MECHANICAL BEHAVIOR OF MICROSTRUCTURES FROM A CHEMO-RESPONSIVE POLYMER NANOCOMPOSITE BASED ON COTTON CELLULOSE NANOFIBERS

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ABSTRACT

This paper reports on the fabrication and characterization of MEMS-scale devices from a mechanically dynamic polymer nanocomposite, consisting of a cotton-derived cellulose nanofibers encased in a poly(vinyl acetate) matrix, with a stiffness modulated by the presence or absence of water. Microtensile testing showed that the Young's modulus (E) of the nanocomposite is initially ~2.7 GPa, but reduces to ~4 MPa upon immersion in water for 7 minutes. A combination of laser-micromachining and lithographic processing was used to produce an intracortical probe with switchable stiffness based on the dynamic nanocomposite. An electrode with area 2800 μm^2 was found to have an impedance of 156 kΩ at 1 kHz. This investigation was the first time that a chemoresponsive nanocomposite based on cotton cellulose nanofibers was used in MEMS-scale structures.

INTRODUCTION

Polymer-based microdevices offer mechanical flexibility, as well as the property of "tunability" during synthesis. However, once the polymer is formed, the properties cannot be reversibly altered. Enhanced device capabilities require polymers with *in situ* property modulation.

Inspired by the dynamic stiffness of the *Cucumaria frondosa* (sea cucumber) dermis, we have developed a family of polymer nanocomposites with a switchable tensile storage modulus regulated *in situ* by the presence or absence of water [1]. The nanocomposite is comprised of stiff cellulose nanofibers (or whiskers) embedded in a soft poly(vinyl acetate), PVAc, matrix. The overall stiffness of the material is in part modulated by surface interactions between hydroxyl bonding groups on the nanofibers, shown schematically in Figure 1 (when dry, fiber-fiber surface interactions are switched "on" and the material stiffens) and in part by the T_g of the matrix. When saturated with a hydrogen-bond forming liquid (i.e., water), the fiber-fiber interactions are switched "off", the matrix is plasticized and the material becomes very compliant, reducing the modulus by approximately three orders of magnitude.

This family of dynamic materials is potentially appealing for the development of intracortical probes for long-term (>20 years) neural recording. Si-based probes have exhibited limited viability (several months), resulting from encapsulation by a cellular sheath that isolates the probe from neurons [2]. The formation of this glial sheath may be produced by an immune response triggered by strain induced by micromotion between the stiff (E=~160 GPa) Si probe and the soft (E=~10 kPa) cortical tissue. Mechanically-flexible polymer-based probes were developed to reduce the induced strain, but were not sufficiently stiff to insert into the brain without assistance by a rigid backbone [3] or gel-filled microfluidic channel [4]. An intracortical probe based on the PVAc nanocomposite may avoid both problems because it would initially be stiff to penetrate the *pia mater* without buckling, and upon deployment would absorb fluids to more closely match the stiffness of brain tissue.
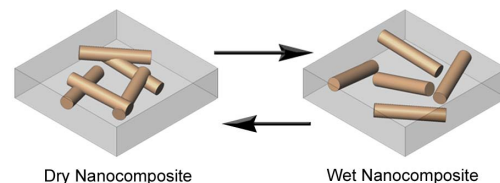

Figure 1: In the dry material, cellulose fibers interact to stiffen the polymer; when wet, interactions between fibers are broken and the material becomes flexible.

The first-generation material, PVAc-TW (Tunicate Whiskers), was a nanocomposite based on PVAc and cellulose whiskers isolated from tunicates, which are filter-feeding sea creatures. A nanocomposite with a whisker content of 16.5 % w/w displayed a room-temperature tensile storage modulus of 5.4 GPa when dry and 12 MPa when at body temperature and saturated with water [1]. We previously showed that this material could be micromachined without affecting its chemoresponsive properties [5]. In an effort to utilize cellulose nanofibers from a more accessible resource, and also to provide an even better match to cortical tissue mechanics, a second-generation material was developed utilizing cellulose

nanofibers from cotton (PVAc-CW, Cotton Whiskers) [6]. Because cotton-derived cellulose nanofibers display a lower length-to-diameter aspect ratio and a lower Young's modulus compared to tunicate-derived cellulose nanofibers, it was expected that water-saturated PVAc-CW would exhibit a reduced stiffness (in both wet and dry states) compared to PVAc-TW.

In this paper, we report the mechanical characterization of microscale PVAc-CW samples to determine whether the dynamic response is observed in micromachined samples with the cotton cellulose fibers. Further, a neural probe with lithographically-patterned metal and insulating layers was fabricated on a PVAc-CW substrate, and electrically characterized.

MECHANICAL TESTING

Sample Preparation

PVAc-CW formulations consisting of both 5% and 15% (by volume) cotton-derived cellulose nanofibers were prepared with the solvent dimethylformamide using a solution-casting technique, then, after solvent removal, compressed to form nanocomposite films with thicknesses ranging from 50-250 μm [6]. These nanocomposites are incompatible with exposure to the wet chemicals used in photolithographic patterning and to temperatures exceeding 120°C. Thus, laser micromachining using a direct-write CO_2 laser at a power setting of 0.5 W was used to pattern microscale test structures.

Microtensile Tester

Using the custom-built test setup shown in Figure 2, a standard microtensile testing technique was used to measure the stress-strain behavior of PVAc-CW samples at room temperature. Strain was applied to the sample with a linear piezomotor while displacement was measured by an indicator with a resolution of 0.5 μm, and the tensile force was measured by a load cell with a resolution of 49 μN. The setup was equipped with a reservoir for immersing the sample-under-test in liquids designed to prevent the samples from drying during testing. The microtensile tester was operated in two modes: tensile mode, in which the sample was pulled at a rate of 1 μm/s to break or until the range of the instrument (200% strain) was exceeded; and dynamic mode, in which the sample was alternately loaded and unloaded within the elastic region to determine the Young's modulus as a function of time.

Tensile Mode Testing

Tensile mode testing of PVAc-CW samples in the dry state showed that increasing nanofiber content within the nanocomposite resulted in an increase in stiffness, with the Young's modulus of PVAc-CW(5%) being ~1 GPa, and that of PVAc-CW(15%) being ~2.7 GPa (Figure 3a). The elongation-to-break of PVAc-CW(5%) exceeded 200%, but increasing the cotton nanofiber content to 15% reduced the elongation-to-break to ~2.2% strain. PVAc-CW(15%) displayed a lower Young's modulus than PVAc-TW, which was more rigid with E=~3.3 GPa [7], but displayed a similar

elongation-to-break. It was expected that by replacing the tunicate-derived cellulose nanofibers with cotton-derived cellulose nanofibers, the stiffness of dry samples would decrease. The greater elongation-to-break of PVAc-CW(5%) samples could be advantageous for clinical applications because the more brittle PVAc-TW and PVAc-CW(15%) samples tend to break if handled incorrectly, whereas the PVAc-CW(5%) samples do not suffer from this problem.
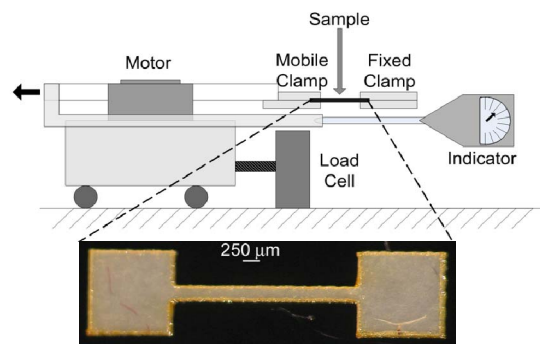

Figure 2: Schematic of custom-built microtensile tester (top), and a sample dogbone test structure (bottom) with a beam 3000 μm x 250 μm x 100 μm.

Accurate measurements of sample width and thickness are essential for accurate stress calculations. Lateral and through-film dimensional changes were measured for PVAc-CW samples to enable width and thickness calculations of water-saturated samples based on the measured dimensions of dry samples. At room temperature, the across-plane dimensions increased by 8.2 ± 1.7%, and through-film dimensions increased by 35.3 ± 3.3% after immersion in DI water for 1 hour, indicating anisotropy in swelling characteristics. These measurements were used to calculate the stress versus strain values for saturated PVAc-CW samples.
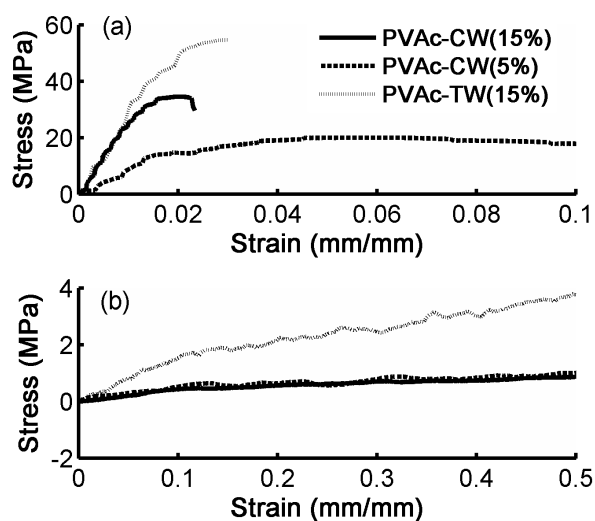

Figure 3: Stress-strain curves of (a) dry PVAc nanocomposites and (b) wet PVAc nanocomposites.

The Young's moduli of water-saturated PVAc-CW(5%) and PVAc-CW(15%) samples were measured to be 3.7 MPa and 4.9 MPa, respectively (Figure 3b), demonstrating that the stiff-to-compliant transition is not significantly influenced by laser micromachining in PVAc-CW-based MEMS-scale structures. Furthermore, the stiffness of both PVAc-CW nanocomposites was significantly less than that for the water-saturated PVAc-TW sample (E=21 MPa). Thus, saturated PVAc-CW samples better match the mechanics of cortical tissue compared to PVAc-TW, and may provide a better long-term solution to single-unit neural recording. Lastly, after drying for 18 hours at 60°C under vacuum, the initial stiffness of soaked PVAc-CW samples was completely recovered.

Dynamic Testing

Samples tested in dynamic mode were cyclically strained at a rate of 1.8 µm/s up to a strain of 0.7%, then allowed to relax and return to the initial position, a process that required approximately 25 seconds per cycle. Samples were placed in the microtensile tester when dry, and after approximately 5 loading/unloading cycles, DI water at 20°C was added to the reservoir. Upon immersion in water, the stiff-to-flexible transition was completed within 7 minutes, as shown in Figure 4.
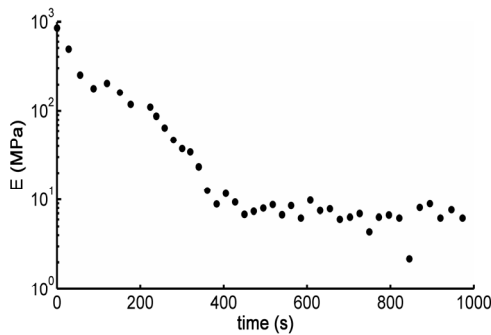

Figure 4: Young's modulus of PVAc-CW(5%) measured over time with sample immersed in DI water at t=0 s.

Buckle testing

It is clear from the microtensile testing that the Young's modulus of PVAc-CW in both stiff and compliant states was lower than similar PVAc-TW samples. As one of the requirements of a probe substrate material is to penetrate through the *pia mater* of the brain without buckling, it was important to determine the buckle strength of the probes, and whether or not the probes are likely to penetrate the brain without buckling. The buckle strength of laser-micromachined mechanical blanks (Figure 5(inset)) with shanks 2000 µm-long x 100 µm-thick x 180 µm-wide was measured by forcing the probe tip into a rigid acrylic block and measuring the corresponding load as a function of displacement. The results, shown in Figure 5, illustrate that the buckle strength of PVAc-CW(5%) samples was ~9 MPa, half that of the PVAc-CW(15%) probes. However, the buckle strength exceeds the previously determined 1.2 MPa required for penetration of the rat pia [8].
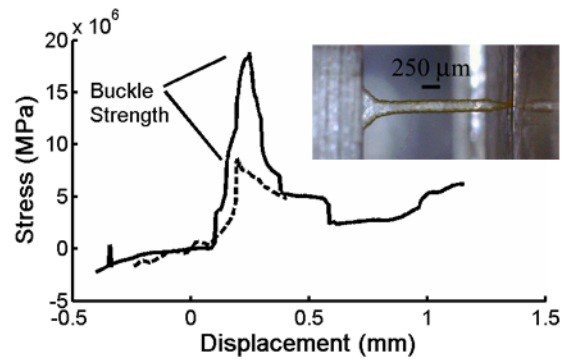

Figure 5: Stress induced as a function of displacement by moving PVAc nanocomposite cortical probes toward a rigid acrylic surface (shown in inset).

DEVICE FABRICATION

After the mechanical behavior of PVAc-CW microstructures was characterized, multi-layer PVAc-CW-based intracortical probes were fabricated using the process in Figure 6.
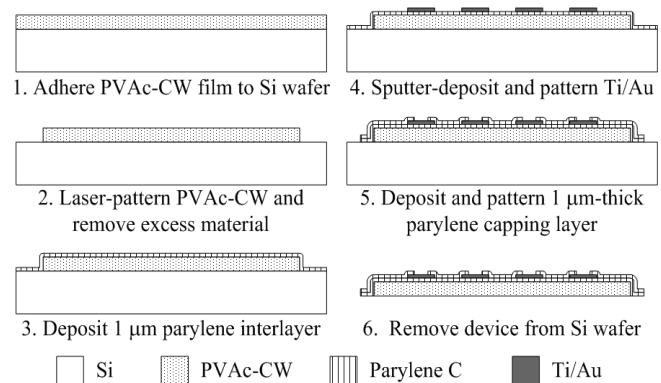

1. Adhere PVAc-CW film to Si wafer
2. Laser-pattern PVAc-CW and remove excess material
3. Deposit 1 µm parylene interlayer
4. Sputter-deposit and pattern Ti/Au
5. Deposit and pattern 1 µm-thick parylene capping layer
6. Remove device from Si wafer

☐ Si   ▨ PVAc-CW   ⫿ Parylene C   ▪ Ti/Au

Figure 6: Cross-sectional process flow for the fabrication of PVAc-CW-based intracortical probes.

The substrate was prepared by adhering the PVAc-CW film to a bare Si wafer, which served as a mechanical substrate for further processing. Modest pressure was applied to the freestanding PVAc-CW film on the Si wafer while heating on a hotplate set to 70°C, exceeding the glass transition temperature of PVAc-CW. The device geometry was then laser-patterned and excess material in the field was carefully removed with tweezers. Next, a 1 µm-thick Parylene C film was vapor deposited to coat the PVAc-CW top surface and sidewalls, as well as field areas. This parylene interlayer served to isolate electrodes and traces from the moisture absorbed by PVAc-CW, as well as to protect the PVAc-CW from wet chemicals utilized in photolithographic processing in subsequent steps.

Next, a 50 nm Ti adhesion layer and 200 nm Au were sputter-deposited, followed by the spin-coating and patterning of a photoresist etch mask. Au etchant and buffered oxide etchant were then used to pattern the Ti/Au features, and the photoresist was removed with acetone. Next, 1 µm-thick Parylene C capping layer was deposited and patterned through a photoresist mask with an oxygen

plasma. In a self-aligned process, the outer geometry of the parylene interlayer was also patterned. Finally, the devices were peeled from the Si wafer.

An optical photograph of a laser-micromachined PVAc-CW(15%) probe with lithographically-patterned Ti/Au and parylene layers is shown in Figure 7. The single-electrode device has a single 60 μm-diam. Au electrode near the probe tip, a 30 μm-wide trace supported by a shank that was 2 mm long, 180 μm-wide, and 50 μm-thick. The connector end of the probe, which includes an exposed window through the parylene layer for electrical connection, was designed to interface with a custom-connector for long-term clinical applications. For the electrical testing reported here, connection was made through a 75 μm-diam. stainless steel wire attached to the contact pad with conductive epoxy, then insulated with silicone.
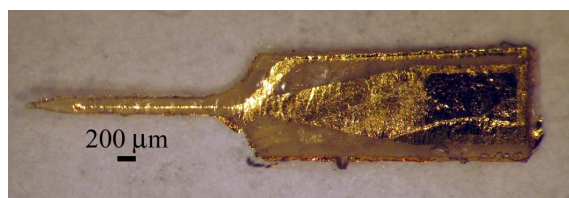

Figure 7: Released PVAc-CW-based intracortical probe.

ELECTRICAL TESTING

Electrochemical measurements of a PVAc-CW probe were made to ensure that the device would be viable for neural recording. The impedance spectra of an electrode with an area of 2800 μm^2 was measured in phosphate buffered saline versus a Pt mesh reference electrode using a computer-controlled LCR meter. The impedance measurements at frequency values scanned from 12 Hz to 200 kHz are shown in Figure 8. At 1 kHz, a biologically-relevant frequency, the magnitude of the impedance was measured to be 157 kΩ, which is comparable with similar electrodes on Si probes [9].
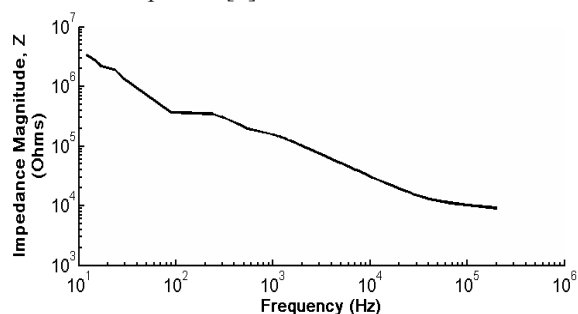

Figure 8: Impedance spectra of PVAc-CW-based probe with 2800 μm^2 Au electrode.

CONCLUSIONS

A chemo-responsive polymer nanocomposite modulated by interactions between its cellulose nanofibers derived from cotton has been formed into microscale devices specifically for application as a substrate material for intracortical probes. It was determined that microstructures patterned from PVAc-CW display a switchable stiffness dependent upon the presence or absence of water, and that in the wet state, nanocomposites utilizing cotton-derived cellulose nanofibers better mechanically match cortical tissue compared to those with tunicate-derived cellulose nanofibers. A fabrication process was developed to integrate conductive electrodes and insulating films onto the PVAc-CW substrate to fabricate an adaptive neural probe. Characterization of the probe showed that electrode behavior is comparable to those on Si substrates.

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