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Flexible, Structured MWCNT/PDMS Sensor for Chronic Vascular Access Monitoring

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Abstract

Graft wall pulsation amplitude sensing can provide a measure of functional status, e.g. in hemodialysis access grafts. Current implantable graft monitoring sensors require graft modification and direct bloodstream contact. We propose a new class of piezoresistive flexible pulsation sensors which can be wrapped around the graft to measure wall movement. These sensors must be highly flexible to prevent graft constriction; typical strain sensors are too rigid and the strain sensing range is too limited for this application. We describe a novel additive manufacturing (AM) method for printing polydimethylsiloxane (PDMS) with an internal porous structure, such that material compliance may be tuned anisotropically for a given sensor geometry. Prototype flexible pulsation sensors (FPS) consisting of structured PDMS with an embedded conductive PDMS sensor layer were fabricated and tested. Initial tests demonstrated reliable sensor response to 1-Hz cyclic elongation of 20%, and a sensor gauge factor of 1.0.

I. Introduction

Over one million vascular grafts are used annually to bypass diseased vessels or for hemodialysis [1]. Many implanted grafts are synthetic and have patency rates of 25 – 90% [2]. Imaging technologies can probe graft status, however these require skilled personnel and are costly for regular graft surveillance. Therefore, a means to easily and non-invasively assess graft flow patency would warn of impending graft failure, greatly enhancing long-term clinical care for vascular graft recipients.

Vascular grafts pulsate with changes in arterial pressure due to their mechanical compliance [1], [3]. Research trends have focused on increasing the compliance to more closely mimic arterial pulsation, reducing mechanical strain and blood flow turbulence [1]. As a graft becomes occluded, its stiffness increases, reducing pulsation magnitude and blood flow. Monitoring pulsation reductions has great potential as the primary measure of graft functional status.

Several approaches to wireless graft monitoring have been proposed including sensors which directly contact the bloodstream [4]. We are developing a new class of flexible pulsation sensors (FPS) which can interface directly with the graft wall, avoiding bloodstream contact and without modifying the mechanical properties of the vascular graft.

Traditional rigid strain sensors are inappropriate for chronic vascular monitoring due to low mechanical compliance and a relatively narrow strain sensing range less than 3%. Vascular grafts may expand up to 20% to match the arterial compliance range [3]. Any mechanical restriction on the graft wall movement can lead to localized turbulence, increasing the graft occlusion rate. To counteract these effects, we propose a new class of polymeric FPS to be wrapped around vascular grafts (Fig. 1). The sensor is constructed entirely from PDMS for long-term biocompatibility and mechanical flexibility. A novel additive manufacturing (AM) process was developed to print PDMS with controlled porosity. This enabled tuning of the axial sensor compliance such that the FPS does not impede graft wall movement during vascular pulsation. An embedded conductive PDMS (CPDMS) layer served as a simple piezoresistive sensor of graft wall displacement. In this work we describe our first experiences in structured PDMS AM, and fabrication of bio-compatible. CPDMS strain sensors.

II. Additive Manufacturing of Pulsation Sensors

To minimally restrict the normal pulsatile motion of graft walls, the FPS needs to have an engineered compliance which trades off sensor flexibility, robustness, and material choices. To accomplish this, we investigated using AM 3D-bioplotting to produce multi-layer PDMS sensors with embedded sensing regions and structured porosity. Porous sensors may have an engineered compliance to match the target tissue mechanical response, and can be seeded with cells or other materials to encourage bio-infiltration (becoming part of the living host) rather than bio-encapsulation (being walled off by scar tissue).

A. 3D Bio-plotting of PDMS

Bio-plotted samples were created using a 3D-Bioplotter System (EnvisionTEC GmbH) extrusion deposition system (Fig. 2). The tool is capable of depositing raw, medical-grade biomaterials that are isolated from the environment by both fine-particle and sterile filters. The PDMS source material is pneumatically dispensed from a container cartridge through a needle tip, which defines the diameter of the individually deposited strands. A high-resolution, computer-controlled, 3-axis system is employed to define the outer contours and inner structure pattern of a 3D-model. Each model is first divided into layers in the z-axis that are defined by the strand diameter, and then setup in the system for plotting.

During deposition, each of the previously defined layers were dispensed under a pressure in the range of 1.5-3.5 bar, at an xy-axis speed controlled to 8 – 60 mm/s. The material cartridge was cooled to 4°C to prevent premature cure of the PDMS, while the deposition platform was heated to 60°C in order to promote curing as strands are placed.

B. Structured PDMS

Conventional techniques cannot easily produce interior structure or 3D porosity throughout the cured PDMS material, since PDMS flows and self-levels prior to curing. There has been recent research in this area, e.g. coaxial PDMS cell seeding [5] and porous PDMS membrane fabrication [6], but these strategies are unsuitable for rapid production of large-scale 3D structures with unity aspect ratios.

AM enables engineered sensors with interior porosity, but relies on layers of consistent height and uncured material spanning gaps without sagging. Unaltered PDMS is unsuitable because even rapid-set and UV-cure formulas have a long gelling time. Conversely, highly viscous PDMS formulations are difficult to degas and cannot be printed through a fine needle.

We studied thixotropic PDMS with 3D-bioplotting equipment. We mixed PDMS (MDX-4210, Dow Corning) with thixotropic agent (A-300-8, Factor II) at various concentrations. Thixotropic PDMS is a stable, non-flowing liquid, but exhibits shear-thinning when compressed. For AM, this is ideal because it allows the material to hold its shape before curing, while permitting fluid flow through small diameter needles without clogging. We found that 0.45 wt.% thixotropic PDMS produced the most reliable printing with the parameters listed in Table 1.

Thixotropic PDMS allowed accurate AM of multi-layer PDMS structures which maintained their porosity (Fig. 3a,b. Structure heights up to 20 layers were produced. To study the repeatability of structured PDMS AM, we printed 10 copies of 2 types of FPS with differing porosity and anisotropic compliance. Structure A was printed with X/Y strand spacing of 1.5/1.2 mm and Structure B had spacing of 1.2/0.8mm. The structures had average pore sizes of 0.8 mm and 1.15 mm. Optical micrograph images were analyzed for average pore size (Fig. 3c). FPS mass was used as a surrogate measure of porosity (Fig. 3d). Compared to the mass of a solid PDMS structure of the same geometry, the two FPS showed a mean porosity of 33% and 81% but with a defined 3D geometry.

C. Conductive MWCNT/PDMS Composite

Multi-walled carbon nanotubes (MWCNTs) produce strain sensitive PDMS [7]. Conductive MWCNT-PDMS (CPDMS) displays piezoresistive properties when agglomerate such that continuous conductive paths bridging millions of nanotubes are formed. These paths are fixed in the cured polymer matrix but some paths are severed as nanotubes are pulled apart, leading to a strain-sensitive piezoresistive sensor response. CPDMS piezo-resistivity is nonlinear and may demonstrate hysteresis [8], however, CPDMS strain sensors can be repeatedly subjected to incredible elongations exceeding 100% without damage.

We produced CPDMS using a modified recipe based on [9]. CPDMS was mixed to varying concentrations of MWCNTs to replicate the findings of prior studies. The sheet resistance of sensor samples was measured by stencil-printing the CPDMS through laser-cut polystyrene stencils onto quartz substrates. After curing, CPDMS samples were peeled from the substrate and clamped between measurement electrodes.

By combining our measurements with other reports of CPDMS mixed by similar methods (Fig. 4) [8] - [10], we modeled the material resistivity ρ_c using an exponential model, e.g.

$$\rho_c = \alpha \cdot N_c^\beta, \quad (1)$$

where N_c was the known MWCNT concentration as a weight percentage, and α and β were empirical constants. Fitting to data (Fig. 4) over a range of MWCNT from 0–12 wt %, $\alpha = 0.0003$ and $\beta = -4.526$ produced an accurate model for the CPDMS resistivity ($r^2 = 0.96$). This model was used to optimize CPDMS doping level, given application-driven sensor geometry.

D. Printed CPDMS Pulsation Sensor

AM was used to fabricate structured FPS prototypes engineered to provide anisotropic compliance (Fig. 5). By varying the strand spacing, a porous FPS was created (Table 2). To maximize uniaxial sensor response and reduce graft wall stricture, narrowly-spaced strands were placed perpendicular to the sensing direction. This produced a strand density 33% lower in the sensing direction, without compromising overall shape or mechanical strength. Strand spacing was chosen by incrementally increasing the spacing until PDMS slump within pores was noted. The sensing layer was 4% MWCNT/PDMS to produce relatively low resistance sensors for electronic interfacing.

Initial studies confirmed a repeatable FPS response to significant elongation. Sensors were clamped in a micropositioner and cyclic strain induced by advancing/retreating the positioner manually. Sensors were biased using a fixed 3V power supply. Paired current/voltage measurements were collected at 10 Hz by a Labview DAQ, which computed equivalent sensor resistance. The FPS was conditioned by cyclic stretching at 1 Hz to simulate regular human heart pulsation rates to stabilize the conductive network of MWCNTs in the polymer matrix. Sensor conditioning took approximately 20 cycles before repeatable sensor response was obtained. After conditioning, the FPS prototypes demonstrated a stable and repeatable response to cyclic elongation (Fig. 6). We calculated sensor Gauge Factor (GF)

$$GF = \Delta R / R_0 \bigg/ \Delta L / L_0 = \Delta R / R_0 \bigg/ \epsilon, \quad (2)$$

by taking the ratio of resistance change R/R_0 to lengthwise strain ϵ . For the 4% CPDMS, we measured GF=1.0 over a 0-20% strain range. This GF is about half that of metal strain sensors—however, metal sensors typically fail at about 3% strain.

III. Conclusion

Flexible pulsation sensors capable of sensing vascular graft occlusion are promising for continuous graft health monitoring. Additive manufacturing combined with thixotropic

PDMS and MWCNT/PDMS composites enabled the fabrication of multilayer pulsation sensors with interior structure and porosity. The sensor GF of 1.0 was measured over cyclic elongation from 0-20% strain, matching the dynamics of arterial vessel wall movement. This new class of sensors is a promising example of novel technology enabled by additive manufacturing methods.

References

- [1]. Greenwald S and Berry C, "Improving vascular grafts: the importance of mechanical and haemodynamic properties," *Journal of Pathology*, vol. 190, pp. 292–299, 2000. [PubMed: 10685063]
- [2]. Abbott WM et al. "Evaluation and performance standards for arterial prostheses," *J. Vasc. Surg.*, vol. 17, pp. 746–756, 1993. [PubMed: 8464095]
- [3]. Gozna ER et al. "Necessity for elastic properties in synthetic arterial grafts," *Can. J. Surg.*, vol. 17, pp. 176–179, 1974. [PubMed: 4275064]
- [4]. Cheong J. H. e. a., "An Inductively Powered Implantable Blood Flow Sensor Microsystem for Vascular Grafts," *IEEE Transactions on Biomedical Engineering*, vol. 59, no. 9, pp. 2466–2475, 2012. [PubMed: 22692871]
- [5]. Townsend-Nicholson A and Jayasinghe SN, "Cell Electrospinning: a Unique Biotechnique for Encapsulating Living Organisms for Generating Active Biological Microthreads/Scaffolds," *Biomacromolecules*, vol. 7, no. 12, pp. 3364–3369, 2006. [PubMed: 17154464]
- [6]. Femmer T, Kuehne AJC and Wessling M, "Print your own membrane: direct rapid prototyping of polydimethylsiloxane," *Lab on a Chip*, vol. 14, pp. 2610–2613, 2014. [PubMed: 24828586]
- [7]. Khan S, Tinku S, Lorenzelli L and Dahiva R, "Flexible tactile sensors using screen-printed P(VDF-TrFE) and MWCNT/PDMS composites," *IEEE Sensors Journal*, vol. 15, no. 6, pp. 3146–3155, 2015.
- [8]. Lee J-B and Khang D-Y, "Electrical and mechanical characterization of stretchable multi-walled carbon nanotubes/polydimethylsiloxane elastomeric composite conductors," *Composites Sci Tech*, vol. 72, pp. 1257–1263, 2012.
- [9]. Liu C-X and Choi J-W, "Patterning conductive PDMS nanocomposite in an elastomer using microcontact printing," *Journal of Micromechanics and Microengineering*, vol. 19, pp. 1–7, 2009.
- [10]. Yan J, Kim B and Jeong YG, "Thermomechanical and electrical properties of PDMS/MWCNT composite films crosslinked by electron beam irradiation," *Journal of Material Science*, vol. 50, pp. 5599–5608, 2015.

Fig. 1. An all-PDMS strain sensor (a) may be wrapped around vascular grafts (b) to measure wall deflection as a surrogate for pulsatile flow rate.

Fig. 2.

3D bioplotting (a) creates 3D structures from liquid materials dispensed (b) from a three-axis print head with controllable deposition speed and pressure. Multi-material structures may be printed such as (c) this test structure consisting of 20 layers of CPDMS and 4 layers of structured thixotropic PDMS.

Fig. 3.

Thixotropic PDMS printed by AM (a) demonstrated controlled inner porosity (b,c). Varying strand spacing produced repeatable production of PDMS structures with 34% and 81% porosity, compared to solid PDMS (d).

Fig. 4. Measured CPDMS resistivity at varying concentrations of MWCNT closely matched previously reported values.

Fig. 5.

Printed FPS with 4 layers of structured PDMS and a piezoresistive CPDMS layer. Variable XY strand spacing provides anisotropic compliance.

Fig.6.

Measured resistance change of FPS prototype to cyclic elongation from 0 – 20%. This test condition simulated the pulsation rate and amplitude of human blood flow through blood vessels or vascular access graft.

TABLE 1.

3d-Bioplotter Parameters for Thixotropic PDMS

Thixotropic PDMS ratio	0.45 wt.% thixotropic agent
Print needle tip size	0.2 mm
Print speed	8 mm/s
Print pressure	3.3 bar

TABLE 2.

Pulsation Sensor Parameters.

Strand width	0.2 mm
Strand spacing – X axis	1.2 mm
Strand spacing – Y axis	0.8 mm
Sensor Dimensions	28.6 × 6.6 mm
Sensor Thickness	0.5 mm