DIRECT INK WRITING OF MICROVASCULAR NETWORKS

Willie Wu\textsuperscript{1}, Christopher J. Hansen\textsuperscript{1}, Alejandro M. Aragón\textsuperscript{2}, Nancy R. Sottos\textsuperscript{1}, Scott R. White\textsuperscript{2}, Philippe H. Geubelle\textsuperscript{2}, and Jennifer A. Lewis\textsuperscript{1,3,*}

\textsuperscript{1} Materials Science and Engineering Department, University of Illinois – Urbana-Champaign, 1304 W. Green St., Urbana IL 61801, USA
\textsuperscript{2} Aerospace Engineering Department, University of Illinois – Urbana-Champaign, 104 S. Wright St., Urbana IL 61801, USA
\textsuperscript{3} Chemical and Biomolecular Engineering Department, University of Illinois – Urbana-Champaign, 600 S. Matthews St., Urbana IL 61801, USA

* e-mail: jalewis@uiuc.edu
* Tel: +1-217-244-4973
* Fax: +1-217-244-2278

The next generation of self-healing polymeric materials will allow multiple healing events through the integration of complex three-dimensional microvascular networks. Traditional techniques for creating these networks, such as soft lithography, do not readily scale to the third dimension. New approaches must therefore be developed to enable the facile construction of three-dimensional microvascular networks. Here, we discuss recent developments in the direct-write assembly of both planar and 3D networks embedded within polymer matrices via robotic deposition of fugitive organic inks. [1,2]

Keywords: Direct ink writing, Microvascular networks, Self-healing

1 Introduction

Self-healing polymers promise to dramatically increase the service lifetime of structural materials, particularly composites under fatigue conditions [3,4]. This concept of self-healing pertains to an expanding number of materials systems, including dicyclopentadiene (DCPD) and Grubb’s catalyst [5], and hydroxy end-functionalized polydimethylsiloxane (HOPDMS) and polydiethoxysiloxane (PDES) [6]. Most self-healing systems are capsule-based, which only provides autonomic healing of a single damage event in a given region. Incorporation of a microfluidic network has the potential to enable repeated healing of multiple damage events independent of their location.

A progression to the next generation, self-healing systems requires the integration of microvascular networks within a polymer matrix. Such networks are composed of a pervasive, interconnected pathway of microchannels whose diameter ranges from ca. 10 μm – 1 mm.
Although the fabrication of microfluidic devices has become increasingly sophisticated, traditional routes, such as soft lithography [7], do not easily scale to three dimensions. Direct ink writing overcomes the inherent limitations associated with this approach by patterning a “fugitive organic” ink within a thermal- or photocurable resin. [1,8] After the surrounding resin is solidified, the ink can be removed from the polymer matrix leaving behind an interconnected network of microchannels in one, two, or three dimensions. [1-2]

Our prior efforts [1-2] have focused on fabricating simple 1D, 2D, and 3D networks, however more complex network architecture are needed for autonomic systems. Here, we report a method for fabricating planar and 3D networks composed patterns, which are generated by: (1) output from a genetic algorithm that optimizes their flow response, (2) mimicking leaf venation, or (3) creating bimodal microchannels in a periodic pattern.

2 Experimental

2.1 Materials system

Fugitive organic inks are created by mixing microcrystalline wax ($M_w=1450$ g mol$^{-1}$, SP 18, Strahl & Pitsch Inc., West Babylon, NY) and Vaseline petroleum jelly ($M_w=840$ g mol$^{-1}$, Vaseline petroleum jelly, Chesebrough-Pond’s, Ladson, NY) on a magnetic stir plate at ~85°C in a 2:3 ratio. This ink composition yields the optimal viscoelastic response to facilitate its deposition at modest extrusion pressure, while simultaneously retaining its filamentary shape even as the ink spans gaps in the underlying layer(s) [1]. The onset of ink melting occurs at ~80°C.

Two types of resins are employed. One consists of a liquid silicone elastomer (Sylgard 170 Dow Corning Corp., Midland, MI), while the other consists of a photo-curable liquid resin (NOA61, Norland Products Inc, Cranbury, NJ). The elastic modulus of the cured polymer matrices are reported to be 2.5 MPa and 1.0 GPa, respectively.

2.2 Robotic deposition of fugitive inks

Two- and three-dimensional structures are printed in a layer-wise build sequence using a 3-axis motion-controlled positioning stage (Figure 1). An air-powered, high-pressure syringe adapter (HP7X, EFD Inc, East Providence, RI) fitted with cylindrical nozzles ranging from 100 to 200 μm in diameter is mounted onto the positioning stage. The air pressure controller enables discontinuous printing via computer control. Customized software (RoboCAD 2.0J) is used to design the structure and to independently control the movement of the x-, y-, and z-axes. Direct deposition into reservoir of the organic resin bypasses the need for resin infiltration into the porous regions between printed features thereby allowing finer structures to be patterned. After curing, the fugitive ink is removed by liquefying it at elevated temperature under a light vacuum. The final structure is composed of an interconnected microchannel network embedded in a PDMS or epoxy matrix.
Figure 1: Schematic representation of the microchannel fabrication process. a.) deposition of a fugitive binary ink in an organic resin; b.) curing of resin; c.) removal of fugitive ink

(a) Optimization of planar microvascular networks using genetic algorithms

Modern computing has adapted the biological process of Darwinian natural selection to allow for numerical optimization through genetic algorithms (GA) [9-12]. GA start by randomly creating a population of sample networks. All the individuals in the initial population are then evaluated with respect to some objective in order to distinguish those individuals with higher fitness. The algorithm then evolves this population by applying selection, crossover, and mutation as genetic operators. The selection operator is where the “survival of the fittest” takes place, as those networks with higher fitness are more likely to be chosen for reproduction. Crossover creates new individuals by intermixing the information of the selected parents. Finally, mutation produces small changes in the newly created individuals. The new population is evaluated and the process is repeated until termination criteria for the algorithm is met. The final population is considered as the optimal one and its individuals are then output to a file format (vector code or g-code) capable of controlling the 3D positioning stage. Following the methods for deposition and writing in epoxy outlined above, the optimized network is fabricated and imaged optically.

(b) Planar microvascular network of leaf venation

An image of a dried Fagus grandfolia leaf is captured using a scanner (Canon U.S.A. Inc, Lake Success, NY) and processed with image editing software (Adobe Systems Inc, San Jose, CA) to enhance the contrast of the skeletal structure. The subsequent image was imported into a commercially available CAD program (Autodesk Inc, San Rafael, CA) in which an overlaying trace image was generated. The trace layer is then converted into position commands for the 3D deposition stage via a custom written software module. The ink is extruded through a 200 μm nozzle onto a polystyrene substrate at a pressure of 2.9 MPa and a speed of 6 mm s⁻¹ to create a PDMS-encapsulated network. Removal of the fugitive ink post cure was achieved by immersing the structure in boiling water.
(c) 3D Multimodal Networks

The bimodal microchannels are patterned into a reservoir containing a photo-curable resin on top of a cured epoxy substrate. The rods are extruded through a 100 μm nozzle at a pressure of 3.8 MPa and a write speed of 4 mm s⁻¹. A z-compression of 85% is used to ensure contact between and adhesion to subsequent layers. The final dimension of the 45 layer structure is 20 mm x 20 mm x 3.85 mm, and the total deposition time was ~2 h. The resin is cured at room temperature (25° C) under ultraviolet light (365 nm) for ~8 hours. The ink is removed post-cure by heating the structure to 85° C with a heat gun and applying a light vacuum to exposed channels. Any remaining ink is removed by flushing the channels with acetone.

3 Results and Discussion

(a) Genetic algorithm optimization of planar microvascular networks

We have produced a planar microvascular network optimized using the genetic algorithm technique outlined above. The output for these networks, optimized for flow within a 20x20 mm² network, is shown in Figure 2(a). This pattern is modified to include an input (source) at the lower-left corner of the network and an output (sink) at the upper-right corner of the network, as shown in Figure 2(b). Upon infiltrating this microvascular network with water, the fluid is observed to fully access all interconnected microchannels (diameter = 100 μm). Pressure measurements are now underway on both a reference network as well as the optimized network shown below to probe the efficiency of this computer-designed network.

![Figure 2: A planar microvascular network optimized via a genetic algorithm approach using the criterion of minimum pressure drop for a given void volume fraction. (a) Computer-generated output of network pattern and (b) corresponding network embedded in epoxy produced by direct ink writing.](image)
(b) Planar microvascular network of leaf venation

Leaf venation is composed of naturally occurring microchannels whose architecture has been highly optimized for water transport [13]. The venation architecture is characterized by a division of labor between the different orders of vein hierarchy. Larger veins serve as fast, long-distance transport channels, whereas smaller veins are responsible for local dispersion of fluid. Redundancy, homogeneous distribution, and high hydraulic conductivity are key attributes of leaf venation that are of great importance for self-healing networks.

To demonstrate the capabilities of direct ink writing, we fabricate 100 μm microchannels that mimic the venation architecture of a *Fagus grandfolia* leaf (Figure 3). This simple architecture is initially selected to focus on accurate reproduction of the leaf network. Systematic variation of the writing parameters is required to ensure that microchannel junctions remain connected without over-deposition of the fugitive ink. Future efforts will include fabricating structures with multiple orders. Additionally, pressure and flow resistance measurements will be carried out to evaluate the effectiveness of such architectures in self-healing applications.

![Figure 3: Planar microvascular network of a simple leaf venation pattern in PDMS](image)

(c) 3D Multimodal Networks

To demonstrate our ability to create multi-modal, 3D microvascular networks, a 45-layer network composed of microchannel of 100 μm and 1 mm in width is fabricated by direct ink writing. Small channels are deposited in a parallel fashion with 150 μm center-to-center rod spacing. Large channels are constructed by co-depositing ten 100 μm rods alongside one another, without any space between adjacent filaments. In subsequent layers, the orientation of the larger channels is maintained, while the smaller channels are rotated by 90°. After 15 layers, the orientation of the large channels is again rotated by 90°. The resulting structure is a periodic network in which the size of the microchannels differs by an order of magnitude (Figure 4a,b). In the optical images, the microchannels remain filled with ink to enhance the contrast between them and the surrounding matrix. The fluorescence image in Figure 4(c) shows a magnified view of a larger channel in a layer below that of the smaller channel network.
Figure 4: Optical (a,b) and fluorescent (c) images of a 45-layer microvascular network composed of microchannels of 100 µm and 1 mm in width

4 Conclusions

Both planar and 3D microfluidic networks have been fabricated by direct-write assembly of fugitive organic inks. Our approach enables the synthetic reproduction of complex architectures, from microfluidic networks embedded in self-healing materials to leaf venation patterns. Efforts are now underway to develop new self-healing polymer materials with embedded microvascular systems that enable autonomic repair of repeated damaged regions in a given location.

ACKNOWLEDGEMENTS

This work was funded by the AFOSR MURI program (Grant # FA9550-05-01-0346). C. Hansen is partially supported by an NSF Graduate Fellowship.

REFERENCES