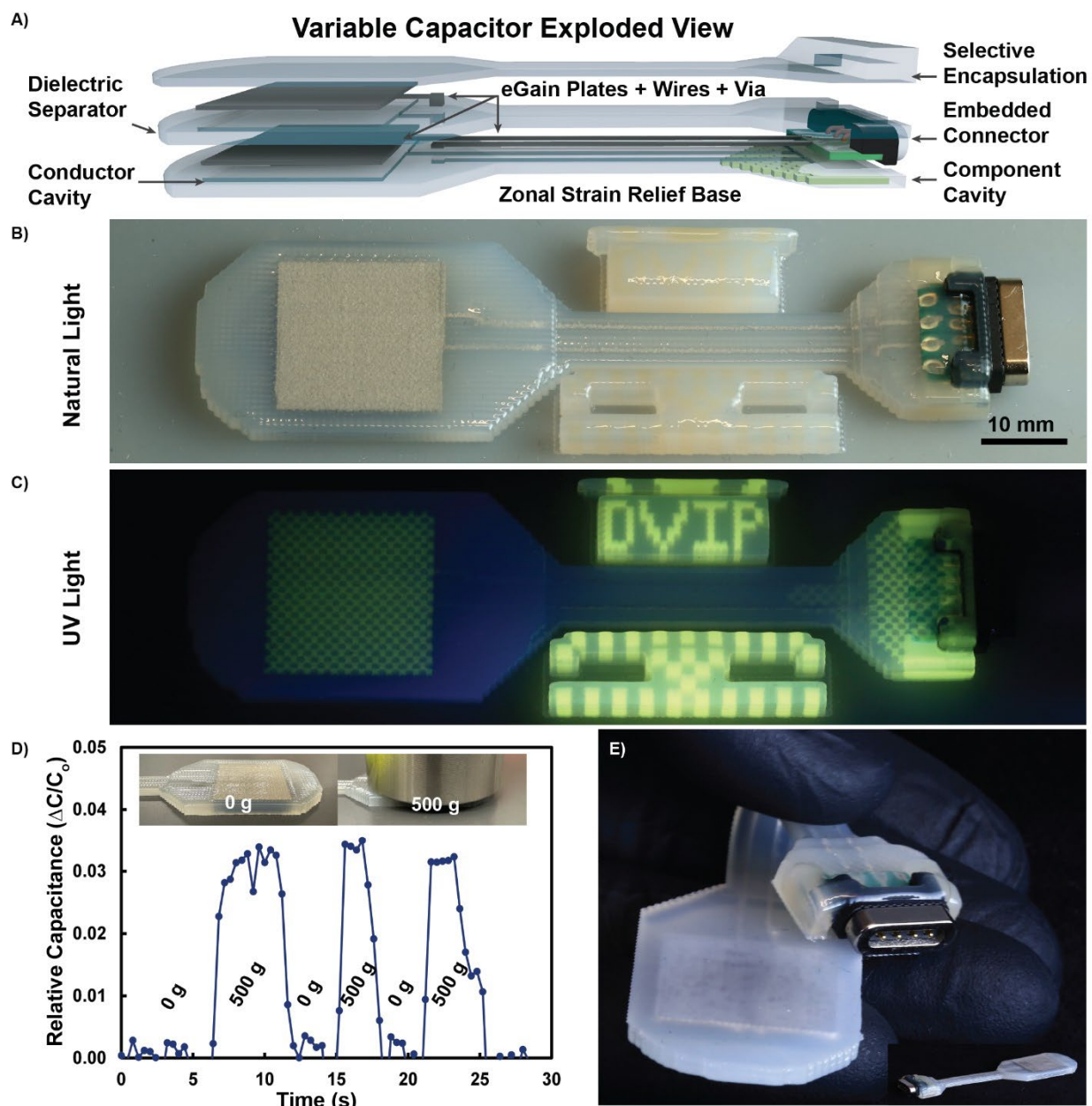


Figure 5.15. A variable capacitance device with multi-layer electronic routing via DVIP. (A) An illustrative exploded view schematic of a multi-layered variable capacitance sensor with partially encapsulated magnetic connector and 3D conductive features. (B) A photo of the completed device under white light, showing the encapsulated component and printed anhydrous eGaIn Emulsion. (C) A photo of the same device under long wave (385 nm) UV light showing the zonal strain reliefs and exemplary digital labeling. (D) A plot of the relative capacitance as a function of time of the device as a 500 g weight is placed on the sensor three times consecutively. (E) A photo of the device during deformation—highlighting the device’s mechanical flexibility and illustrating its potential for integration into soft, conformable systems.

As a final demonstrative use case of the DVIP process, we fabricated a variable capacitance sensor consisting of printed liquid metal plates separated by a printed dielectric layer in the z-direction, with electrical connections routed to a magnetic connector via vertically printed vias. The magnetic connector, over 4 mm thick, was selectively encapsulated using the DVIP system's capability to print thick 3D structures by stacking 12 consecutive layers, resulting in a total thickness of 5.5 mm. **Figure 5.15A** shows a schematic of the device architecture, highlighting the bottom section with predefined cavities for conductive ink and connector placement. After component placement, the liquid metal emulsion was deposited in 2 steps, interleaved with simultaneous deposition of stiff and soft elastomers. Since DVIP is a non-contact deposition process, we were able to print vertical vias greater than 1 mm in a single step by repeatedly depositing droplets into defined cavities bridging layers, from an elevated standoff distance. **Figures 5.15 B-C** show the completed device under white light and long-wave UV illumination, respectively. The images highlight the conductive liquid metal traces routed through vertical vias across the stretchable region to the parallel-plate capacitor, along with the yellow zonal strain relief that surrounds the magnetic connector and encapsulates the sensor pad. To test device function, we measured capacitance over time using an LCR analyzer as a 500 g weight was applied to the sensing surface in three consecutive cycles (**Fig. 5.15D**). **Figure 5.15E** highlights the device's mechanical flexibility, illustrating its potential for integration into soft, conformable systems.

5.4 CONCLUSION

In summary, we have demonstrated a new parallelizable method for multi-material, drop-on-demand printing of viscoelastic inks. Our DVIP method is capable of jetting elastomeric and conductive inks with low-shear viscosities that are three orders of magnitude greater than inkjet printing. An open-source electronic control system was created for multi-material raster image

processing, which is scalable to larger microvalve arrays. UV-curable elastomers were formulated with optimized rheological stability and dynamic stretching performance tailored for the DVIP process. These materials were co-printed to fabricate composite structures with tunable stiffness ranging from 700 kPa to 18 MPa. We also developed a DVIP-compatible, anhydrous eGaIn emulsion as a stretchable conductive ink. A 3-axis gantry system was configured to co-deposit three distinct materials and robotically place electrical components, enabling automated fabrication of functional stretchable electronic devices. Incorporating zonal strain relief around rigid components significantly improved mechanical durability, allowing devices to withstand thousands of stretch cycles with minimal mechanical or electrical degradation.

5.5 CONTRIBUTIONS

R.W.R. designed the droplet-based raster image processing (dRIP) controller, created the firmware, electrically integrated the dRIP controller into the robotic gantry controller, and produced the dRIP documentation. T.A.B. and J.A.L. prepared the manuscript. Michael Rosnach created the schematic illustration in Figure 5.1A. T.A.B. did all other work.

CHAPTER 6

CONCLUSIONS

My PhD research led to the development of printable soft electronic inks and novel digital manufacturing approaches for fabricating mechanically robust stretchable electronics, overcoming the fundamental challenge of integrating rigid electronic components within soft, compliant matrices. Through systematic advances from instrumented biosensors to scalable printing platforms, design principles, material formulations, and fabrication methods were established for stretchable electronics that exhibit reliable operation under cyclic deformation. The principal findings of my PhD research are summarized below.

1. Direct ink writing (DIW) electronics for instrumented heart-on-chip devices

Tissue-compatible cardiac microphysiological devices capable of detecting micronewton-level forces were created by direct ink writing of six custom-designed inks. Thermoplastic polyurethane (TPU)-based inks served as the core ink constituent for printing insulating elastomeric matrices and piezoresistive sensors with a gauge factor of 2.5. Through systematic optimization of TPU solids content and THF:DMF solvent ratios to control ink wetting and spreading behavior insulating layers as thin as 1.5 μm with sensor layers less than 10 μm thick could be co-printed by DIW. These layers were subsequently modified by printing 30 μm PDMS ridges, with an optimal spacing of 60 μm , to drive cardiac tissue alignment via their surface topology. These thin composite cantilevers exhibited sufficient compliance to undergo substantial deformation by monolayers of cardiac tissue during contraction, resulting in a measurable resistance change. This change was correlated to the tissue's contractile stress

through a mechanical model and validated by directly comparing both electrical and optical readouts.

2. Hybrid DIW of soft electronics

Building upon the intrinsically stretchable TPU ink design platform, we created conductive electrodes by introducing silver platelets at high volume fraction ($\phi \sim 0.36$), exhibiting remarkable conductivity up to 3×10^6 S/m. This shear-thinning viscoelastic ink is suitable for direct ink writing electrodes less than 200 μm wide. Comprehensive electromechanical characterization revealed that the conductive ink could withstand strains up to 240% before electrical failure, while reliably returning to their baseline resistance after being stretched to 30% strain.

By integrating robotic pick-and-place of rigid electronic components with direct writing of TPU and Ag-TPU inks, we created a hybrid printing platform for producing soft electronic devices. As exemplars, we printed flexible and stretchable LED arrays, body-worn strain sensors, and capacitive-based shoe insoles. Through systematic characterization of electrically interconnected components under uniaxial strain, we discovered that their strain at electrical failure could be increased by more than seven-fold (to 120%) via strategic incorporation of an adhesive layer around each electrical component. This adhesive layer locally increased the elastomer thickness in critical regions and enhanced component retention. These findings led us to hypothesize that devices of even greater robustness could be fabricated via zonally controlling the mechanical properties of the printed matrices.

3. Droplet based viscoelastic ink printing

To address the above challenge, we developed a droplet-based viscoelastic ink printing (DVIP) method capable of patterning multiple elastomeric inks with tunable mechanics via raster

image processing. DVIP employs heated, mechanically actuated microvalves with orifice diameters ranging from 100 to 300 μm , which eject pressurized viscoelastic fluids with viscosities exceeding 60,000 $\text{mPa}\cdot\text{s}$. DVIP therefore expands the range of printable ink viscosities by more than three orders of magnitude over conventional inkjet printing. We designed and implemented an open-source electronic control system capable of driving arrays of microvalves to deposit patterns defined by bitmap images. The process enables simultaneous deposition of two materials through sequences of linear raster moves, effectively allowing material deposition through arbitrary array sizes and thus unlocking the ability to decouple multi-material pattern complexity from print time. To create zonally architected stretchable electronics, several advances were achieved:

i) UV-Curable Thiolene DVIP Inks and Architected Mechanics

Both stiff and soft thiol-ene-based elastomeric inks were specifically formulated for DVIP. These inks exhibit rheological stability at 80°C for more than 30 min and cure rapidly upon exposure to UV light. These attributes ensure both reliable nozzle heating without clogging and immediate ink solidification after printing. Through systematic rheological tuning using fumed silica as a filler coupled with comprehensive droplet characterization using high-speed imaging, we identified that inks possessing a characteristic shear yield stress (τ_y) of approximately 40 Pa and a storage modulus (G') around 1000 Pa formed droplets with the optimal balance between coalescence and shape retention behavior. We printed geometric patterns with architected mechanics and demonstrated tunability across a wide range, where the elastic modulus of the pure control materials varied from 700 kPa with more than 300 percent elongation to over 18 MPa with 40 percent elongation. These zonally architected

substrates exhibited intermediate properties between the pure stiff and soft materials, validating our ability to precisely control mechanical behavior via geometric design.

ii) Stretchable conductive liquid metal emulsions

To overcome the inherent high-strain electromechanical hysteresis observed in all conductive composite inks, we created a printable liquid metal ink that is compatible with DVIP. To circumvent the characteristically high surface tension of eutectic gallium-indium (eGaIn) liquid metal that typically prevents reliable jetting, we developed an emulsification approach using a polymer-laden organic solvent. The resulting ink could be reliably jetted at room temperature and remained stable for periods exceeding three weeks under ambient conditions. The ink demonstrated excellent compatibility with thiol-ene elastomer substrates and exhibited an electrical conductivity of 2.69×10^5 S/m upon mechanical activation.

iii) Stretchable electronics via DVIP

Stretchable electronic devices with unprecedented mechanical durability were fabricated with precise zonal stiffness control via DVIP. This Drop-on-Demand process enables voxelated control over high and low stiffness thiol-ene regions within the printed electronic devices. Devices with and without zonally graded interfaces were created to explore their effect on protecting the interfaces between rigid components and soft electrodes, which are highly susceptible to stress concentration. Devices based on zonal strain relief exhibited dramatically improved dynamic electrical performance and mechanical robustness—withstanding 5000 consecutive cycles of 25% uniaxial strain while maintaining no baseline drift in resistance with a repeatable 0.1Ω amplitude of cyclic resistance change. In stark contrast, devices fabricated without zonal strain relief exhibited significant resistance drift after merely 50 strain cycles under the same conditions, i.e. a 100-fold decrease in electrical fatigue life. We further

demonstrated the versatility of this approach by creating multi-layer 3D stretchable electronics with vertical vias for interlayer interconnection, printed variable capacitance sensors, and successfully embedded PCB modules within stretchable devices.

In summary, my Ph.D. research has established printable viscoelastic inks and scalable platforms for multi-material 3D printing of intrinsically stretchable electronic devices with embedded rigid electrical components, protected through digital architecting of elastomer mechanics. In the future, this platform may be harnessed for printing the next generation of customizable human-machine interfaces.

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