THREE DIMENSIONAL TRANSFORMATION OF PARYLENE THIN FILM STRUCTURES VIA THERMOFORMING

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ABSTRACT

Non-planar, three dimensional structures, not possible with conventional microfabrication processes, were achieved using post-fabrication thermal annealing of thin film Parylene-C structures facilitated by a mold ("thermoforming"). We demonstrate thermoforming of Parylene-Parylene and Parylene-metal-Parylene (PMP) structures for increased structural and mechanical functionality such as strain relief, formation of open-lumen sheath structures, and conformation-matching of curved surfaces that broaden applications for Parylene MEMS. Characterization of the material and mechanical properties as a function of thermoforming temperature is also presented. Thermoformed Parylene consistently retained bulk/surface chemical material properties following the treatment regardless of temperature, and thermoforming at higher temperatures increased structural stiffness, which is attributed to increased crystallinity of the polymer. By varying the thermoforming process parameters, the final shaped structure can be mechanically and structurally tuned for broad range of applications, most notably, structured implantable neural interfaces with integrated channels for tissue ingrowth and improved integration.

INTRODUCTION

Thermoforming of polymers for biomedical applications was previously reported to form microfluidic and lab-on-a-chip devices [1]. Common thick-film thermoplastics, such as polystyrene, were used to achieve substrate material shaping for a variety of applications. Typically, thermoforming processes involve the use of molds and pressure to hold a sample in a specific shape during heating (above its glass transition temperature but below the melting point) which softens the material and facilitates shaping. Subsequently, the cooling process locks in the new shape [1]. Within the thermoforming temperature range, polymeric chains experience increased mobility and are free to move and undergo thermally induced reorganization [2]. Although this process was well characterized for common polymers (e.g. PET, PLA), the potential of this technique for shaping Parylene C, a biocompatible thermoplastic polymer [3], was introduced recently.

Parylene C has garnered much attention as a structural and encapsulation material for biomedical devices attributed to its many favorable features: including biocompatibility, chemical inertness, dielectric properties, moisture barrier properties, and low Young's modulus. Thermal treatment of Parylene-based devices was explored for the micromolding of microchannels [4], hot-embossing of patterns [5], and simple thermoforming of Parylene into curved shapes [6-8]. In addition to the formation of structures, thermal annealing of Parylene C was explored to improve encapsulation and adhesion properties [9]. Here, formation of complex three dimensional (3D) shapes via thermoforming, together with analysis of the resulting surface and mechanical properties of thermoformed Parylene are reported for the first time.

Thermoforming of Parylene C involves heat treatment of the film between the glass transition and melting temperatures, which are ~60-90°C and 290°C, respectively [4]. By annealing Parylene between these temperatures while simultaneously holding the final desired shape, complex, functional structures can be realized. It is important to note that Parylene C undergoes thermal oxidation at elevated temperatures >125°C in an oxygen-rich atmosphere [10]; thus, all thermal treatment must be performed under vacuum with nitrogen backfill to ensure the absence of oxygen.

The utility of thermoforming was realized for shaping an as-fabricated, flat surface-micromachined Parylene channel into a 3D sheath lined with electrodes as an implantable cortical recording probe [11]. In addition to structural shaping, the added benefits of annealing Parylene-Parylene layers, such as enhanced adhesion [12], supports thermoforming as a means to attain 3D structural and mechanical functionality to Parylene-based devices to expand Parylene MEMS applications.

EXPERIMENTAL METHODS

Thermoforming of two multi-layered thin film structures was performed: Parylene-Parylene (dual layer) and Parylene-Metal-Parylene (PMP) sandwiches (Figure 1). These thin film combinations are commonly encountered in practical device structures and were selected for this reason.
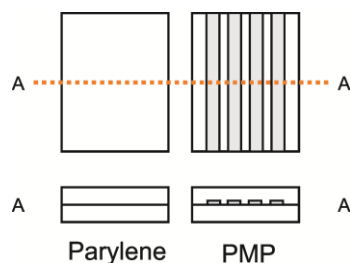

Figure 1: Top and cross-sectional drawings illustrating test samples used in thermoforming experiments: (left) Parylene on Parylene samples and (right) Parylene-metal-Parylene (PMP) sandwiches.

To obtain the final desired shape, films were wrapped around or placed on molds (i.e. stainless steel, aluminum, or tungsten; Figure 2), or held in place with aluminum foil. Fixtured samples were then thermoformed in a vacuum oven (Lindberg/Blue V0914A, 10 mTorr) with nitrogen backfill (10 SCFH). The oven was ramped at a rate of

~1.3°C/min to the desired final thermoforming temperature. Fixtured Parylene samples were annealed for 1 hour at different temperatures (100, 120, 140, 160, 180, and 200°C) to elucidate temperature related effects. Samples were slowly cooled overnight also under vacuum and nitrogen backflow to ensure that thermal degradation does not occur during the cooling process. After cooling, the molds and fixtures were easily removed to reveal the final structure without the use of dedicated release layers.
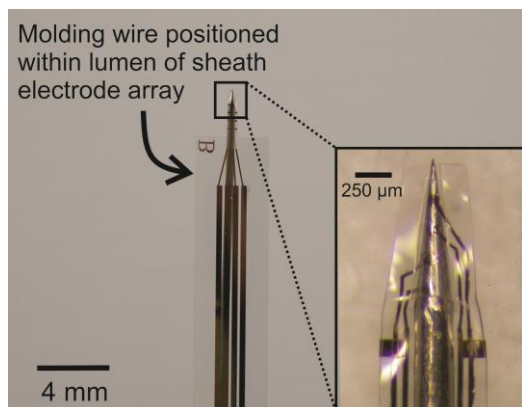

Figure 2: Thermoforming fixture consisting of a microwire inserted into a Parylene channel to form cone shaped sheath electrodes for neural recordings. The microwire was positioned in the lumen of the cone to maintain the final desired shape during the thermal treatment.

Chemical and mechanical properties were characterized as a function of varying temperatures. To assess effects on bulk chemical properties, Fourier transform infrared spectroscopy (FTIR) (Nicolet iS 10 FT-IR Spectrometer) was used to identify any molecular changes or additions to the bulk material following thermoforming. Changes to surface properties were also assessed by measuring contact angle on the heat-treated Parylene surfaces (10 μL droplet, Ramé-Hart Model 290-F1). Mechanical properties, notably molded structure stiffness, were also of interest to see if thermoforming could not only affect structural but also mechanical functionality. Structural stiffness measurements were obtained on thermoformed Parylene cone structures using a nanoindenter (Berkovich tip, MTS Nano Indenter XP).

RESULTS AND DISCUSSION
Thermoformed Structures

Vacuum thermoformed structures intended for a variety of applications were achieved. To form 3D neural interfaces, sheath-shaped structures consisting of Parylene-Parylene and PMP samples were formed by the insertion of a microwire mold into an as-fabricated Parylene microchannel (Figure 3a-c). The 3D shape formed by thermoforming the microchannel is clearly observed in the SEM image (Figure 3b), forming a hollow, tubular structure that would be difficult to fabricate using conventional microfabrication techniques. Thermal treatment of Parylene also yielded bonded PMP structures without the need for applied pressures (Figure 3d). However, the bonded structures contained unbounded voids and did not uniformly survive the scotch tape test indicating the need for additional research to optimize the bonding parameters.
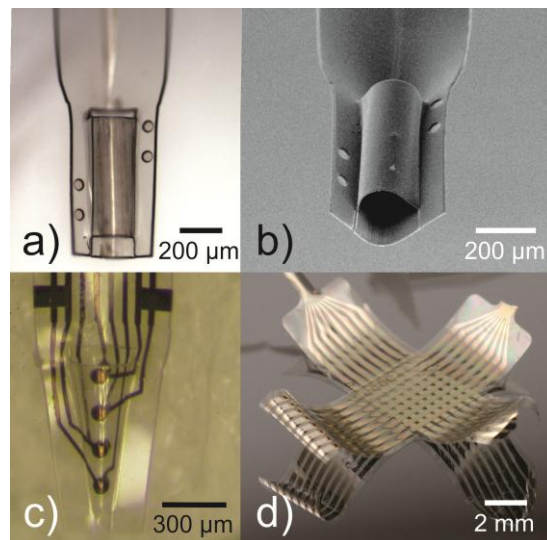

Figure 3: Thermoformed Parylene and PMP samples: (a) cylindrical sheath for promoting neural integration, (b) SEM of cylindrical sheath showing 3D structure, (c) PMP cone for cone shaped sheath electrodes, and (d) curved PMP cables bonded at the central crossing point.

In addition to forming primary structural elements for Parylene-based devices, secondary structures such as a strain-relief coil in Parylene-based flexible cables were demonstrated (Figure 4a). Thermoforming could also be repeated in sequential processes; secondary elements were formed in a second sequential step without affecting the previously molded primary structures (Figure 4b).
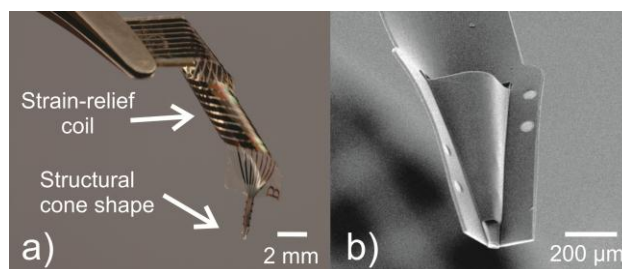

Figure 4: (a) Thermoformed PMP neural probe formed by sequential thermoforming processes where the cone was formed first followed by the strain-relief coil. (b) SEM image of thermoformed cone.

Parylene-based electrode arrays were thermally shaped to allow for conformation matching of physiological surfaces. An electrode array was curled 360° which allows wrapping around nerve fiber bundles (Figure 5a) and a sensor array was curved to match the shape of the retina (Figure 5b).
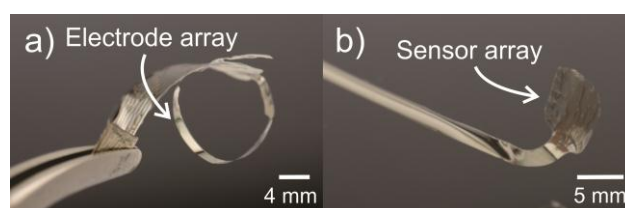

Figure 5: Shaped PMP samples: (a) coiled and (b) curved electrode arrays.

It is important to note that thermoforming is associated with bulk dimensional changes in Parylene. This is of particular concern when the precise pitch of structures after thermoforming must fall within tight tolerances. Direct electrical connections can be established with flexible Parylene ribbon cables using commercially available zero-insertion force (ZIF) connectors [13], but requires a specific contact pad spacing for proper alignment between connector pins and contact pads. However, it was observed that thermoformed PMP samples exhibited altered contact pad pitch that prevented proper pin-pad alignment (Figure 6). Shrinkage was largely limited to inter-lead Parylene spaces and resulted in an overall ~5% reduction of the total lead spacing in thermal-treated samples. This shrinkage error propagates with the increasing number of channels and therefore must be compensated in larger lead count connections. For 32-count linear contact pad arrays in Parylene cables (0.5 mm pitch; Figure 6a), a significant change in dimension was encountered whereas in 8-count arrays (0.5mm pitch; Figure 6b), the dimensional change was tolerated. This shrinkage was accounted for in future versions of Parylene ribbon cables.
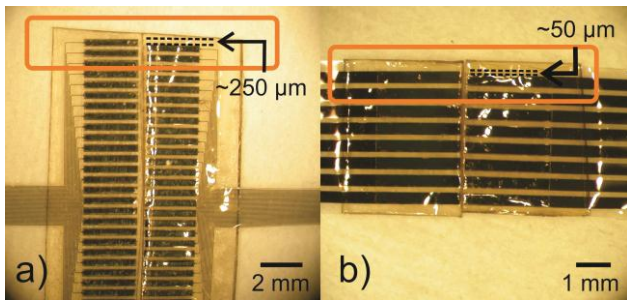

Figure 6: Optical micrographs comparing PMP contact pad arrays shown as-fabricated (left) and after thermoforming (right). (a) Pitch shrinkage observed in thermoformed PMP samples for large lead count (32 channels). (b) Reduced pitch shrinkage observed for 8 channel cable.

In cases where oxygen was inadvertently introduced into the vacuum chamber, oxidative degradation of Parylene was observed. The normally transparent appearance of Parylene would instead be marked by a brownish hue. These samples were noticeably brittle and did not retain the flexibility of samples thermoformed in oxygen-free conditions. Such mechanical changes are undesirable and highlight the importance of the vacuum and nitrogen backfill conditions.

Chemical and Mechanical Characterization

FTIR spectra were acquired on samples treated at low (100°C) and high (200°C) thermoforming temperatures. Compared to the control, no new peaks were observed, indicating that thermoforming does not significantly change bulk chemical functionality (Figure 7). This observation is further supported by contact angle measurements. Samples treated across a range of thermoforming temperatures exhibited similar measured contact angles differing only by a few degrees and indicated that the surface energies (hydrophobicity) were relatively unchanged following thermal treatment (Table 1). These results suggest that the thermoformed films remain largely unchanged in their bulk and surface chemical properties.

Mechanically, the treated films exhibited changes in stiffness, which were noted qualitatively and quantitatively. The stiffness of shaped sheath structures processed at different temperatures was measured and compared to that of a mechanically opened sheath that was not thermally treated. Increased stiffness of the formed structure was observed as a function of increasing thermoforming temperature (Figure 8). This is consistent with reports in literature in which the stiffness increase arises from an increase in film crystallinity following thermal treatment due to the development of additional crystalline domains within the polymer's amorphous regions [14] and the introduction of a new second crystalline phase [2]. It was also reported that the film crystallinity increases with increasing treatment temperature; this is confirmed by structural stiffness results, where a sample thermoformed at 200°C exhibited a measured stiffness increase up to sixty times that of an untreated sample. Thus, mechanically tuning a thermoformed structure to the required stiffness is possible by selecting the appropriate annealing temperature.
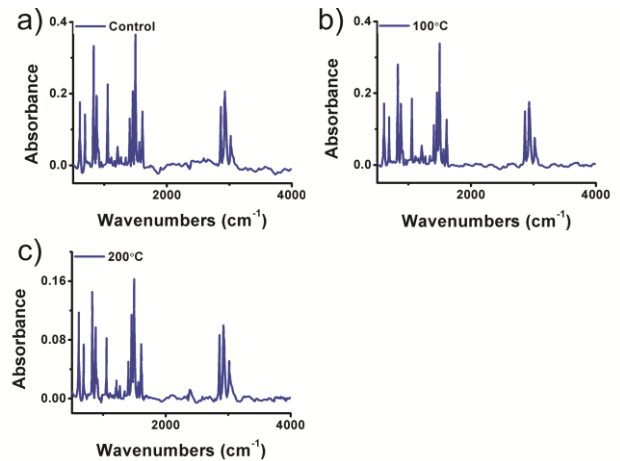

Figure 7: FTIR spectra of (a) untreated Parylene film (control) and films after thermoforming at (b) 100°C and (c) 200°C for 1 hour indicating no bulk chemical changes in the material following thermal treatment.

Table 1: Measured contact angles of thermoformed samples indicating insignificant surface energy changes.

Treatment Temperature (°C)	Contact Angle (°)
Control	80.3
100	75.8
120	80.2
140	77.8
160	79.1
180	85.8
200	82.1

The effect of increased crystallinity due to thermoforming also contributes additional benefits specific to long term reliability for chronic *in vivo* applications; more crystalline films were reported to possess greater tensile strength, improved thermal resistance [14], and improved water barrier properties [2].

CONCLUSION

A post-fabrication, thermal molding ("thermoforming") process was developed to form non-planar, 3D structures with high aspect ratio from Parylene thin films that would otherwise be difficult to attain with standard planar microfabrication processes. Thermoforming was conducted under a vacuum environment with temperatures above the glass transition and below of the melting temperatures of Parylene C, and resulted in 3D structures with wide applicability, including bonded and shaped structures, and those formed in sequential steps. The effects of thermoforming on the chemical and material properties were characterized. Thermoformed results retained bulk/surface chemical properties and exhibited increased mechanical stiffness due to increased crystallinity at higher temperatures. These results indicate the potential to achieve structures with a broad range of mechanical stiffnesses simply by controlling thermoforming parameters.
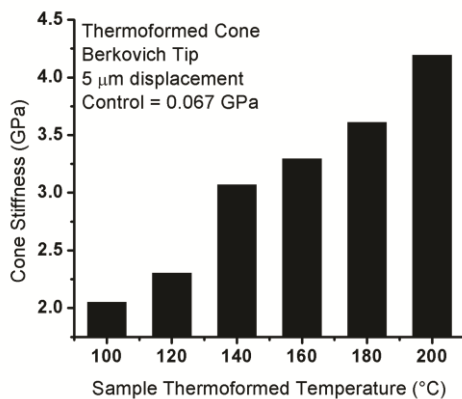

Figure 8: Stiffness measurements of thermoformed Parylene cone structures obtained from nanoindentation measurements. As the treatment temperature is increased, the cone stiffness also increases, demonstrating the increased rigidity of the final thermoformed structure.

Additional experiments are being performed to study the relationship between treatment temperature and duration to further tune the thermoforming process to achieve specific mechanical qualities and investigate improvement of moisture barrier capabilities, especially for *in vivo* applications.

ACKNOWLEDGEMENTS

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