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3D Printed Edible Hydrogel Electrodes

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Abstract

We report on a hand-held reactive printing device used to pattern highly conductive, edible hydrogel wires formed from gellan gum, gelatin, cross-linkers and a common salt (NaCl). The conductivity of the gels when printed (190 ± 20 mS/cm) closely matched the conductivity recorded for cast systems (200 ± 19 mS/cm). Printing was observed to reduce the elastic modulus and failure strains of hydrogels under compression, but printed gels retained sufficient integrity for application as flexible conductive lines. We demonstrate that hand-held printing can utilize to pattern soft conductor elements within a simple electronic circuit.

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3D Printed Edible Hydrogel Electrodes

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ABSTRACT

We report on a hand-held reactive printing device used to pattern highly conductive, edible hydrogel wires formed from gellan gum, gelatin, cross-linkers and a common salt (NaCl). The conductivity of the gels when printed (190 ± 20 mS/cm) closely matched the conductivity recorded for cast systems (200 ± 19 mS/cm). Printing was observed to reduce the elastic modulus and failure strains of hydrogels under compression, but printed gels retained sufficient integrity for application as flexible conductive lines. We demonstrate that hand-held printing can utilize to pattern soft conductor elements within a simple electronic circuit.

INTRODUCTION

Silicon based electronics are largely incompatible with living tissue, having no biodegradation pathways and a mismatch in mechanical compliance. Despite this, silicon based electronics are already in use in a wide variety of medical devices such as pacemakers[1] and cochlear ear implants[2]. These systems rely on encapsulating electronic circuits within soft and impermeable plastics, which provide a physical barrier between the electronics and the body. Because of their construction, the systems never fully integrate with their host tissue, and remain at risk of fibrosis and infection throughout the life of the implant, or until they are surgically removed[3]. Replacing traditional electronic materials with soft and bioresorbable alternatives provides the potential of a new generation of implantable and edible electronics that are ultimately biodegraded with no long-term health consequences. For example, bioelectronics offer a possible solution to pill retention as simple gastrointestinal (GI) monitoring devices can be constructed from bioresorbable materials [4- 8].

Hydrogels are hydrophilic polymer networks, able to absorb 99% (w/w) water[9]. Biopolymer-based hydrogels are a promising material for bioelectronics development as they are often biocompatible[10], 3D printable[11] and possess unique chemistries that can be tailored for specific medical applications[12]. Gelatin and gellan gum are two hydrogel-forming biopolymers commonly used as food additives to products such as yogurt, ice cream and jelly[9, 13]. These gels are generally soft and mechanically weak, but may be rendered tough like rubber using the ionic-covalent entanglement (ICE) approach[14, 15]. ICE gels are constructed through the enmeshing of independently cross-linked ionic and covalent networks, resulting in synergistic strengthening[16].

Herein, we describe a simple method of producing simple bioelectronics through the hand-held extrusion of ICE hydrogels. Our gels are formed from a combination of edible and bioresorbable materials, gellan gum, CaCl_2 , gelatin and the covalent cross-linker genipin with conduction imparted by the inclusion of the common bodily salt NaCl. The printing of the gel was achieved through the reactive printing of biopolymer and cross-linker components, using a

method recently published by our research group[16]. Facile, 3D printed, edible wires were produced, analyzed and used in simple demonstration circuits.

EXPERIMENT

Materials

The ICE gels were prepared using gelatin, (porcine, type A, Bloom number 300, molecular weight 87.5 kDa, Sigma Aldrich, USA, lot number: 119K0062) and gellan gum (low acyl, Gelzan-CM, CP Kelco, lot number: 1I1443A). 25% (w/v) genipin (Challenge Bioproducts, Taiwan) in 60% (v/v) ethanol (Ajax Finechem, Australia) and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Sigma Aldrich, Australia, lot number: MKBG9652V) solutions were used to crosslink the gelatin and gellan gum respectively.

Conducting ICE gels were prepared in salts solutions of NaCl (Sigma Aldrich, Australia, lot number: MKB9892V) dissolved in Milli-Q water (resistivity, 18.2 M Ω .cm).

Hydrogel preparation

A 0.5 % (w/v) solution of gellan gum (GG) was supplemented with 0.875 % (w/v) porcine gelatin (Sigma, SLBK6158V) and mixed at 70 °C. The gelatin cross-linking species genipin (98 %, Challenge Bioproducts Co.) was added at 0.22 % (w/v) (25 % w/w gelatin) and mixed for 3 min. Cast ICE gels were formed by the addition of CaCl_2 to the hot mixture to a final concentration of 50 mM, followed by immediately transferring the solution to prepared moulds.

Hand held extrusion printing

Hand-held printing of ICE gels was achieved using a recently published method[17]. Briefly, a syringe loaded with 500 mM CaCl_2 was loading into a Legardo 180 syringe pump (KD Scientific Inc.). A 45 cm line of silicon tubing was used to connect this syringe to a customized luer-locking coaxial needle tip (Ramehart) with inner diameter 200 μm , outer diameter 1 mm. A 10 mL Luer-lock syringe (Harpool) was then filled with the gelatin-gellan gum-genipin solution and attached to the second port of the coaxial needle. The biopolymer and CaCl_2 solutions were then printed in a 10:1 ratio, forming cylinders for mechanical testing, or linear channels for electrochemical analysis. All gels were allowed to fully cure for 48 h at 21 °C prior to testing.

Compression testing

Compressive mechanical analysis was conducted on a Shimadzu EZ-S mechanical analyzer. Samples cured in cylindrical wells measuring 10 mm (h) x 16 mm (d) were transferred to the instrument and compressed at a rate of 25 mm/min to a maximum strain of 80 %.

Rheometry

Shear rheometry was performed using a Physica MCR 301 shear rheometer (Anton Paar) equipped with 15 mm parallel plates. Samples were cast into cylindrical wells measuring 5 mm

(h) x 15 mm (d), and tested under a dynamic amplitude sweep mode between 0.01% and 100% strain at a constant angular frequency of 5 Hz.

Impedance analysis

Electrical impedance spectroscopy measurements were carried out according to the methods described previously by Warren et al[18]. Using a custom instrument the impedance of the gel samples was obtained between frequencies of 1 Hz and 100 kHz. Impedance analysis was performed using a waveform generator (Agilent U2761A) by applying 1V (AC signal) across a circuit with a known resistor (R_k) and measuring the voltage drop across the gel sample and R_k with a two channel oscilloscope (Agilent U2701A).

DISCUSSION

Development of printing formulation

The genipin-gelatin-gellan gum ICE hydrogels form conductors, as has been previously reported[19], with polymer loadings of 1 % (w/v) GG, 1.75 % (w/v) gelatin alongside 0.44 % (w/v) genipin and 5 mM CaCl_2 . However, initial trials printing this formulation were observed to suffer from poor flow behaviors and intermittent tip-clogging, attributed to the high viscosity of the solution. Stevens *et al.*[20] reported an optimal printing of pure gellan gum solutions when 0.5 % (w/v) gellan gum and 500 mM CaCl_2 solutions were printed in a 10:1 ratio, resulting in final gels of 0.45 % (w/v) GG and 50 mM CaCl_2 . As a result ICE gel precursor solutions were reduced to 0.5 % (w/v) GG, 0.875 % (w/v) gelatin and 0.22 % (w/v) genipin. Using this formulation and heating solutions to 40 °C prior to printing was found to enable hydrogel printing, including the formation of printed line patterns (Figure 1, C). This formulation was applied for further testing.

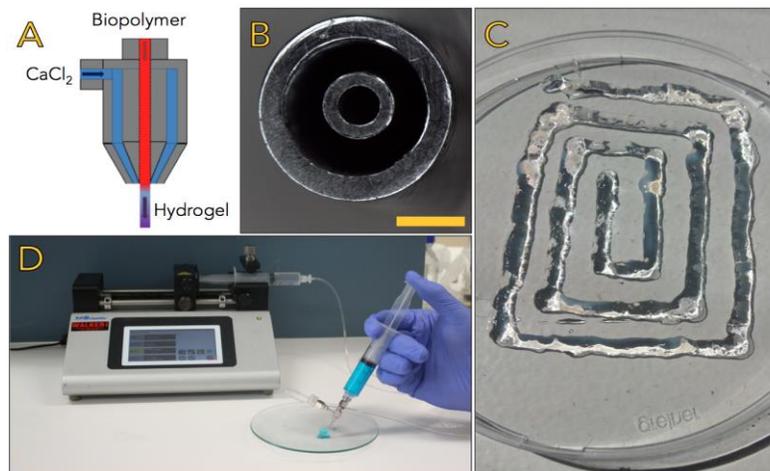


Figure 1. Schematic diagram showing the flows of CaCl_2 and biopolymer solutions through the print head (A). Close up of the tip of the coaxial print head (B). Demonstrated of a printed line of gel using the hand-held extruder (C). Hand-held device in use (D).

Assessment of printed gels

Using the identified printing formulation, ICE hydrogels were printed into cylindrical and linear forms, akin to the moulds used for cast gels. The printed and cast gels were then compared in terms of their mechanical and electrical performance, Fig.2. Mechanical testing under compression showed a significant reduction in compressive modulus, ultimate strength and ductility after printing. Rheological measurements performed in shear, however, indicated the reverse trend. In this case, printed gels providing a higher response in storage and loss moduli. Furthermore, the position of the linear viscoelastic region (LVE), indicative of shear ductility. We attribute these findings to the printing process causing inhomogeneous deposition of the hydrogel, with incomplete binding between sequentially deposited layers acting as a crack initiation site under compression. This leads to rapid failure of the network with lower required force input. Additionally, these internal boundary layers are thought to increase the total energy dissipation observed under shear resulting in a 184 % increase in loss modulus. In both cases, it is apparent that the reactive printing process has a noticeable impact upon the mechanical properties of gels, a factor that should be considered in future applications.

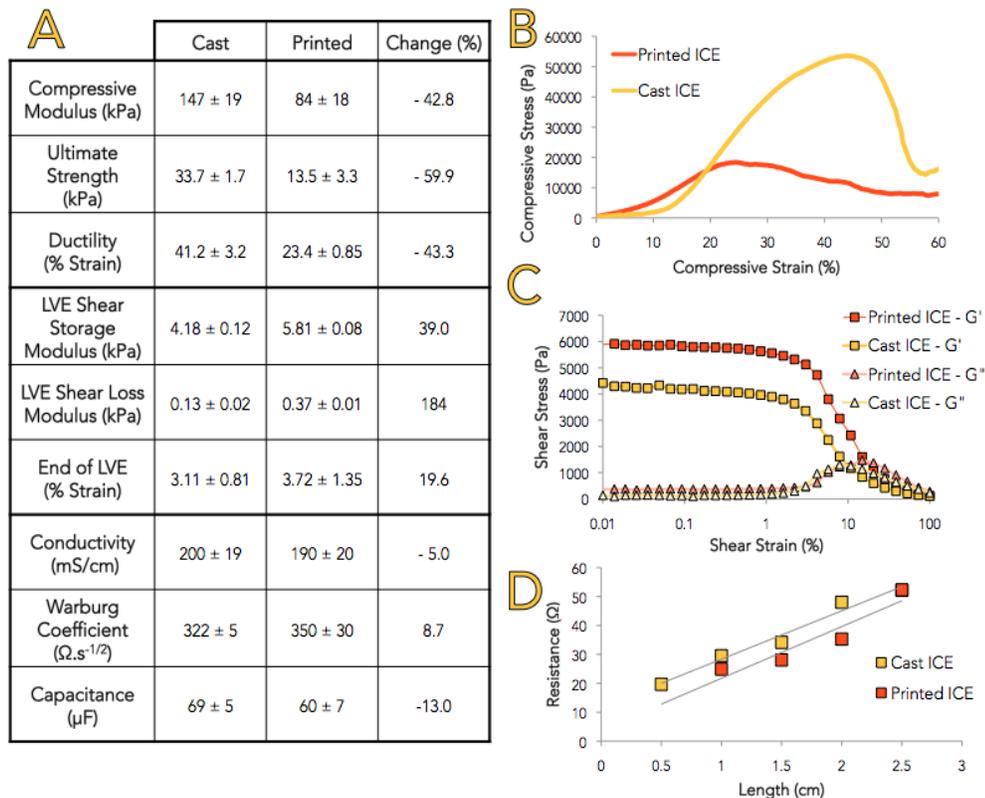


Figure 2. Mechanical and electrical properties of the ICE gels after casting or printing (A). Graphs present typical results from compression tests (B), rheometry (C) and samples of ICE gel resistances as a function of gel length (D).

The cast and printed gels were immersed in saturated NaCl solutions and the electrical properties analyzed using the methods described above and equivalent circuit modelling. The results in Fig.2 A,D show that printed and cast gels had a conductivity of 190 ± 20 and 200 ± 19

mS/cm respectively. The Warburg coefficient of the printed and cast gels was 350 ± 30 and $322 \pm 5 \Omega/s^{1/2}$, respectively. Lastly, the capacitance of the printed and cast gels was 60 ± 7 and $69 \pm 5 \mu\text{F}$, respectively. These results indicate that no change in electrical properties was observed as a result of extrusion printing of the materials.

Demonstration circuit

ICE hydrogels were hand-printed between two reticulated vitreous carbon (RVC) electrodes, leaving a small gap such that the gels did not provide a complete connection (Fig.3A). After soaking gels with NaCl, the gap was bridged with a light emitting diode (LED) and an external power supply was used to apply an electrical potential across the two RVC electrodes. The charging and discharging of these high surface area electrodes drives ionic conduction in the bulk gel (Fig.3B), which can be used to power the LED (Fig.3C). This simple example of ICE hydrogels acting a conductive element demonstrates their potential for application in more complex, bioresorbable devices.

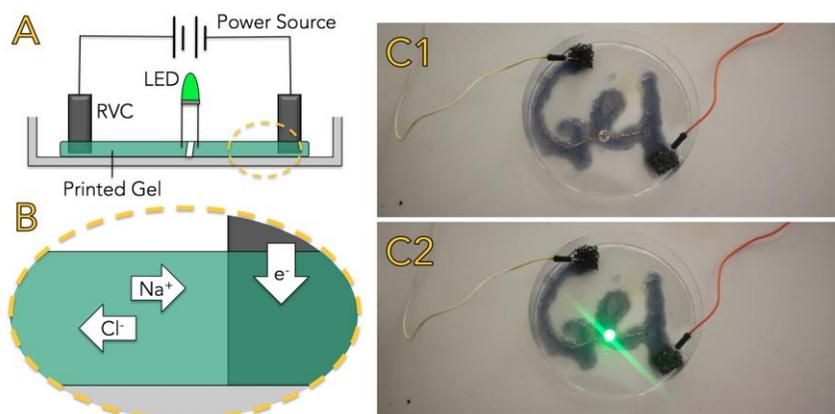


Figure 3. Schematic of a circuit in which ICE gels act as a conductor to complete a circuit between RVC electrodes and a LED light (A). Electrons delivered to the RVC drive the flow of Na^+ and Cl^- ions through the gel (B). Photograph of the setup at rest (C1) and when a voltage is applied (C2).

CONCLUSIONS

This paper demonstrates a simple method for constructing highly conductive, bioresorbable wires using a hand-held extrusion printer. The printed wires were constructed using food grade materials of gellan gum-gelatin-genipin with NaCl as an ionic conductor. The gels were able to maintain their electrical performance after printing, displaying a conductivity of $190 \pm 20 \text{ mS/cm}$. This work contributes to the future development of edible and bioresorbable devices for improved GI monitoring and other edible electronic devices.

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