Characterization and Modification of Adhesion in Dry and Wet Environments in Thin-Film Parylene Systems

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Abstract—**Parylene C is a thin-film polymer used as a bio-compatible barrier layer in biomedical implants and implantable MEMS; free-film Parylene C may serve as both the substrate and insulation in polymer-based microdevices, a growing branch of biomedical technology. The adhesion of vapor deposited Parylene C, particularly when exposed to wet, *in vivo* environments, is a critical determinant of device lifetime for such polymer-based implants. This paper explores several novel strategies for improving the adhesion of multi-layer Parylene structures, including thermal annealing and the use of several chemical interposer layers. Interfacial adhesion of Parylene-Parylene and Parylene-platinum-Parylene films was examined using a standard T-peel test to quantify adhesion and measure film integrity under chronic exposure to saline up to two years. Improved adhesion and barrier properties in Parylene-Parylene films resulted from the inclusion of diamond-like carbon and ethylene glycol diacrylate layers. Thermal annealing improved Parylene film integrity in wet environments but was insufficient for improving the integrity of Parylene-platinum interfaces. A 100-fold increase in adhesive strength at such interfaces was achieved using a commercially available adhesion promoter, and the corresponding improvements in resistance to moisture driven delamination were observed. X-ray diffraction and X-ray photoelectron spectroscopy results are provided to highlight the role of film morphology and surface composition in adhesion integrity.** [2018-0076]

Index Terms—Adhesion, AdPro Plus®, annealing, DLC, EGDA, Parylene, T-peel test, XPS, XRD.

I. INTRODUCTION

PARYLENE C, referred to here as Parylene and known generically as poly-(para-chloro-xylylene), is a semicrystalline hydrophobic polymer formed as a thin, conformal, and pinhole-free film using a unique chemical vapor deposition (CVD) technique. Parylene is recognized for its chemical inertness, electrical resistivity, low moisture permeability, and proven biocompatibility. For several decades, thin Parylene coatings have been used as waterproof insulation for electronics intended for use in harsh environments, a category that now increasingly includes biomedical implants. Parylene has been used extensively to coat silicon, metal, and glass surfaces intended for extended *in vivo* use, including neural recording probes [1], coronary stents [2], implantable electronics [3], [4] and dental implants [5]. In addition, Parylene is used as a substrate material from which to microfabricate biomedical implants because of its low Young's modulus and flexibility. Despite well touted barrier properties, Parylene coatings and thin film Parylene devices exposed to wet environments for extended durations can suffer from moisture permeation and delamination; this limitation has motivated a significant body of work seeking to improve the lifetime and reliability of these coatings by increasing the strength of Parylene adhesion to surfaces of interest. Many strategies have been investigated to improve Parylene adhesion, including physical modifications (e.g. melting, anchoring, surface roughening), thermal modifications (e.g. annealing), chemical modification (e.g. surface plasma treatment) and inclusion of chemical interposer layers (e.g. silane A-174 and plasma polymerized adhesion layers) [6]–[8]. An exhaustive search of literature reported techniques, with mechanical tensile and peels strength serving as a proxy for coating adhesion, is summarized in the supplemental material.

Due to its widespread use in biomedical implants, Parylene has emerged as a key material in the growing field of polymer-based biomedical microdevices comprising microelectronic, microfluidic and micromechanical systems wherein the bulk structure is composed of the thin-film, flexible polymer. Examples include polymer-based neural probes [9], [10], cochlear implants [11], [12], retinal electrodes [13], [14], and pressure sensors [15], [16]. Devices frequently feature a simple symmetric design: a base layer of flexible polymer, a thin layer of patterned metal (frequently platinum), and a top, insulating layer of polymer. This approach is motivated by evidence that reductions in size and mechanical rigidity of an implant can mitigate the physiological foreign body response, and enable chronic *in vivo* performance. Thin and flexible polymer-based devices offer an enticing alternative to rigid and sharp implants of silicon and metal, and Parylene, owing to its extensive history in biomedical applications and compatibility with standard micromachining processes, is a prime choice among available materials [14], [17]–[19].

TABLE I

COMPARISON OF WET ADHESION FORCES REPORTED IN THE LITERATURE FOR PARYLENE INTERFACES

Test	Interface	Adhesion Treatment	Force	Environment	Reference
Tensile	Pt/PxN	None	~0.15 Pa	3 hrs in boiling saline	[42]
		GDMP	~3.3 Pa	2 hrs in boiling saline	
	Si/PxC&PxC/Si	230 ºC, 30 min, 800 N	> 2.98 MPa	1 week in acetone	[29]
			> 3.45 MPa	1 week in IPA	
			> 1.63 MPa	1 week in BHF	
			> 1.15 MPa	1 week in AZ400k	
			> 2.51 MPa	1 week in MF319	
Peel 90º	Cr/PxC	None	0	30 min in PBS at 37 º C	[32]
		140 ºC, 3 h	0		
		X	20 mN/mm		
		X, 140 ºC, 3 h	150 mN/mm		
	Au/PxC	Ti	35.5 mN/mm	48 hrs in PBS	[39]
	Au/PxC	DLC	6.3 mN/mm		
	Au/PxC	Ti/SiOx	5.1 mN/mm		
	Au/PxC	A-174	157.5 mN/mm		
	Au/PxC	TMS	Delaminated		
	Ti/Pt/PxC	O$_2$ plasma	70 mN/mm	1 h in boiling saline	[41]
		O$_2$ plasma + TMS	210 mN/mm		
		Ar plasma + TMS	210 mN/mm		
Peel 180º	PxC/PxC	None	10 mN/mm	30 min in PBS at 37 º C	[32]
		140 ºC, 3 h	>100 mN/mm		
		X	2 mN/mm		
		X 140 ºC, 3 h	3 mN/mm		
	PxC/PxC	None	210 mN/mm	24 hrs in PBS at 37 º C	[37]

GDMP = glow discharge polymerized methane
PxC = Parylene
PBS = phosphate buffer solution
PxN = Parylene N
TMS = trimethylsilane
X = CH$_2$NH$_2$ or CHO, aldehyde and aminomethyl side group

As with examples of Parylene coated rigid structures, thin-film Parylene devices are also subject to delamination after extended exposure to wet, *in vivo* conditions. While a few reports describe Parylene-based thin-film devices functioning *in vivo* for longer than a year [9], these examples are uncommon. Numerous reports describe moisture intrusion and subsequent delamination of Parylene films over periods of weeks and months. These failure modes reflect poor adhesion of CVD Parylene to pre-deposited Parylene films, or at Parylene-metal-Parylene interfaces [20]–[22]. Adhesion between Parylene layers is dominated by physical adsorption and, to an extent, chemical reaction with free radicals, whereas adhesion at Parylene-metal interfaces is typically mediated by a combination of hydrogen bonding and Van der Waals forces [18], [23], [24]. In either case, the formation of chemical bonds through use of an intermediary linker is possible. For example, Driesche *et al.* [25] have reported the use methacrylate-based coupling agents to support Parylene-gold adhesion. Without the use of such an adhesion promoter bonds are easily broken by water molecules, creating a serious problem under *in vivo* conditions where the interfaces encounter bodily fluids [23]. Delamination under wet conditions may be induced by water vapor condensing within voids created by surface particulates present during CVD [4]. Stringent attention to surface cleanliness may reduce the risk of this phenomenon, but even when deposited under cleanroom conditions, Parylene coatings still exhibit voids in which water vapor can nucleate and condense. In addition, there are reports that coating failure can be hastened by application of electric current across insulated

metal features [20], [22], the action of compounds generated during inflammatory responses [26], and the presence of internal stress between layers [27]. Parylene structure and adhesion can likewise be effected by the chemical and physical demands of typical sterilization processes, required for clinical use *in vivo* [28].

While there are many proposed methods for improving adhesion between Parylene and non-polymeric substrates, there are relatively few reports describing methods to improve Parylene-Parylene adhesion [29]–[37] or Parylene-metal-Parylene adhesion [8], [31], [32], [35]–[43] in thin-film devices, and robust chronic adhesion remains elusive. Table 1 shows the techniques reported in the literature for improving Parylene adhesion to different materials under 'wet' conditions, referring to chronic exposure to water and/or saline. Table S1 summarizes an exhaustive search of the literature for methods to improve adhesion under dry conditions. By far the most common approach is the use of thermal annealing [10], [13], [27], [44]–[48]. The application of temperature and pressure during annealing can induce polymer-polymer bonding through entanglement of polymer chains [29], [30], and the high temperature can alter Parylene crystal structure, limiting the rate of moisture diffusion [27], [49]. Less common are reports of chemical linkers or adhesion promoting layers appropriate for Parylene multilayer structures. While silane A-174 (3-trimethoxysilylpropyl methacrylate) is commonly used to improve Parylene adhesion to glass and silicon, the adhesion mechanism relies on the presence of hydroxyl groups absent from Parylene surfaces, and as such the

compound does not promote strong adhesion between Parylene layers [31]. Also, A-174 cannot be used when sacrificial photoresist layers are present [50]. Other chemical adhesion layers have been presented to aid Parylene coating of metals such as gold through a thiol-linker group [25]. Currently, there is no commercially available chemical linker demonstrated to improve Parylene-Parylene bonding. An alternative approach entails the use of non-linking interposer layers; under this approach a thin-film is deposited prior to CVD Parylene, which improves adhesion and/or operational lifetime by modifying surface energy, providing improved barrier properties (see work with Al_2O_3 [37]), or supporting adhesion to an intermediate layer (e.g. thin-film metal). Plasma-polymerized films have been used for years to improve the properties of Parylene coated bulk metal structures [8], [23], [51], though once again there are scant references to this approach for thin-film polymer-based devices.

There is no commercially available compound, or state-of-the-art protocol, established that adequately improves Parylene-Parylene thin-film adhesion, beyond the broad recommendation to thermally anneal Parylene films. Several ideas presented or proposed in the literature, including plasma treatments and interposer layers [8], [31], [36]–[39], have not been rigorously compared and most have not been tested under chronic wet conditions. This represents a critical deficit in current research, as thin-film polymer-based microdevices are increasingly proposed for biomedical implantation because they are soft and flexible, yet moisture intrusion and delamination remain frequently reported failure modes.

This study investigates and characterizes strategies to improve the adhesion of Parylene-Parylene films and to extend the operational lifetime of thin-film Parylene devices under chronic exposure to moisture, specifically in a simulated physiological saline environment. The purpose is to advance realization of a reliable, generalizable method. This work has specific application to the creation of polymer-based microdevices intended for chronic *in vivo* implantation. We compared a combination of thermal annealing strategies and the use of several interposer films. Samples of Parylene-Parylene bilayers were prepared with different adhesion strategies; the adhesive strength of those interfaces were measured quantitatively under 'dry' conditions, and as a function of soaking duration in warm saline (simulated *in vivo* conditions) for up to two years. We measured adhesive strength with 180° T-peel test, and recorded the number of days of exposure in a 'wet' environment before each strategy failed. The efficiency of thermal annealing was examined as function of annealing time, and we report x-ray diffraction data as an examination of the corresponding morphological change in the Parylene films. Three chemical interposer layers were selected: amorphous diamond-like carbon (DLC), ethylene glycol diacrylate (EGDA), and a proprietary commercial compound sold under the brand name AdPro Plus®. DLC and EGDA have been previously reported to improve the barrier properties of flexible polymer films, though there is no quantitative report of their effect on Parylene-Parylene adhesion. These materials were included as they hypothetically offer improved adhesion and/or moisture barrier properties [52]–[55]. AdPro Plus® is a Parylene-metal

TABLE II
MATERIAL COMBINATIONS

Interface	Abbreviation
Parylene-Parylene	PP
Parylene-platinum-Parylene	PMP
Parylene-AdPro Plus®-platinum-Parylene	PAdMP
Parylene-platinum-AdPro Plus®-Parylene	PMAdP
Parylene-AdPro Plus-platinum-AdPro Plus®-Parylene	PAdMAdP
Parylene-ethylene glycol diacrylate-Parylene	PEGDAP
Parylene-diamond-like carbon-Parylene	PDLCP

adhesion promoter designed to improve adhesion of noble metals to Parylene C and is the only promoter designed specifically for this function to our knowledge. We compared the adhesive strength and operational lifetime of Parylene-Parylene films with interposer layers of DLC and EGDA, and interposer layers of platinum supported by AdPro Plus®. Platinum was chosen owing to its widespread use in polymer-based biomedical microdevices, a result of its high biocompatibility and corrosion resistance. For purposes of control we also examined the adhesion strength and operational lifetime of Parylene-platinum-Parylene films without AdPro Plus®, and with and without thermal annealing treatments. Devices were prepared with large area coverage of platinum films, an unfavorable scenario compared with functional thin-film devices, which feature very limited exposed metal.

While the formulation of AdPro Plus® is proprietary and not disclosed, we provide an empirical examination of its performance compared with experimental controls: thermal annealing treatments common in current research, and EGDA and DLC interposer layers, strategies motivated by recent academic research. This work represents the most rigorous examination of strategies to improve adhesion in multi-layer Parylene-Parylene devices.

II. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

This study examined wet and dry adhesion in Parylene-Parylene and Parylene-platinum-Parylene film systems. Table 2 lists the seven material combinations prepared and tested along with corresponding abbreviations used in this article.

A. Sample Fabrication

Test structures for T-peel testing were fabricated using common polymer micromachining techniques. Structures consisted of a well-defined bonded area (4.3 × 3 mm) connected to two Parylene flaps (12 μm thick) each perforated with a 3.3 mm clamping hole (Fig. 1).

Figure 2 illustrates the layer-by-layer process by which samples were prepared. First, Si carrier wafers were dehydrated at 110 °C then coated in a base layer of Parylene (12 μm) by CVD (PDS 2010, Specialty Coating Systems (SCS), Indianapolis, IN) (Fig. 2a). PMP samples were prepared by sputter depositing platinum (2000 Å, LGA Thin Films, Santa Clara, CA) through a photoresist mask (2 μm, AZ 5214 E-IR; Integrated Micro Materials, Argyle, TX) followed by lift-off
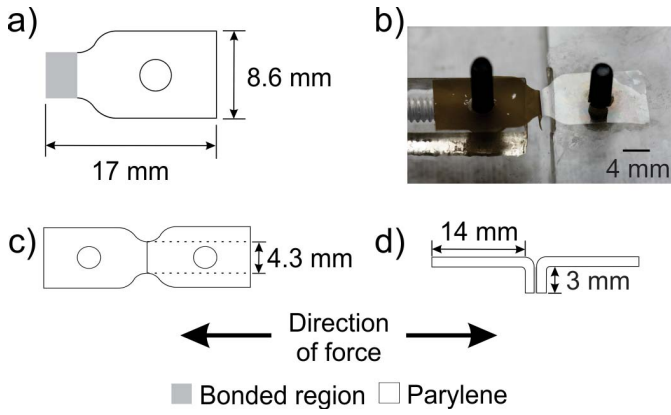
Fig. 1.   a) Sample schematic of T-peel test structure, b) test structure in T-peel pulling apparatus, and c) top and d) lateral views of a sample under testing.
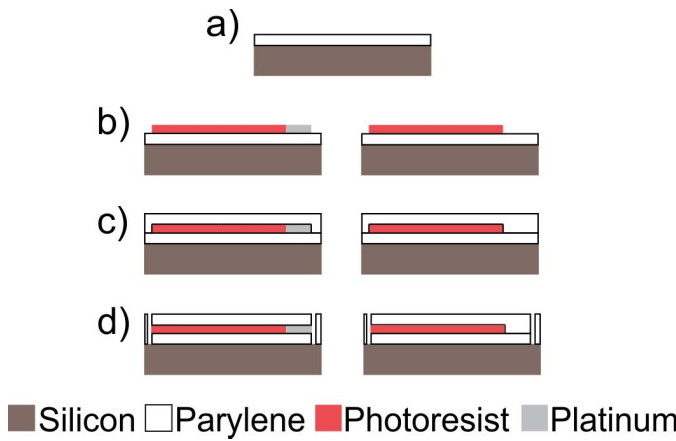

Fig. 2.   Cross-sectional view of the fabrication process for PMP (left) and PP (right) T-peel tests samples.

to define the bonded area. A 4 μm thick film of photoresist (AZ 4400; AZ Electronic Materials, Branchburg, NJ) was patterned lithographically to create a sacrificial spacer (Fig. 2b), prior to depositing the top Parylene layer (12 μm) by CVD (Fig. 2c); the sacrificial layer assisted separation of the two Parylene layers containing the clamping regions. The sample outline and clamping holes were etched using O$_2$ reactive ion etching (100 W:100 mTorr:5 min cycles; RIE-80 Plasma Etching System, Oxford Plasma Technology, UK) through a thick photoresist mask (30 μm, AZ 4620; AZ Electronic Materials, Branchburg, NJ) (Fig. 2d). The sacrificial photoresist was removed with acetone, and then the released samples were rinsed with isopropanol and water (Fig. 2e).

B. Adhesion Layers

1) Ethylene Glycol Diacrylate: Ethylene glycol diacrylate is a cross-linked anchoring layer that can be grafted to a Parylene surface by initiated chemical vapor deposition (iCVD). This technique allows for thin, uniform films to be deposited conformally in a single step and without use of solvents [56]. EGDA was selected for investigation as a Parylene-Parylene adhesion layer, owing to recent reports

demonstrating EDGA films as durable and moisture resistant when grafted to Parylene, despite a 30-day soak in 1× phosphate buffered saline (PBS) [52]. PEGDAP samples were prepared using an iCVD process described in detail elsewhere [52], [56], [57] in which a benzophenone photoinitiator is used to attach a thin (10-20 nm) EGDA film to the base Parylene layer. Successful EGDA deposition was confirmed by a decrease in water-droplet contact angle, indicating a more hydrophilic surface (55° ± 2°, compared to 90° typical for native Parylene) [52]. Samples were then processed to completion as described in A, with care taken to avoid any cleaning or surface treatment after EGDA deposition.

2) Diamond-Like Carbon: Diamond-like carbon (DLC) is a conformal, hard, chemically inert, and low friction coating consisting of an amorphous form of carbon with diamond bonds [53], [58]. Because of its potential as a barrier layer, this film was also evaluated as a potential adhesion promoter in Parylene-Parylene films. The 0.23 μm thick film was deposited by Morgan Advanced Materials using ion-beam plasma-enhanced CVD with a hydrogen concentration ranging from 30% to 40%. After receiving the coated wafers, the DLC film was cleaned by O$_2$ plasma, and samples were then processed to completion as described in A.

3) AdPro Plus®: AdPro Plus® is a biocompatible, proprietary adhesion promoter available from Specialty Coating Services, designed to improve adhesion between Parylene and metals, such as, platinum, titanium, gold, etc. [21]. Wafers were sent to SCS for treatment with AdPro Plus® and deposition of the bottom and/or top Parylene layers depending on the interface, then returned for final processing. Samples were prepared with AdPro Plus® at each Parylene-platinum interface, and samples were prepared with the adhesion promoter present at both interfaces. No cleaning or surface treatment was performed after the promoter deposition to avoid removal or damage of the AdPro Plus® layer.

C. Thermal Annealing

A subset of test structures was thermally annealed in an attempt to improve adhesion between layers and reduce moisture permeation, by way of an induced change in crystallinity and pore size. Several annealing durations were evaluated to determine the effects of annealing on the adhesion of PP and PMP samples. As reported by Charmet *et al.* [7], heating Parylene above its melting point results in an amorphous morphology which is susceptible to moisture intrusion, thus samples were annealed at 200 °C for 24, 48 and 72 hours under vacuum, then cooled to room temperature overnight. The use of a vacuum was necessary to prevent oxidation of Parylene, which occurs at temperatures higher than 125 °C in the presence of oxygen [59]. During the annealing process, flaps of the T-peel structures were separated using a Teflon film to avoid thermal bonding of the layers.

D. T-Peel Tests

Adhesive strength was measured using a T-peel test based on ASTM standard D1876-08 [60]. Test structures were peeled apart at 180° using a custom motorized stage while force
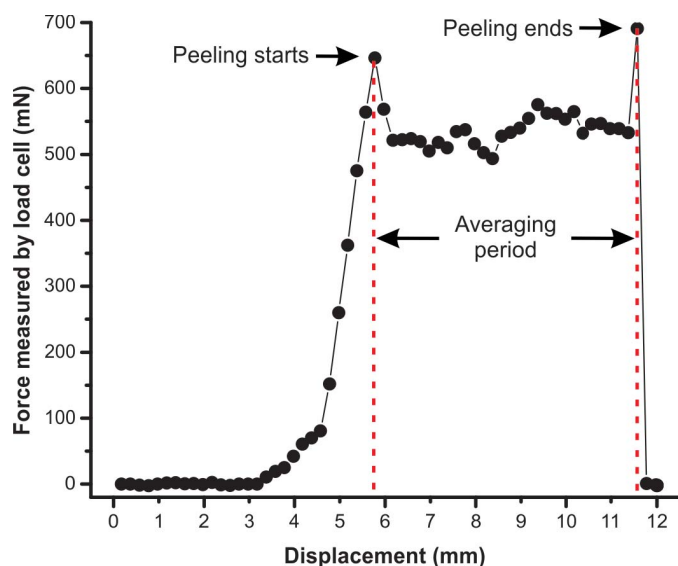
Fig. 3.   Representative raw T-peel test data.

Fig. 4.   XRD 2θ scans of un-annealed and annealed Parylene films.

was measured using a 50 g load cell (Omega, Stamford, CT, USA). Samples were clamped onto the stage with one end fixed to a stationary post and the other to a movable post driven by a stepper motor. The motorized stage was driven at 2 mm/sec to slowly peel apart the interface at the bonded region (Fig. 1). A characteristic T-peel measurement is shown in Fig. 3. The force registered by the load cell increases as the bonded area begins to peel (first peak), then stabilizes to a relatively constant force during peeling, and drops to zero as the interface is fully separated.

The peeling strength (mN/mm) is defined as the mean force recorded on the load-cell, averaged over the period between local maximums which denote the start and end of the peeling (marked by dashed red-lines in Fig. 3), divided by the width of the bonded area. Four samples from each experimental group were tested without exposure to solution (exempting PDLCP, for which only two samples were measured), and four samples were tested at each time point in the soaking study (as described in E).

E. Long-Term Soaking Study

Approximately 60 samples of every combination of experimental parameters (14 experimental groups in total) were immersed in 1× concentration PBS at 37 °C to mimic physiological conditions. The degradation of the bond was measured by T-peel test at time points 1, 4 and 7 days during the first week. Then, samples were tested weekly for a month, and then monthly for 2 months. After completion of a 3-month soak, samples were tested every 3 months until the samples delaminated or until 1 year had elapsed. Then, samples were tested every 6 months until delamination or until 2 years had elapsed.

F. XPS

After T-peel tests Parylene interfaces were cleaned and rinsed with isopropanol and deionized water, then analyzed
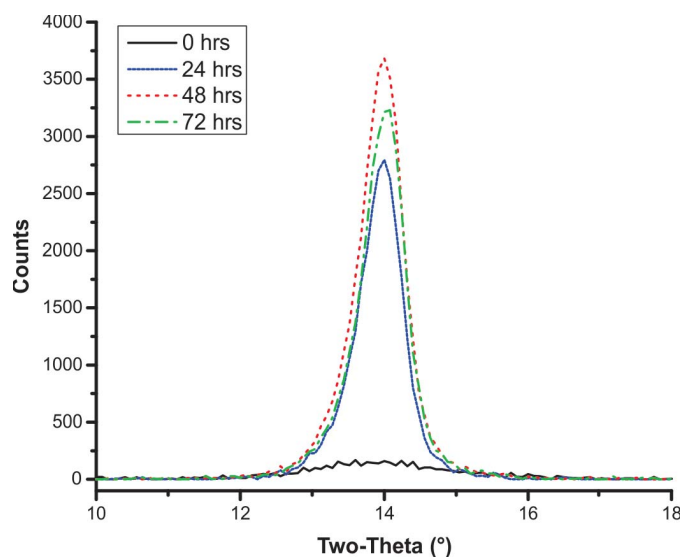
using X-ray photoelectron spectroscopy (XPS), to determine fractional atomic composition. The XPS measurements were performed with a Kratos Axis Ultra DLD instrument (Kratos Analytical, UK) with a monochromatic Al Kα x-ray source, and probed the top 5 nm of each surface.

G. XRD

The crystallinity of Parylene films, prior and post annealing, was characterized by X-ray diffraction (XRD), using an Ultima IV Powder Diffractometer (Rigaku, USA). Glass slides were coated with 12 μm of Parylene and were cleaned with isopropanol and deionized water prior to measurements. The scans were measured from 10° to 18° (incident angle) in order to measure the Parylene diffraction peaks, which are known to appear around 14° [61].

III. RESULTS

A. Crystallinity/XRD Analysis

The XRD spectra of un-annealed and annealed Parylene films for different anneal times is shown in Fig. 4. The diffraction peaks appeared at $2\theta \approx 14°$ for all tested samples.

The crystallite size of the Parylene films was calculated using Scherrer's equation, which is given by:

$$\text{Crystallite size} = \frac{0.9\lambda}{\text{FWHM} \cos\theta} \tag{1}$$

where λ is the wavelength of Cu Kα X-ray source, FWHM (full width half maximum) is derived from the measured peak, and θ is the Bragg angle (degree of the diffraction peak). The FWHM values were calculated by fitting a Gaussian function to the peaks using OriginPro software (Northampton, MA).

The FWHM decreased as anneal time increased, whereas the crystallite size of un-annealed Parylene increased after a 24-hour anneal and then was unchanged for 48 and 72 hour anneal. The percentage of crystallinity is related to the intensity of the Bragg peak as the peak intensity increases the

TABLE III
PROPERTIES OF PARYLENE (N=1) AT DIFFERENT ANNEAL TIMES

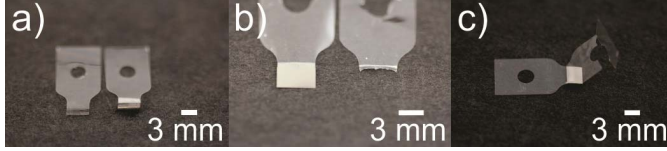| Anneal Time (hours)	FWHM (°)	Crystallite Size (nm)
0	2.07±0.02	3.94±0.08
24	0.74±0.02	11.11±0.60
48	0.75±0.02	10.88±0.58
72	0.74±0.02	11.08±0.60

Error bars reflect instrument precision.

Fig. 5. Failure modes presented at day 0 during testing for a) typical PMAdP peeled apart sample with no tearing, b) PMAdP sample torn at the interface and b) 48h-annealed PAdMAdP sample torn at the clamping hole.

crystallite concentration in the polymer increases as well [61]. The percentage is calculated as the ratio of the area of the crystalline peak to the whole area, amorphous plus crystallized area [62], [63]. Thus, the film that was annealed for 48 hours has the greatest percentage of crystallinity.

B. T-Peel Tests

Thermal annealing resulted in dramatic increases in the peeling force for the majority of the experimental groups, and increased the stiffness of the Parylene layers. As such, while most samples peeled apart at the bonded interface during T-peel testing (Fig. 5a), we also observed two modes of failure: tearing at the interface (Fig. 5b) and at one of the clamping holes (Fig. 5c). This was observed for several PP, PMP and PEGDAP samples, and therefore the reported values must be strictly considered a lower bound of peeling strength.

C. Parylene-Parylene Samples

The adhesive strength of PP samples as a function of annealing time is presented in figure 6a for samples annealed for a duration of 24, 48, and 72 hours at 200 °C. The mean force required to peel apart PP samples increased from ~38 to ~74 mN/mm following a 24-hour anneal, increased further to ~155 mN/mm following a 48 hour anneal, and diminished for a 72 hour anneal. These samples were not subject to long-term soaking and thus these experiments are referred to as dry testing.

Fig. 6b shows how adhesive strength decreased as a function of total time immersed in saline. Un-annealed samples suffered a catastrophic loss in adhesion following just a single day of soaking, and delaminated completely after 4 weeks, whereas annealed samples exhibited greater moisture resistance and longer lifetimes. The 48-hour annealed samples notably maintained minimal to no loss in adhesion over 2 years. Owing to the results of these experiments, a 48-hour anneal was used in all subsequent testing where annealed samples were prepared.
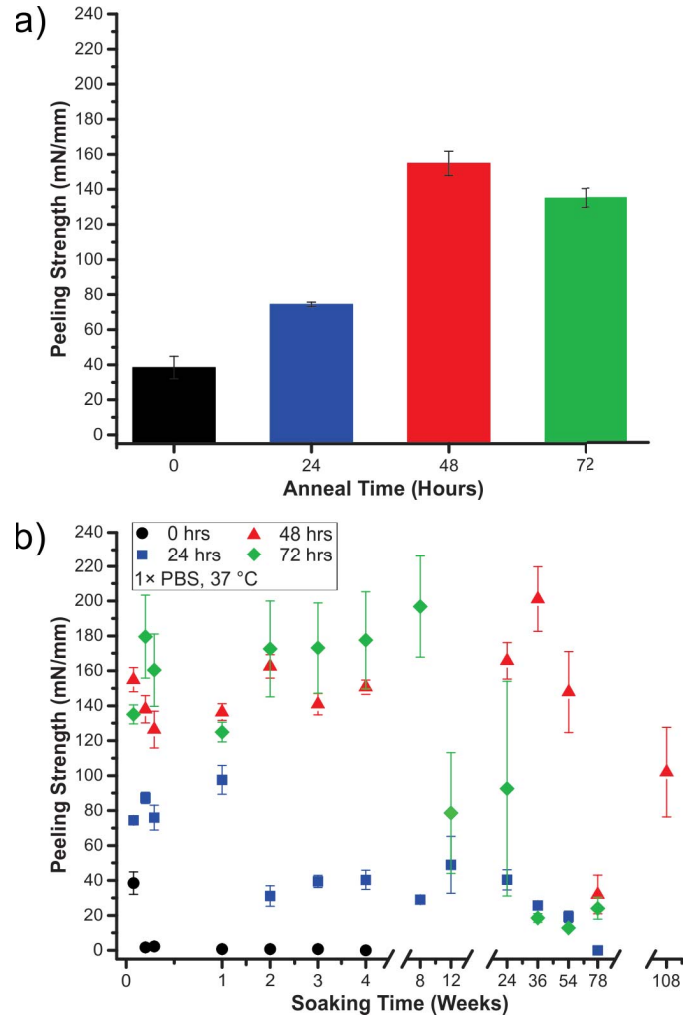

Fig. 6. Average force per unit length required to peel apart annealed and un-annealed samples of Parylene-Parylene layers (mean±SE, n=4): a) peeling strength as a function of thermal annealing time for dry samples, and b) peeling strength as a function of time soaked in warm saline.

D. Parylene-Platinum-Parylene Samples

The inclusion of metal (specifically platinum) between Parylene layers resulted in a dramatic decrease in adhesion; un-annealed PMP samples were peeled apart with just ~3 mN/mm prior to soaking (Fig. 7a), while soaked samples delaminated after just 4 days in saline (Fig. 7b). Annealing significantly increased adhesion (to a peeling force of ~22 mN/mm), however, even annealed PMP samples exhibited weaker adhesion than un-annealed Parylene-Parylene samples. Annealed PMP samples exhibited gradual adhesion loss during soaking and delaminated after 3-weeks.

Figure 8 shows the different mechanisms of adhesion failures for annealed (Fig. 8a) and un-annealed (Fig. 8b) PMP samples, after 3 weeks and 4 days, respectively. In annealed samples, the metal film delaminated completely from both base and top layers of Parylene. Wrinkling of the metal film demonstrated that significant stress was introduced by the annealing process. In un-annealed samples, the top (second) layer of Parylene consistently separated from the metal film,
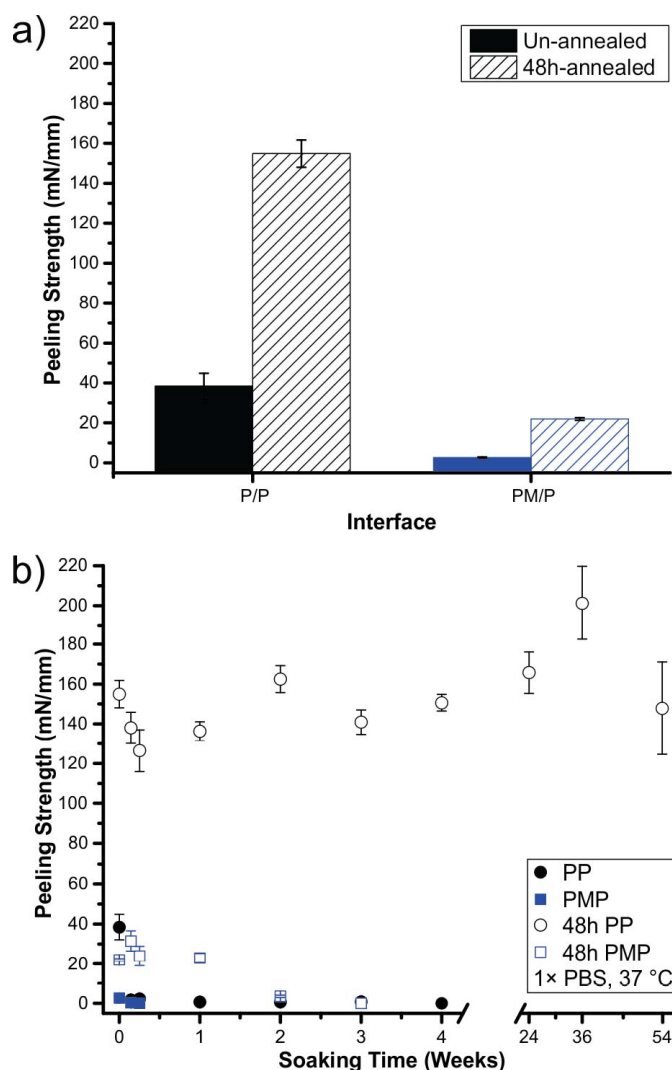
Fig. 7. Average force per unit length required to peel apart annealed and un-annealed samples of Parylene-Parylene (PP) and Parylene-platinum-Parylene (PMP) layers (mean ± SE, n=4): a) Peeling strength of dry samples; b) Peeling strength as a function of time soaked in warm saline.
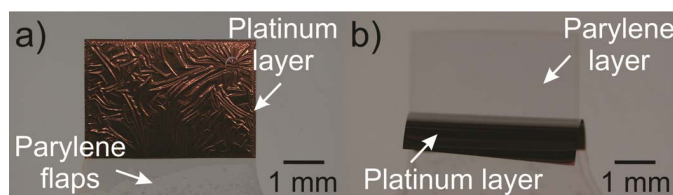

Fig. 8. Delaminated a) 48h-annealed and b) un-annealed PMP samples after a 3-week and 4-day soak in PBS, respectively.

while the adhesion between the metal film and base (first) layer of Parylene remained intact.

E. Parylene Samples With Adhesion Layers

Un-annealed samples with EGDA and DLC adhesion layers exhibited improved adhesion, compared to un-annealed Parylene-Parylene samples. The mean peeling force for un-annealed PEGDAP and PDLCP samples was ~99 and ~58 mN/mm respectively (Fig. 9a). Annealing
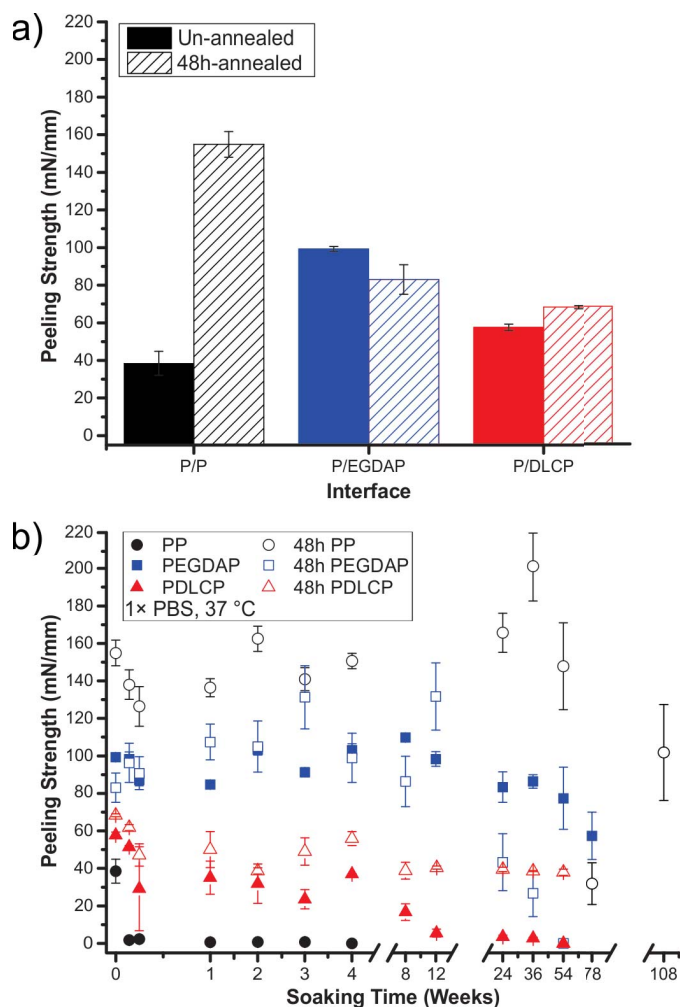

Fig. 9. Average force per unit length required to peel apart annealed and un-annealed samples of Parylene-Parylene (PP), Parylene-Ethylene glycol diacrylate-Parylene (PEGDAP), and Parylene-Diamond-like carbon-Parylene (PDLCP) layers (mean ± SE, n=4): a) Peeling strength of dry samples; b) Peeling strength as a function of time soaked in warm saline.

improved the adhesion of PDLCP samples marginally but not for PEGDAP samples; average peeling force for annealed PDLCP samples increased to ~68 mN/mm, while the peeling force decreased to ~83 mN/mm for annealed PEGDAP samples (Fig. 9a).

Un-annealed PEGDAP samples exhibited minimal to no loss in adhesion over a period exceeding 54 weeks soaking in PBS, whereas annealed PEGDAP samples exhibited a loss in adhesion strength after 12 weeks and completely delaminated after a year in PBS. Un-annealed PEGDAP samples still retained integrity up to at least 82 weeks of simulated *in vivo* environment (Table 4). The peeling force for un-annealed and annealed PDLCP samples dropped in the first 4 days and then it stabilized after a 4-week soak in PBS up to a month and year for un-annealed and annealed samples, respectively. Following an 8-weeks soak in PBS, un-annealed PDLCP samples presented a loss of adhesion and were completely delaminated after a year. Following T-peel tests, we observed that delamination consistently occurred at the interface between the top (second) Parylene layer and

TABLE IV

STATUS OF SOAKING STUDY

Interface	Soaking Time (Weeks)
PP*	4
Annealed PP*	108
PEGDAP	85
Annealed PEGDAP*	54
PDLCP*	54
Annealed PDLCP	72

* Tests completed.

TABLE V

TIME TO INTERFACE FAILURE: WITH & WITHOUT ADHESION PROMOTER

Interface	Soaking Time (Weeks)
PMP	4 days
Annealed PMP	2
PAdMP	4 days
Annealed PAdMP	3
PMAdP	24
Annealed PMAdP	2
PAdMAdP	3
Annealed PAdMAdP	2

DLC layer for un-annealed and annealed PDLCP samples. PDLCP samples were curled after release due to the stress of the film. Table 4 summarizes the survival times of samples subject to soaking until the submission of this manuscript.

F. Platinum Samples With Adhesion Promoter

Figure 10 displays the results of T-peel measurements on 'dry' samples of Parylene-platinum-Parylene films with AdPro Plus® deposited below, above, and on both sides of the metal film. Samples with the adhesion layer deposited prior to sputtering the platinum film (PAdMP) exhibited very weak adhesion, similar to untreated PMP samples (∼3 mN/mm). In contrast, samples with the adhesion layer deposited after sputtering the platinum film (PMAdP), and samples with the adhesion layer deposited both before and after the platinum film (PAdMAdP), exhibited excellent adhesion (mean T-peel measurements of 336 and 143 mN/mm respectively). The T-peel measurement of un-annealed PMAdP samples was the highest recorded among all sample combinations. Thermal annealing of these samples yielded unexpected results, adhesion strength of PAdMP samples *increased* to produce T-peel measurements of ∼52 mN/mm, while adhesion strength of PMAdP and PAdMAdP *decreased* to 94 and 87 mN/mm respectively. Most samples peeled apart during testing and the top (second) Parylene layer detached from the metal, however, all un-annealed PMAdP and annealed PMAdP and PAdMAdP samples tore at the interface and clamping holes, respectively.

Results from soak-testing reflected these same trends, and are compiled in Table 5. Un-annealed PAdMP samples failed after just 4 days of immersion in saline (similar to untreated PMP samples), but, if annealed, withstood 3 weeks before suffering delamination. Un-annealed PMAdP samples exhibited excellent resistance to moisture, but failed after just 2 weeks immersion in saline if annealed. In annealed samples, the metal film delaminated completely from both base (first)
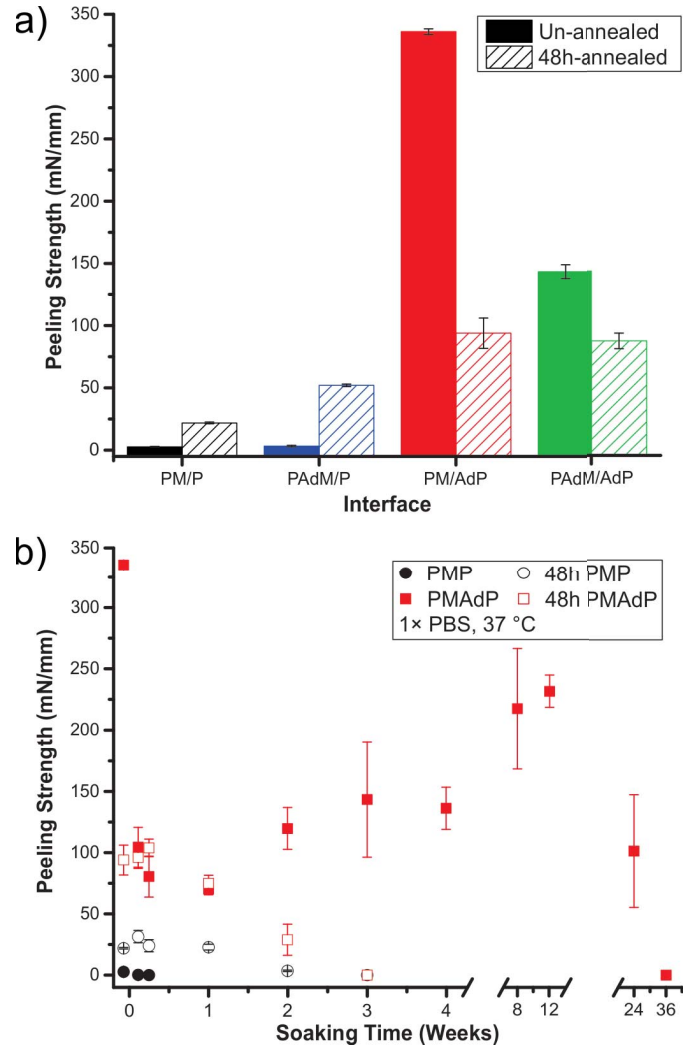

Fig. 10. Average force per unit length required to peel apart annealed and un-annealed samples of Parylene-platinum-Parylene layers with and without AdPro Plus® adhesion promoter (mean ± SE, n=4). Samples featured AdPro Plus® between the base Parylene and metal layer (PAdMP), between the metal and top Parylene layer (PMAdP) and on both sides of the metal layer (PAdMAdP): a) Peeling strength of dry samples; b) Peeling strength as a function of time soaked in warm saline.

and top (second) layers of Parylene while in un-annealed samples, the top (second) layer of Parylene separated from the metal film.

G. XPS Analysis

Table 6 shows the results of XPS, detailing the atomic composition at the failing surface of the platinum interfaces after peel tests. Samples are presented corresponding to different time points in the soaking study. The presence of oxygen in platinum containing samples is likely the result of the O_2 plasma cleaning process used after metal deposition and prior to the deposition of AdPro Plus®.

The most notable feature of this dataset is the presence and strength of the platinum signal. In no sample was platinum detected on the top (second) layer of Parylene following t-peel testing. Instead, platinum was detected only on the bottom (first) layer of Parylene, with the exception of the

TABLE VI
ATOMIC COMPOSITION OF THE METAL COMBINATIONS

Interface	Layer	%C	%O	%Cl	%Pt
Parylene reference		90.00	0.00	10.00	0.00
PAdM/P	Top	89.21	1.30	9.49	0.00
(dry)	Bottom	63.06	20.25	8.37	8.32
48h PAdM/P	Top	89.95	1.05	9.00	0.00
(dry)	Bottom	89.98	0.00	10.02	0.00
PM/AdP	Top	62.57	25.05	3.46	0.42
(1 day)	Bottom	56.33	26.45	0.00	17.22
48h PM/AdP	Top	60.22	27.63	2.36	0.00
(2 weeks)	Bottom	41.02	33.42	0.00	25.56
PAdM/AdP	Top	90.09	0.00	9.91	0.00
(dry)	Bottom	85.31	3.16	10.50	1.02
48h PAdM/AdP	Top	66.09	24.76	3.25	0.00
(2 weeks)	Bottom	72.03	18.44	0.00	9.54

annealed PAdMP sample for which no platinum was detected; this is consistent with visual observation that the stressed platinum film delaminated entirely from both Parylene layers. This dataset was useful for examining the relative strength of platinum-Parylene bonds. Notably, the platinum film consistently and preferentially remained on the bottom layer. Beyond this, variation between results proved too severe to draw precise conclusions about the surface composition.

IV. DISCUSSION

Our results confirm both the relatively weak adhesion between untreated Parylene layers, and the susceptibility of Parylene coatings to adhesive failure and delamination under wet conditions. This phenomenon has been noted extensively, both in literature and anecdotally, yet Parylene remains an important insulator for biocompatible implants. For free-film devices, such as those tested here, the susceptibility is exacerbated as both sides of the film offer a conduit for moisture penetration.

Experimental testing of annealed samples show that the thermal treatment dramatically improves both Parylene-Parylene adhesion and barrier properties. This is in agreement with prior reports, and the mechanism can be understood as thermally induced entanglement of the polymer chains and an increase in crystallinity which reduces moisture permeation. The use of a 48-hour anneal has been commonly reported, again both in the literature and anecdotally by other researchers, and the comparison of the 24-hour, 48-hour and 72-hour datasets shows this protocol is well supported by the data. While improvements in adhesion and barrier properties are evident after 24 hours, continued annealing more than doubles the adhesive strength, while the lack of improvement at the 72-hour mark suggests whatever crystallization or morphology change is occurring is accomplished at the end of 48 hours. This is further supported by the XRD data (Fig. 3); the sharpest diffraction peaks were observed for samples annealed for 48-hours, with less crystallinity observed for 24- and 72-hour annealed samples.

We measured incredibly weak adhesion of Parylene to platinum films, and the thermal annealing method improved the adhesive strength and barrier properties only

slightly. Our experiments examined only platinum, and specifically sputter-deposited platinum, so we are hesitant to generalize to all metals or even platinum films deposited by other methods, however, the likely cause of this weak adherence is the mismatch in surface energy between the hydrophobic Parylene layer and the hydrophilic platinum layer (in agreement with Hwang *et al.* [64]), and such a mechanism would likely apply to other metals as well. Despite improvements following annealing, the lifetime of annealed PMP samples requires further improvement to achieve long term Parylene-based implants. This result is of serious concern; the majority of both polymer bioMEMS and Parylene coated medical devices incorporate conductive metal layers, and platinum specifically is a common choice.

The use of EGDA and DLC interposer layers increased the lifetime of Parylene-Parylene devices under soaking conditions. Annealing produced minimal improvement, and neither the inclusion of DLC or EGDA was comparable to annealed PP in adhesive strength or lifetime (Fig. 9). We will note that there was a considerable period of time (6 months) between the DLC deposition and the final Parylene insulation, and this risked oxidation or contamination of the DLC surface. DLC was not tested with a platinum layer as this would require a titanium adhesion layer between interposer layer and platinum, which would introduce a confounding factor. EDGA was not tested with a platinum layer as the solvents required for metal-liftoff were expected to attack the adhesion layer.

AdPro Plus® was chosen for testing because it is advertised exclusively for improving adhesion at Parylene-metal interfaces. Results of both soak and T-peel tests show a dramatic improvement in barrier properties and adhesion for Parylene-platinum-Parylene samples, but also revealed a critical sensitivity to temperature that may complicate processing. Un-annealed PMAdP samples exhibited the strongest adhesive force of any sample tested in this study (Fig. 10), and a greatly extended lifetime (>24 weeks) under saline soaking conditions. However, annealed PMAdP samples incurred a significant *decrease* in both adhesion and lifetime, as did annealed PAdMAdP samples. As the only difference between the un-annealed and annealed samples was the heat treatment itself, we are confident that this loss in adhesion can be ascribed to the action of the temperature on the AdPro Plus®. Our hypothesis is that the adhesion promoter denatures under high temperature, and this is supported by the failure of the PAdMP samples, which delaminated almost immediately. The deposition of platinum and associated lithography can drive samples to temperatures above 100 °C, and it would appear this is sufficient to disable the adhesion promotor. These results are further supported by the XPS data; the bottom layer of the un-annealed PAdMP exhibits a small platinum signal that vanishes following annealing, suggesting the platinum film lost adhesion after heat treatment. Conversely, the bottom layer of the un-annealed PMAdP samples exhibit a strong platinum signal, that *increases* following annealing, suggesting the platinum film lost adhesion to the top layer after heat treatment. In all cases, we see that the platinum film is retained on the bottom layer of Parylene, suggesting stronger adhesion of metal deposited on Parylene than Parylene deposited on metal.

We note that prior work by Charmet *et al.* [7] examined a combination of thermal treatment (350 °C) and the use of silane A-174 adhesion promotor at the interface between silicon and CVD Parylene. Their results indicated no decrease in adhesion or insulation integrity with the addition of the heat treatment. The heat sensitivity of AdPro Plus® appears to be intrinsic to this specific formulation, and is not a general result of combining thermal treatment with chemical adhesion layers.

In almost all experiments, adhesion failure occurred between the top (insulating) layer of Parylene and the bottom layer regardless of material (e.g. base layer Parylene, platinum, EGDA, DLC). This agrees with previous findings that, absent the formation of a chemical bond, Parylene typically adheres poorly as deposited, particularly to smooth surfaces or materials with significant differences in surface energy [65], [66]. We also observed very strong adhesion between deposited platinum and the bottom (base) layer of Parylene. This may be a result of the O_2 plasma descum performed prior to sputtering, which can roughen surface morphology and induce hydrophilicity in Parylene. Finally, we also note that the samples tested featured large-area platinum films, relative to smaller patterned structures commonly used in devices. Therefore, the presence of PP interfaces between metal features, such as, traces and electrodes, may improve overall adhesion of the structure.

V. Conclusions

The adhesion of thin ($\sim$10 μm) CVD Parylene films to pre-deposited layers of Parylene and metal is insufficient for robust insulation intended for chronic exposure to wet environments. Thermal annealing of Parylene under vacuum significantly improves both the barrier properties of the bulk medium and the adhesion of Parylene-Parylene interfaces, enabling samples to survive for up to 2 years in saline, and the benefits of the annealing process are exhausted after 48-hours at 200 °C. Annealing, however, is insufficient for improving the adhesion at Parylene-platinum interfaces. Interposing materials, including diamond-like carbon and ethylene glycol diacrylate, can provide improvements in both the moisture resistance and adhesion at Parylene-Parylene interfaces without reliance on heat treatments. The inclusion of AdPro Plus® between platinum films and insulating Parylene layers improved adhesion and moisture resistance by an order of magnitude beyond that of either annealed or un-annealed Parylene-platinum-Parylene films, however the adhesion proved very sensitive to elevated temperatures, and may not be compatible with additional processing.

Broadly, we note that despite its reported barrier properties, very thin Parylene layers are susceptible to moisture intrusion and subsequent insulation failure/delamination. Methods which reduce water vapor permeation, including the use of moisture resistant interposer layers and crystallization under thermal annealing, can significantly reduce this effect and dramatically extend the lifetime of Parylene-based or Parylene-insulated devices exposed chronically to water or saline. Reducing moisture intrusion alone is insufficient if there is

significant mismatch in surface energy between Parylene and the target, which in this study included sputtered platinum. Methods that roughen the Parylene surface, or induce hydrophilicity, such as O_2 plasma exposure, appear to significantly improve adhesion. Improving dry and wet adhesions of Parylene to metal is critical for long-term stability of material interfaces in Parylene-based medical implants.

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