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The Suitability of 3-D Printed Eutectic Gallium-Indium Alloy as a Heating Element for Thermally Active Hydrogels

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Abstract

We report the use of a novel extrusion tip that allows for the omnidirectional printing of eutectic gallium-indium (eGaIn) alloy onto the surface of hydrogel materials into complex 2-dimensional patterns. The use of these printed soft "wires" as an electrothermal heating element for soft robotics purposes was explored. Heating of the eGaIn structures encapsulated in an alginate/acrylamide ionic-covalent entanglement hydrogel was measured by a thermal imaging camera. It was determined that eGaIn is a suitable material for use in future soft robotics applications as an electrothermal heating element to actuate thermally responsive N-isoproylacrylamide hydrogels.

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The Suitability of 3-D Printed Eutectic Gallium-Indium Alloy as a Heating Element for Thermally Active Hydrogels

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ABSTRACT

We report the use of a novel extrusion tip that allows for the omnidirectional printing of eutectic gallium-indium (eGaIn) alloy onto the surface of hydrogel materials into complex 2-dimensional patterns. The use of these printed soft “wires” as an electrothermal heating element for soft robotics purposes was explored. Heating of the eGaIn structures encapsulated in an alginate/acrylamide ionic-covalent entanglement hydrogel was measured by a thermal imaging camera. It was determined that eGaIn is a suitable material for use in future soft robotics applications as an electrothermal heating element to actuate thermally responsive N-isoproylacrylamide hydrogels.

INTRODUCTION

The field of soft robotics has seen the benefit of tough hydrogel materials in a variety of applications in fields such as biomedical, waste management, soft robotics, and others [1-4]. Recently, stimuli responsive hydrogels such as thermally responsive N-isopropylacrylamide (NIPAM) have been determined to be suitable materials to serve as actuators for many soft robotics applications [5, 6]. However, a practical method of actuation has yet to be determined for these materials, but one approach would be to use electrothermal heating by incorporating a soft conductor. Recently, liquid metal eutectic gallium-indium (eGaIn) alloy has been explored in various applications and has shown great potential as a compliant conductive material [7, 8]. One notable advantage of eGaIn, aside from its metallic conductivity and low toxicity, is the spontaneous formation of a passivating oxide layer that allows for the formation of stable microstructures [9, 10].

In previously reported work, the use of eGaIn in many applications has revolved around the ability to manipulate this oxide layer [11]. However, the inherent properties of eGaIn have made it difficult to process and many devices have required the use of complicated multi-step processes incorporating micro-molding techniques [12]. Newly developed techniques, such as embedded printing, have simplified the process but the material’s unfavorable interaction with hydrous surfaces, described as the formation of a “slip-layer,” has restricted its use to primarily silicone based substrates such as PDMS [13, 14]. In this study, we describe the use of a custom extrusion tip that can print eGaIn onto hydrous surfaces in continuous complex 2-dimensional patterns. The eGaIn is then encapsulated into the completely 3D-printed hydrogel device and its capability as an electrothermal heating element to actuate thermally responsive NIPAM hydrogels is assessed.

EXPERIMENTAL

Acrylamide, NIPAM, alginic acid sodium salt (medium viscosity), calcium chloride, α-keto glutaric acid photo-initiator, and N,N' – methylenebisacrylamide (MBAA) crosslinker were purchased from Sigma Aldrich, Australia. Ethylene glycol was purchased from ChemSupply, Australia. All aforementioned reagents were used as received and all solutions were prepared using Milli-Q water (resistivity ~18.2 Ω). All hydrogel precursors were prepared as per previously described methods [15]. The precursor gels were then placed into 5mL syringe barrels and centrifuged for 12 minutes at 4400 rpm to remove air bubbles.

Gallium and indium of 4N purity were purchased from Changsha Santech Materials Co., Ltd. and SmaTree Australia respectively. The eGaIn alloy was made by heating the metals at a ratio of 75% wt. gallium / 25% wt. indium in an inert atmosphere while stirring.

The custom built extrusion tips were modeled in SolidWorks 2015 and fabricated with a Realizer SLM50 printer using Ti6Al4V titanium alloy powder ranging from 20-60 μm particle size.

Fabrication of the eGaIn hydrogel device used a custom built extrusion printer based on a CNC-milling machine and the Gcode to create the devices was written in a Linux Gedit program. All materials were extruded out of a 5mL syringe by a T-NA08A25 Zaber linear actuator. The printed structure was cured with a Dymax BlueWave 75 Rev 2.0 UV system with a 19+ W cm^{-2} light source. After curing, the samples were immersed in a 0.1M $CaCl_2$ solution for 24 hours followed by immersion in Milli-Q H_2O for 24 hours. To electrothermally heat the device, the eGaIn tracks were connected to a Tektronix PWS4305 programmable DC power supply. Two samples were made and voltages of 2, 3, or 4 Volts were applied for 15 minutes. Each sample was immersed in Milli-Q H_2O afterwards for 45 minutes and samples were weighed before and after heating. As the device was heated, temperature was recorded via thermal imaging by a Micro-Epsilon TIM 160 thermal imager with analysis done in the TIM Connect Software and OriginPro.

RESULTS AND DISCUSSION

When attempting to print eGaIn with conventional EFD extrusion tips, the material would bead up and a continuous printed line could not be achieved. The custom extrusion tip to print the eGaIn was designed with the idea that the material needed to omnidirectionally flow into its own skin (Figure 1). The design of the tip allows for a small reservoir of the eGaIn to remain at the end of the tip and be extruded into itself through the gaps engineered into the sides of the extrusion tip. This novel design allows for the printing of continuous lines of the eGaIn in complex 2-dimensional shapes. Printing was even possible on top of substrates that exhibit an unfavorable surface interaction. The resolution of the printed wires is closely associated with the prong-to-prong distance of the tip and remained at approximately 900 μm for the experiments reported in this study.

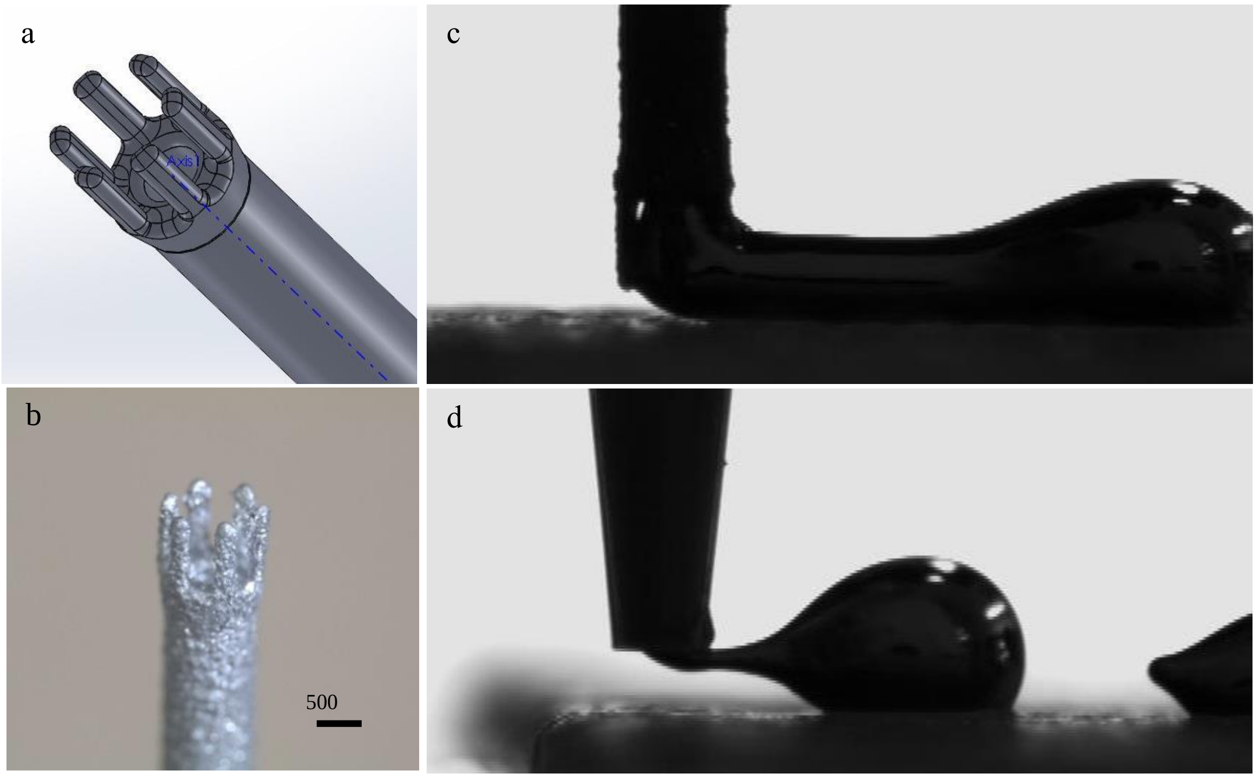

Figure 1. a) The CAD model of the custom extrusion tip that was subsequently manufactured from titanium alloy (b). c) Printing of the eGaIn material with the custom titanium tip allows for the liquid metal to flow laterally into its own skin to produce a continuous "wire" that cannot be achieved with a conventional extrusion tip due to beading (d).

The reported device was fabricated with a non-thermally responsive alginate/acrylamide hydrogel for proof of concept and to assess the viability of using eGaIn as an electrothermal heating element. Acrylamide crosslinks covalently with MBAA to form a covalent network through free radical polymerization when exposed to UV light, whereas the alginate crosslinks ionically in the presence of divalent cations to form the ionic network of the ionic-covalent entanglement (ICE) gel. Initially, the base layer of ICE gel was printed and then the syringe was swapped and the eGaIn wires were printed. Lastly, the gel around the wires as well as a top layer of gel was extruded to encapsulate the eGaIn inside the device (Figure 2). Prior to UV curing, copper wires were inserted into the printed gel precursor to allow for electrical connection to an outside power source. After curing, the gels were immersed in a 0.1M $CaCl_2$ solution to allow the alginate to fully cross-link and then soaked in water to remove excess ions.

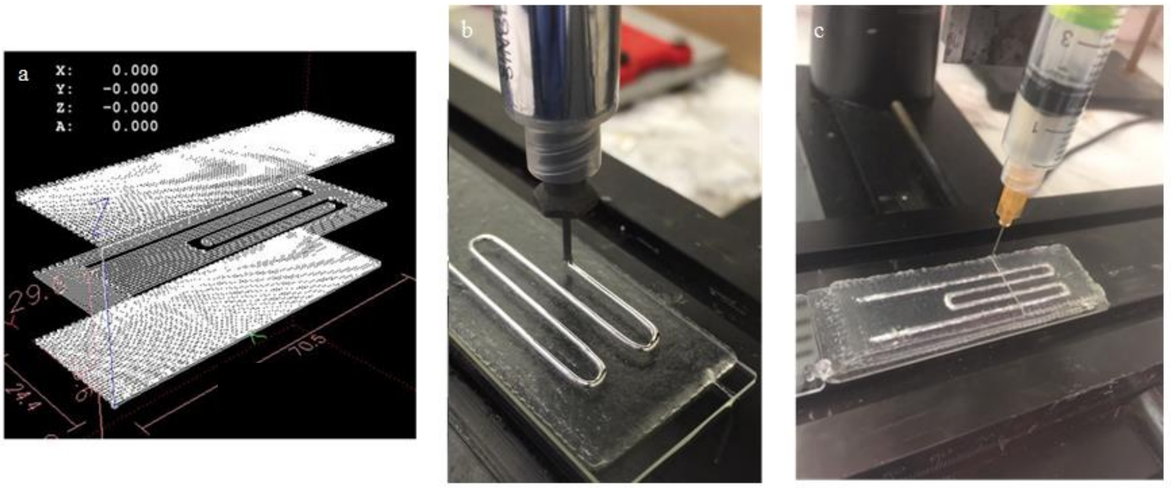

Figure 2. a) The printing process of the device where the Gcode is interpreted by the LinuxCNC software and the paths that the nozzle will take are produced in three layers. b) The eGaIn wires are printed onto the hydrogel surface after the base layer is produced. c) The top layer of hydrogel is then printed onto the structure to encapsulate the eGaIn.

To investigate the potential use of eGaIn to actuate thermally responsive NIPAM hydrogels, 2 samples were made and potentials of 2, 3, and 4 Volts were applied for 15 minutes to observe the temperature change. The goal was to find the appropriate voltage necessary to increase the temperature of the gels to above the lower critical solution temperature (LCST) of NIPAM (~31 °C). With a potential difference of 2 and 3 Volts applied, a maximum temperature of only 26 and 30 degrees could be achieved. When 4 Volts was applied the sample was heated above the LCST and shows that it can be used to actuate NIPAM based hydrogels. An average loss of water content of 4% was measured throughout the experiment.

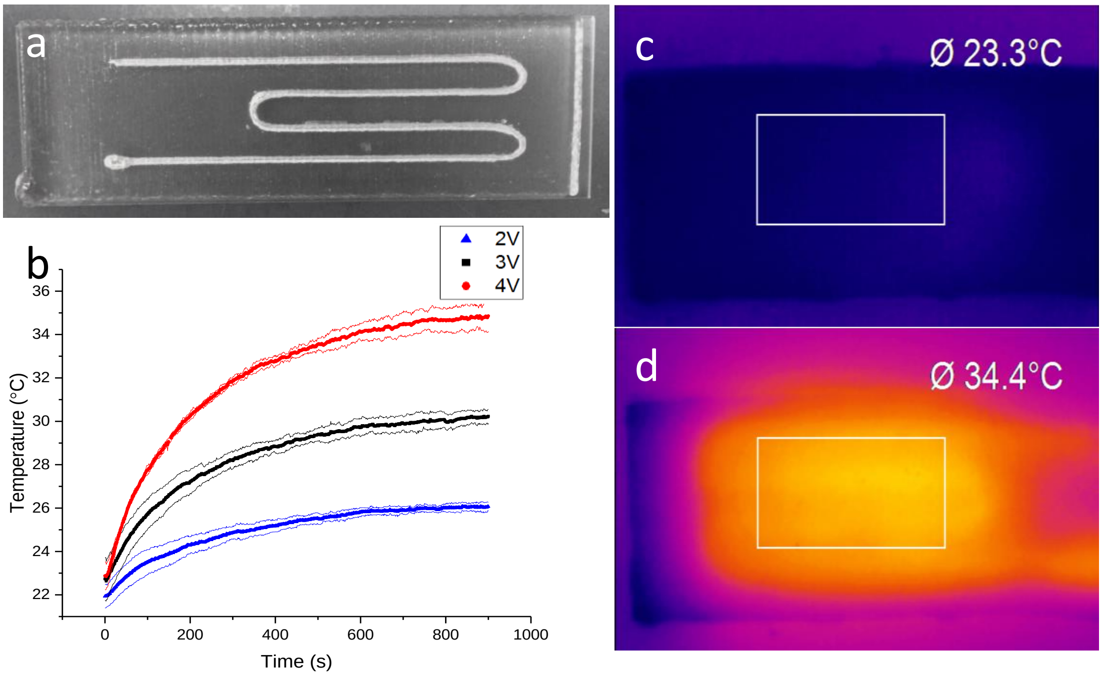

Figure 3. a) The 3D-printed hydrogel device with eGaIn wires immediately after printing. After the insertion of connecting wires and post-processing previously described, a potential difference of 2, 3 and, 4 Volts were applied and the temperature change was recorded over time (b). Three separate heating cycles were conducted at each applied voltage. Average temperature of the selected region (box) was recorded with an IR camera and is shown at 0 (c) and 900 seconds after a voltage of 4V was applied (d).

CONCLUSIONS

A method of extrusion printing eGaIn with a custom designed extrusion tip was developed that allows the user to print complex 2-dimensional patterns. This technique was used to print “wires” onto hydrous surfaces that normally exhibit a highly unfavorable surface interaction. These wires were then encapsulated into a hydrogel device to assess the suitability of eGaIn as a thermal heating element in hydrogel devices. It was observed that the temperature of the device could be heated to above the LCST of NIPAM by applying a potential of 4 Volts thus showing its potential to serve as a mechanism to actuate thermally responsive materials in soft robotics devices. In the future, efforts to increase the heating rate such as improving eGaIn wire resolution, patterning, hydrogel porosity, and composition of the eGaIn itself will be explored.

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