# ANNEALING EFFECTS ON FLEXIBLE MULTI-LAYERED PARYLENE-BASED SENSORS

*Brian J. Kim[1], E. Peter Washabaugh IV[2], and Ellis Meng[1]*
[1]Department of Biomedical Engineering, University of Southern California, Los Angeles, CA, USA
[2]Department of Biomedical Engineering, University of Michigan, Ann Arbor, MI, USA

## ABSTRACT

To mitigate long term, soaking-induced delamination failure of multi-layered Parylene C devices, a post-process annealing step can be employed to increase adhesion between the Parylene layers. However, it has been shown that annealing of Parylene thin films can alter the bulk properties of the polymer, and thus impact final device performance. To elucidate these effects, the mechanical and electrochemical properties, and sensing performance of untreated and annealed Parylene C-platinum electrochemical impedance-based force sensors were compared. Annealing reduced the height (~3%) and increased the stiffness of the Parylene C sensing channel structure (~1.6x), affecting the sensor's mechanical response. Furthermore, the electrode surface was smoothed as built-in residual stresses were removed during annealing, altering the sensor's electrochemical properties. Together, these phenomena resulted in a 24% reduction in sensor sensitivity. These results indicate that heat-based effects cannot be ignored for Parylene-metal device systems, including neural microelectrode implants, and that mechanical and electrochemical properties and performance must be determined after heat treatment, such as annealing and sterilization.

## INTRODUCTION

Initially used as an encapsulation coating for implantable devices, Parylene C (from here on referred to as Parylene) is now frequently chosen as a structural material for implantable or other biomedical devices because of its biocompatibility, flexibility, and compatibility with microfabrication techniques [1]. The introduction of techniques to form three dimensional structures from Parylene thin films [2] has further expanded the potential for Parylene as a MEMS material; novel Parylene microdevices and microsystems have been developed that leverage the polymer's properties for biomedical applications [3].

However, it is well established that these multi-layered Parylene-MEMS encounter a failure mode under continuous soaking conditions (i.e. *in vivo*) via delamination between Parylene-Parylene and Parylene-metal interfaces that is attributed to liquid intrusion that weakens these layer interfaces. To mitigate this, many efforts to increase the adhesion between the Parylene layers have been explored [4]; one of note is a simple post-process annealing treatment at temperatures greater than the glass transition point of Parylene (~60-90°C [5]) to allow for increased entanglement between the chains of the Parylene layers [6]. However, heat treatment of Parylene thin films has been found to cause significant chain reorganization and thus material changes to the bulk polymer [7], which may in turn impact device performance. These heat-induced modifications to Parylene can further extend beyond the annealing step; any process in which the film experiences temperatures greater than the glass transition point (e.g. autoclave sterilization) can alter the properties of the bulk polymer and thus the final device performance.

To explore the annealing effects on multi-layered Parylene device performance, we present an investigation of the post-annealing performance of a distributed Parylene-based force sensor array consisting of an electrolyte-filled Parylene microchannel sensing structure encasing a linear array of platinum (Pt) electrodes [8]. Deflection of the top surface of the microchannel by an applied force induces changes in the volumetric conduction path between the electrodes, altering the measured electrochemical impedance (Figure 1); thus device performance is closely associated with both the mechanical response of the Parylene microchannel and the electrochemical properties of the electrode surface. Annealing was found to induce changes in both aspects of the sensor, thereby affecting final sensor performance. Our results indicate that annealing effects cannot be ignored for mechanically or electrochemically sensitive Parylene-MEMS devices; device properties and performance must be characterized following any heat-based process.

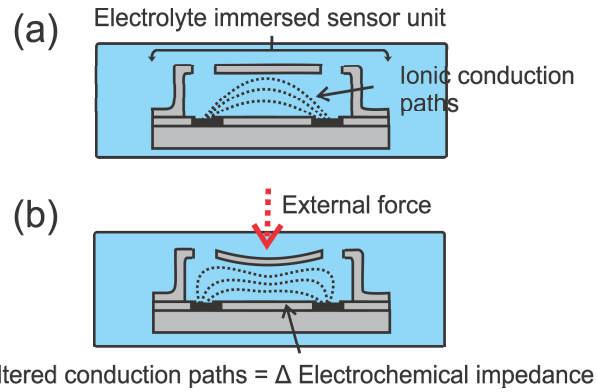


*Figure 1: Illustration of sensor transduction mechanism (a) during steady state and (b) during an applied external force. Applied forces deflect the top surface of the microchannel to induce a change in the volumetric conduction path, and thus electrochemical impedance. This mechanism highlights the importance of the mechanical and electrochemical sensor properties on performance.*

## EXPERIMENTAL METHODS

The Parylene-based force sensor array consists of a Parylene microchannel (100 µm x 4.15 mm x 24 µm) encasing a linear array of eight electrodes (each measuring 100 x 130 µm); electrode pairs constitute a single sensor (Figure 2). As mentioned previously, the sensors utilize an electrochemical transduction principle; force-induced disruptions of the ionic conduction path between the electrode pairs alters the measured electrochemical impedance. The impedance is acquired at a specific measurement frequency ($f_{measurement}$ = 1 kHz), selected such that it is sufficiently high enough to bypass the double layer capacitance ($C_{dl}$), isolate the solution resistance, and thus capture the disruptions in the ionic conduction path.

The sensor array was designed to measure the interfacial forces between an implanted rigid neural probe and surrounding tissue. To improve the sensor's *in vivo* lifetime, devices were annealed to prevent delamination resulting from chronic soaking in saline. More specifically, sensor arrays were placed within a vacuum oven (10 mTorr), which was ramped at 1.6°C/min to 200°C. Following a thermal soak time of 48 hours, the devices were cooled overnight (~15 hours) under vacuum, and then removed for post-process characterization. All untreated sensors were tested following removal off wafer.

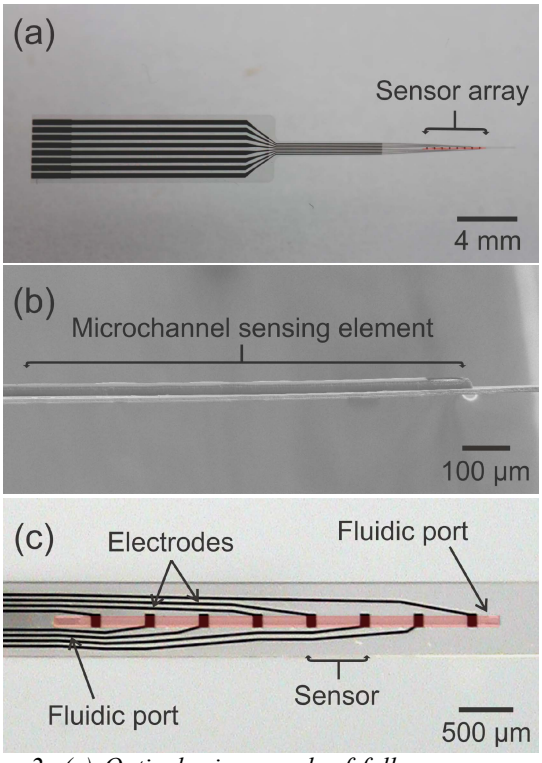


*Figure 2: (a) Optical micrograph of full sensor array and integrated Parylene cable. Microchannel structure is highlighted in pink. (b) SEM image of a sideview of the 20 µm Parylene microchannel sensing structure. (c) Zoomed in top-down image of Parylene microchannel (pink) indicating the electrodes and fluidic ports on opposing ends of the structure.*

The bulk material and mechanical properties of the Parylene-Pt sensors were assessed before and after annealing via scanning electron microscopy (SEM), profilometry, and load-deflection tests of the sensing structures immersed in an electrolyte solution (1x PBS). For load-deflection tests, a motorized z-axis stage and an inline load cell with a flat-tipped deflection probe was used to measure both channel deflection and load forces (Figure 3). A similar testing setup along with real-time electrochemical impedance measurement utilizing a precision LCR meter and LabVIEW graphical user interface was also used to assess device performance by analyzing sensor calibration sensitivities.

Two point electrochemical impedance spectroscopy (EIS; 1x PBS, 20 Hz–1 MHz), a commonly used electrochemical technique to assess electrode surface properties, was used between adjacent electrodes to determine changes to the electrochemical properties of the sensing electrodes.

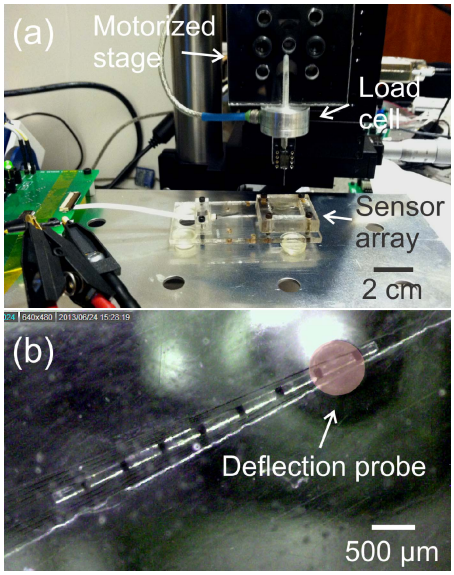


*Figure 3: (a) Load-displacement setup for mechanical and calibration testing of Parylene force sensor array. (b) Optical micrograph taken using a camera underneath testing setup illustrating deflection probe (pink) displacing into sensor element.*

## RESULTS AND DISCUSSION

### Mechanical Characterization

SEM analysis revealed no significant qualitative differences between the two samples (Figure 4a, b). However, profilometric measurements indicated a ~3% reduction in the height (~1 µm) of the microchannel structure following annealing (Figure 4c), analogous to bulk shrinkage effects previously observed in lateral thin film structures [9]. Analysis of the electrode spacing indicated no significant shrinkage of the pitch of the electrodes (data not shown).

Load-deflection tests revealed a ~1.6x increase in the stiffness of the structure following annealing (Figure 5), likely due to a combination of microchannel height shrinkage and an increase in the elastic modulus of annealed Parylene

bulk polymer attributed to increased polymer crystallinity [10].

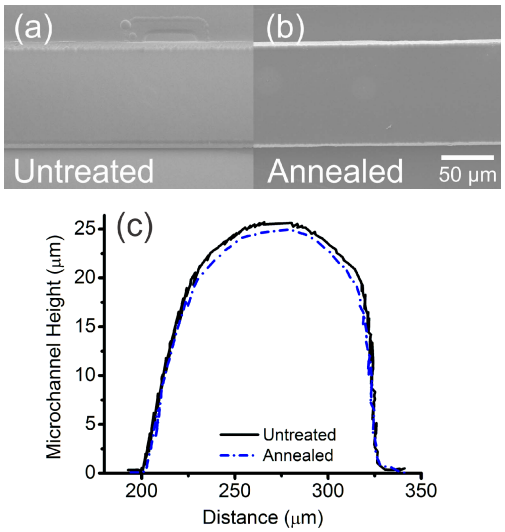


*Figure 4: SEM images of top-down views of (a) untreated and (b) annealed sensing structures. (c) Representative profilometry measurement of untreated and annealed Parylene microchannel sensing structure illustrating ~3% shrinkage following annealing.*

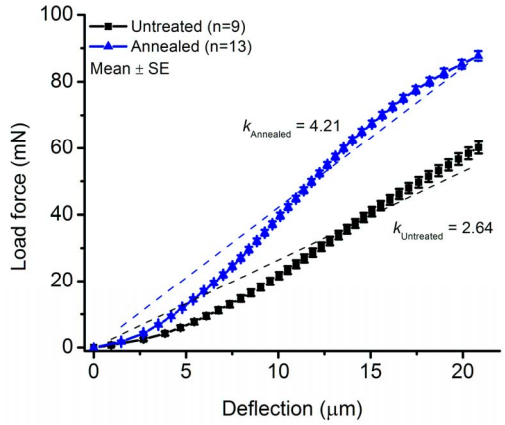


*Figure 5: Results of load-deflection tests comparing untreated and annealed sensors illustrating an increased structural stiffness of ~1.6x after annealing.*

**Electrochemical Characterization**

EIS results indicated a slight increase in the impedance magnitude and narrowing of the phase plot, attributed to a decrease in double layer capacitance, or $C_{dl}$, of the simplified Randles electrode-electrolyte system circuit model (Figure 6a, inset). $C_{dl}$ reduction within the model is often seen as a consequence of the smoothing of the thin-film metal during annealing [11], which removes surface roughness but in turn also reduces electroactive surface area. Despite these slight differences, the measurement frequency (peak of phase plot) remained consistent following annealing (Figure 6b). The minimal effect on the electrochemical properties of the electrodes (relative to the mechanical changes) can be hypothesized to be correlated with electrode size-dependent phenomena in altering electrode surface properties; annealing effects on electrochemical properties of Pt on Parylene electrodes have been demonstrated to be magnified in devices with smaller electrode sizes (Ø = 40 µm) [12].

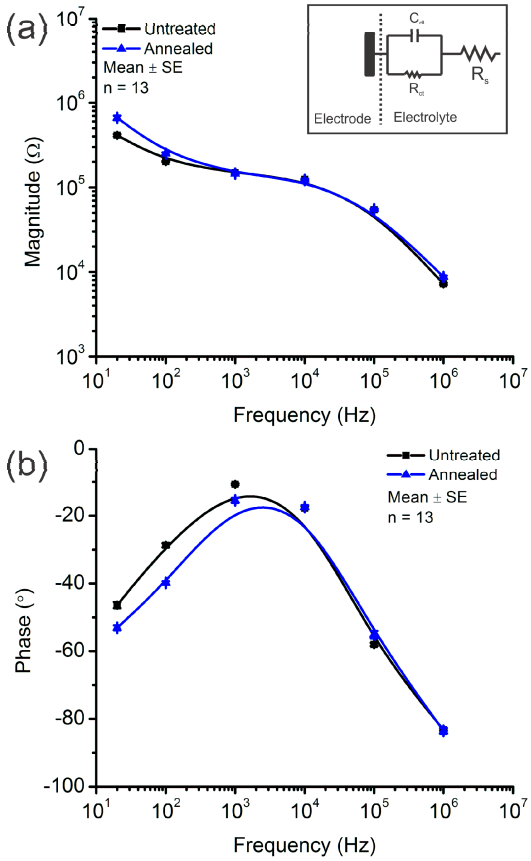


*Figure 6: EIS plots of (a) impedance magnitude and (b) phase for electrodes of untreated (black) and annealed (blue) Parylene sensors. A slight increase in impedance magnitude and narrowing of the phase peak following annealing corresponds to a decrease in the $C_{dl}$ within the simplified Randles circuit model (a, inset). Dashed line in (b) corresponds to the measurement frequency chosen as the peak of the phase plot.*

**Sensor Performance**

A combination of the mechanical and electrochemical changes following annealing significantly altered sensor performance during calibration (Figure 7). Device sensitivity was decreased from $\alpha_{untreated} = 1.25\times10^{-3}$ (normalized impedance/mN) to $\alpha_{annealed} = 9.25\times10^{-4}$ (normalized impedance/mN). A reduction in the sensitivity of the sensor by 24% after the annealing process follows the increase in stiffness of the sensing structure. For a stiffer channel, applied forces induce smaller channel deflections, thus reducing sensor sensitivity. Finite element modeling studies utilizing COMSOL to model the observed changes following annealing elucidated that the increase in stiffness of the Parylene film contributed the most (rather than microchannel

height reduction or decrease in electroactive surface area) to the differences of sensor performance for these devices (data that shown).

Additional work is underway to assess the benefits of annealing on sensor longevity in wet environments via soak testing. Also, previous work has demonstrated annealing temperature dependence on altering the properties of Parylene films [9]; experiments are underway to correlate the degree of intra-Parylene layer adhesion with annealing temperature to determine the optimal process parameters for improving chronic wet performance of multi-layered Parylene devices.

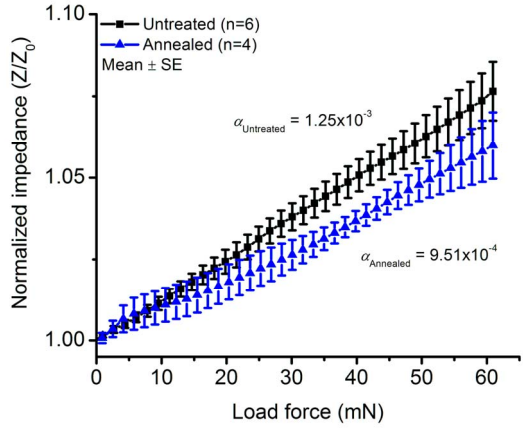


*Figure 7: A marked difference in sensor calibration performance (reduction of ~24%) was observed due to the combination of mechanical and electrochemical effects of annealing on Parylene sensors. Sensitivity (α) units are in normalized impedance/mN.*

## CONCLUSION

Effects of annealing on a Parylene-based force sensor array utilizing the combination of a fluid-filled transduction microchannel and electrochemical sensing scheme was elucidated. Annealing was found to increase the stiffness of the Parylene microchannel, attributed to increased crystallinity of the polymer chains and the reduction of the height due to bulk shrinkage effects, and slightly decrease the electroactive surface area of the Pt electrodes, caused by the smoothing of the thin film metal surface. A combination of these effects was exhibited in a modified sensor calibration curve with a decreased sensitivity of 24% following annealing. The present study demonstrated that high-temperature processes or environments (relative to the glass transition point of the polymer) can modify device performance, which must be considered during sensor design and for proper sensor operation.

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## CONTACT

*E. Meng, tel: +1-213-8213949; ellis.meng@usc.edu