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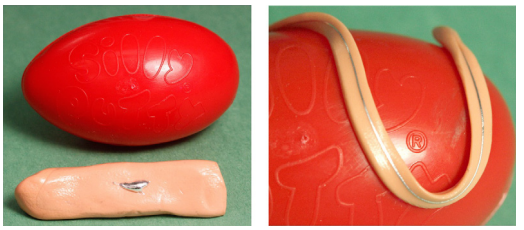
Drawing liquid metal wires at room temperature

Yiliang Lin [1], Collin Ladd [1], Siyao Wang, Andre Martin, Jan Genzer, Saad A. Khan, Michael D. Dickey *

Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695-7905, USA

GRAPHICAL ABSTRACT



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ABSTRACT

This paper describes an extremely facile method to fabricate metallic wires at room temperature. The wires form by stretching viscoelastic polymer substrates supporting a drop of gallium-based liquid metal. Stretching the polymer causes the metal to also elongate due to the adhesion between the two materials. The diameters of the resulting wires, which can be as small as 10 μm, decrease with increasing strain. This method is inspired by the process used for drawing optical fibers, which involves pulling a pre-form cylinder of molten glass until it thins to the size of a fiber. In contrast, the process here is done at room temperature and realized without the need for large forces. Moreover, geometries beyond simple wires are possible including parallel, core–shell, branched, and helix structures. The resulting wires can be elastic (stretchable), viscoelastic (soft), or plastic (stiff) depending on the chemistry and post-processing of the polymer. Wires can make electrical contacts by allowing the metal to sink through the viscoelastic polymer onto a substrate containing electrodes. In addition, removing the polymer substrate after elongation produces freestanding liquid metal wires stabilized by the surface oxide on the metal. Rheological studies show that polymers with a variety of properties can be utilized to form these wires including viscoelastic materials and gels. The ability to form metallic wires in a simple manner may find uses in soft and stretchable electronics, or enable new applications, such as 'wires on demand' for repairing electrical connections.

1. Introduction

This paper describes an extremely simple method to fabricate metallic wires at room temperature with a wide

* Corresponding author.
E-mail address: mddickey@ncsu.edu (M.D. Dickey).
[1] Y.L. and C.L. contributed equally to this work.

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range of mechanical properties. The wires form by manually stretching a polymer slab supporting a droplet of gallium-based liquid metal. Both the liquid metal and polymer substrate elongate during stretching to form wires in a process similar to drawing optical fibers (i.e., pulling a preform cylinder of glass softened by heat [1]). Others have taken inspiration from this high temperature process to elongate metals [2], optical materials [3], and semiconductors [4] to make nanostructures [4], probes [5], and sensors [3]. Here, we show it is possible to form metallic wires by hand at room temperature by utilizing materials that are inherently deformable and soft. Utilizing such a simple strategy forms conductive, metallic wires with diameters as small as tens of microns, embedded core–shell structures, parallel networks of wires, branched structures, and helices. Moreover, depending on the chemistry of the polymer substrates, the resulting metallic wires may be stretchable, rigid or soft by crosslinking the polymer after formation of the wires.

The fabrication of conventional electrical wires begins typically with a spool of metal 'rod' (e.g. copper) formed via high temperature processing. A series of pulleys and dies elongate the rod under tension using large forces until the diameter reduces to a suitable value; elevated temperatures can reduce the required forces [6]. The wires are often braided and then coated with plastic insulation via extrusion of polymer at elevated temperatures. The resulting wires are stiff due to the mechanical properties of the metal. We sought a simpler process to make insulated wires on demand, at room temperature, with a wide range of mechanical properties. The goal is not to replace conventional cabling, but rather provide an alternative method to make conductive traces that takes advantage of the unique properties of liquid metal.

Metals that are liquid at room temperature have two features that are appealing within the context of making wires: (1) they can be mechanically manipulated at room temperature, and (2) the resulting wires maintain metallic conductivity even at large deformation and are therefore useful for soft and stretchable electronics [7,8] Here, we utilize eutectic gallium indium (EGaIn) due to its low melting point (m.p. ~15.5 °C) [9,10], low-toxicity [11] and high conductivity ($\sigma = 3.4 \times 10^4$ S/cm) [12]. Various microfluidic systems and soft electronics utilize this liquid metal [13], such as soft memristors [14], stretchable wires [7,8], antennas [15–19], electrodes [20,21], pumps [22], capacitors [23,24], soft circuit boards [25], hyperelastic pressure sensors [26], self-healing circuits [27,28], soft curvature sensors [29], and stretchable interconnects [30,31]. EGaIn forms a surface oxide that is important for two aspects of this work: (1) It allows the metal to adhere to the polymer during elongation, and (2) it mechanically stabilizes the metal to maintain high aspect ratio geometries that would be prohibited by surface tension due to Plateau–Rayleigh instabilities.

Various processes have been introduced for patterning liquid metals in polymers [32], such as stencil lithography [33,34], imprint lithography [35], injection [10,15], microcontact printing [36] and direct-writing [37]. Most existing patterning techniques are relatively low resolution (>100 μm). Patterning at higher resolution may enable new applications such as dense wire bundles or electrodes with length scales commiserate with cells. The method here is distinguished by its simplicity and ability to make both metallic structures with small diameters and high aspect ratios. Metallic structures with high aspect ratios are desirable for conductive fibers, wires, interconnects, and cables. It is possible to make conductive fibers of liquid metal by melt processing or electrospinning hollow fibers filled with metal [7,38], although these processes require tools that are not widely available. It is also possible to create conductive fibers utilizing conductive particles [39] (e.g. Ag particles [40] and CNTs [41]), although no other material offers the combination of conductivity and elasticity provided by liquid metals.

Here, we demonstrate that it is possible to draw either exposed or encapsulated wires of EGaIn at room temperature in a one-step process without any specialized equipment. The simple stretching approach can achieve liquid metal structures with diameters smaller than the resolution of many existing techniques to pattern liquid metal lines. Rheological and mechanical measurements confirm the properties of both the starting materials and resulting wires, which helps elucidate the mechanism of wire formation.

2. Result and discussion

Fig. 1 highlights a simple approach for making metallic wires at room temperature. First, a syringe extrudes EGaIn on a polymer substrate (in this representative example, ~50 microliters of metal on ~10 g of Silly Putty™). Stretching the putty by hand (Fig. 1(b)) extends both the polymer and the metal, resulting in an elongated structure with a diameter that decreases with strain (Fig. 1(c)). Supporting information (SI) Video S2 shows a wire being stretched. Using typical strain rates of ~1 cm/s, EGaIn wires with diameters approaching the tens of micron-scale form within seconds using this strategy. Due to the soft and stretchable property of putty, conductive, metallic wires can be manipulated into a variety of geometries. Fig. 1(d) provides an example of one such shape.

We hypothesized that if the metal adheres well to the putty, the diameter should correlate with the strain of the polymer. Fig. 2(a) plots the diameters of the wires as a function of the strains on the polymer substrate (Experimental Section in SI). Approximating the geometry of the EGaIn lines as cylinders and accounting for conservation of mass, results in Eq. (1),

$$V = \frac{1}{4}\pi d_0^2 l_0 = \frac{1}{4}\pi d_1^2 l_1 = \frac{1}{4}\pi d_1^2 n l_0 \quad (1)$$

which simplifies to Eq. (2),

$$d_1 = d_0 n^{-\frac{1}{2}} \quad (2)$$

where V is the volume of the metal, d_0 and d_1 is the diameter of the EGaIn lines before and after stretching, and l_0 and l_1 is the length of EGaIn lines before and after stretching. We define n as the stretch ratio (l_1/l_0) of the EGaIn lines. Eq. (2) also holds for truncated cylinders. As predicted by Eq. (2), the diameters of the EGaIn lines measured experimentally vary linearly with the inverse square root of the

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