



Characterization of Polydimethylsiloxane (PDMS) Properties for Biomedical Micro/Nanosystems

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Abstract. Polydimethylsiloxane (PDMS Sylgard® 184, Dow Corning Corporation) pre-polymer was combined with increasing amounts of cross-linker (5.7, 10.0, 14.3, 21.4, and 42.9 wt.%) and designated *PDMS1*, *PDMS2*, *PDMS3*, *PDMS4*, and *PDMS5*, respectively. These materials were processed by spin coating and subjected to common microfabrication, micromachining, and biomedical processes: chemical immersion, oxygen plasma treatment, sterilization, and exposure to tissue culture media. The PDMS formulations were analyzed by gravimetry, goniometry, tensile testing, nanoindentation, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Spin coating of PDMS was formulation dependent with film thickness ranging from 308 μm on *PDMS1* to 171 μm on *PDMS5* at 200 revolutions per minute (rpm). Ultimate tensile stress (UTS) increased from 3.9 MPa (*PDMS1*) to 10.8 MPa (*PDMS3*), and then decreased down to 4.0 MPa (*PDMS5*). Autoclave sterilization (AS) increased the storage modulus (σ) and UTS in all formulations, with the highest increase in UTS exhibited by *PDMS5* (218%). PDMS surface hydrophilicity and micro-textures were generally unaffected when exposed to the different chemicals, except for micro-texture changes after immersion in potassium hydroxide and buffered hydrofluoric, nitric, sulfuric, and hydrofluoric acids; and minimal changes in contact angle after immersion in hexane, hydrochloric acid, photoresist developer, and toluene. Oxygen plasma treatment decreased the contact angle of *PDMS2* from 109° to 60°. Exposure to tissue culture media resulted in increased PDMS surface element concentrations of nitrogen and oxygen.

Key Words. polydimethylsiloxane, PDMS, Poly(dimethylsiloxane), mechanical properties, micromachining, microfabrication, MEMS, microsystems, contact angle, sterilization, tensile strength, structural properties, nanotechnology, nanosystems

1. Introduction

Recent advances in microelectromechanical systems (MEMS) technology are providing new opportunities for a variety of biological and medical applications (Bashir, 2004; Rebello, 2004; Roy et al., 2001; Ziaie et al., 2004). Microfabrication and micromachining-based approaches offer the potential to tackle biomedical problems within the same size scale of cells and subcellular structures (Desai, 2000; Itoh, 1999; Kane et al., 1999; Mata et al., 2003). Consequently, there has been an increase in re-

search and development of MEMS-based devices in the biomedical arena for a variety of applications ranging from diagnostics (Fujii, 2002; Mastrangelo et al., 1998; Paranjape et al., 2003; Wu et al., 2001) to therapeutics (Borenstein et al., 2002; Chung et al., 2003; Ferrara et al., 2003; Santini et al., 1999; Tao and Desai, 2003). However, the development of these applications through established MEMS manufacturing approaches is hindered by inherent characteristics of traditional silicon-based processes such as high costs and limited access to clean room environments (Roy et al., 2001; Whitesides et al., 2001). Moreover, the most successful silicon-based microfabrication process has been photolithography, which is expensive, works for a limited set of materials, and is often limited to planar surfaces (Deng et al., 2000; Quake and Scherer, 2000; Xia and Whitesides, 1998).

The diversity of applications and commercialization of MEMS has encouraged the MEMS community to find processes and materials that enable mass production while reducing costs. Likewise, the increasing number of biomedical MEMS (BioMEMS) applications has led to a divergence from traditional silicon-based processing, and the pursuit of more biologically friendly materials. New fabrication techniques such as Soft Lithography have fostered the use of biocompatible materials such as polymers (Whitesides et al., 2001; Xia and Whitesides, 1998). The practicability of polymers for fabrication with both rapid prototyping and mass production techniques as well as lower cost relative to silicon and glass make them particularly attractive for the development of BioMEMS (Deng et al., 2000; Quake and Scherer, 2000). Polycarbonate (PC), polymethylmethacrylate (PMMA), polyvinylchloride (PVC), polyethylene (PE), and polydimethylsiloxane (PDMS) are some of the polymer candidates for the low cost, mass production of BioMEMS devices (Despa et al., 1999; Duffy et al., 1998; Lee et al., 2001; Lin et al., 1998; Wei et al., 2005).

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PDMS is a silicone elastomer with desirable properties that make it attractive for the development of MEMS and microfluidics components for biomedical applications (Jo et al., 2000; Mata et al., 2002b; McDonald and Whitesides, 2002; Unger et al., 2000). It is chemically inert, thermally stable, permeable to gases, simple to handle and manipulate, exhibits isotropic and homogeneous properties as well as lower cost than silicon, and can conform to submicron features to develop microstructures (McDonald and Whitesides, 2002; Ng et al., 2002; Xia and Whitesides, 1998). The use of PDMS for BioMEMS applications has been largely driven by the development of Soft Lithography techniques such as micro-contact printing, replica molding, micro-transfer molding, micro-molding in capillaries, and solvent-assisted micro-molding (Xia and Whitesides, 1998). These techniques usually require the use of PDMS to create an elastomeric stamp or mold that incorporates microstructures for transfer of patterns onto a subsequent substrate. In addition, PDMS is transparent, non-fluorescent, biocompatible and nontoxic, and has been traditionally used as a biomaterial in catheters, drainage tubing, insulation for pacemakers, membrane oxygenators, and ear and nose implants (Visser et al., 1996).

The extensive biomaterial foundation of PDMS in conjunction with the increasing interest in low cost, mass-produced, microfabrication compatible, polymeric MEMS make it formidable and promising material for current and future BioMEMS applications. Consequently, there is significant interest in examining the compatibility of PDMS with both MEMS technology and biomedical applications. Therefore, we investigated the structural and surface properties of Sylgard[®] 184 (Dow Corning Corporation, Midland, MI), which is a widely used commercially available brand of PDMS. This paper reports on the effects of various biomedical, microfabrication, and micromachining processes on the characteristics of PDMS Sylgard[®] 184. More specifically, this paper attempts to convey relevant information on particular properties of PDMS that will accelerate its wider adoption for the development of BioMEMS devices and applications.

2. Materials and Methods

2.1. Experimental design

PDMS Sylgard[®] 184 (Dow Corning Corporation) is a heat curable PDMS supplied as a two-part kit consisting of pre-polymer (base) and cross-linker (curing agent) components. The manufacturer recommends that the pre-polymer and cross-linker be mixed at a 10:1 weight ratio, respectively. In this study, PDMS (Sylgard 184) pre-polymer and cross-linker were combined at various weight ratios designated as *PDMS1*, *PDMS2*, *PDMS3*, *PDMS4*,

and *PDMS5*, corresponding to 5.7, 10.0, 14.3, 21.4, and 42.9 wt.% cross-linker, respectively. The different PDMS formulations were formulated to investigate possible alterations in PDMS properties due to deviation from the recommended 10:1 weight ratio, which corresponds to our *PDMS2* notation.

The surface and structural properties of the different PDMS formulations were analyzed to investigate the effects of common biomedical, microfabrication, and micromachining processes including: (a) spin coating—to quantify the effect of the amount of cross-linker on thickness profiles; (b) chemical immersion—to characterize and quantify the effect of various chemicals used in microfabrication and micromachining on both surface microtexture degradation and long-term surface hydrophilicity; (c) exposure to oxygen plasma—to quantify its effect on long-term surface hydrophilicity; (d) sterilization—to characterize and quantify the effect of various sterilization procedures on surface microtexture degradation, long-term surface hydrophilicity, surface chemical composition, and mechanical properties; and (e) exposure to tissue culture media—to characterize changes in the surface chemical composition. The PDMS formulations were analyzed by gravimetry, goniometry, tensile testing, nanoindentation, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Fourier Transform Infrared Spectroscopy (FTIR). Statistical significance was defined at the 95% confidence interval using a One Way Analysis of Variance (ANOVA) test performed in Sigma-Stat Statistical Software Version 2.0 (SPSS, Chicago, IL). A summary of the various processes and respective analysis tools is presented in Table 1. It should be noted that not all PDMS formulations were investigated for effects of the different processes. The basis for choice of specific PDMS formulations for certain processes was based on equipment availability. Nevertheless, *PDMS2* was used in all investigations since it is the standard formulation recommended by the manufacturer.

2.2. Processes

Spin coating. Spin coating is a common microfabrication method for producing polymer films of controlled and uniform thickness (Linderholm and Asberg, 2000; Lotters et al., 1997). *PDMS1*, *PDMS2*, *PDMS3*, *PDMS4*, and *PDMS5* formulations were prepared (mixed and degassed) and poured to cover about 2/3 of a smooth 100 mm-diameter, <100>-oriented n-type silicon wafer with a 2 μ m thick thermally grown SiO₂ layer, and spin coated using a 400 *Lite* spinner (Laurell Technologies, North Wales, PA) at 200 revolutions per minute (rpm). In addition, *PDMS2* (the recommended formulation) was spin coated at 50, 75, 100, 200, 500, and 1000 rpm. The spin coating procedure was performed for 90 seconds (sec)

Table 1. Processes and analysis tools for various PDMS formulations

Process → (Analysis tool) ↓	Spin coating ^a	Chemical immersion ^b	Oxygen plasma exposure ^c	Sterilization ^a	Culture media immersion ^c
SEM	x	x		x	
Gravimetry		x			
Goniometry		x	x	x	
Nano-indentation				x	
Tensile testing				x	
XPS				x	x
FTIR				x	

^aFormulats tested: *PDMS1*, *PDMS2*, *PDMS3*, *PDMS4*, and *PDMS5*.

^bFormulats tested: *PDMS1*, *PDMS2*, *PDMS3*, and *PDMS4*.

^cFormulats tested: *PDMS2*.

with an acceleration of 85 rpm/sec until the desired speed was reached. Substrates were cured in a *C-005* convection oven (Lindberg/Blue M, Asheville, NC) at 95 °C for 30 minutes (min) followed by 24 hours (hr) at room temperature (~25°C). This process was repeated twice to obtain a total of three spin-coated substrates for each condition. After curing, the cross-linked PDMS films were peeled from the silicon wafers, and 2 mm² pieces were cut from seventeen locations around the wafer in a region 3 mm from the edge to the center of the wafer. The thickness of the cut PDMS sections was measured using SEM.

Chemical immersion. Exposure to different liquid chemicals is a common practice in microfabrication and micromachining processes. To study the effect of common liquid chemicals on PDMS, changes in hydrophilicity were investigated using smooth PDMS substrates, and changes in weight and degradation of patterns using micro-textured PDMS substrates.

PDMS2 samples comprising channel micro-textures with 11 μm high, 45 μm wide channels separated by 5 μm wide ridges (PDMS Channels) were produced by Soft Lithography as reported elsewhere (Mata et al., 2002a). Substrates were subsequently cut into 1 cm² specimens and immersed in chemicals at room temperature for time periods similar to those commonly used in microfabrication and micromachining processes. Table 2 presents a summary of the chemicals, their concentration, time of sample immersion, and effects of immersion. After rinsing in deionized (DI) water for 10 min and drying in air for 5 min, PDMS substrates were analyzed using SEM and gravimetry.

Surface hydrophilicity was also analyzed as a function of chemical immersion on smooth PDMS substrates (PDMS Smooth) by measuring their surface wettability with water. *PDMS1*, *PDMS2*, *PDMS3*, and *PDMS4* substrates were produced in the same manner as those for the spin coating process, cut into 1 cm² specimens, immersed in the chemicals at room temperature, and rinsed

as described above. Long-term (>24 hr after immersion) surface hydrophilicity of PDMS was quantified using goniometry.

Oxygen plasma exposure. Oxygen plasma is used in biomedical processing to facilitate surface modification. Two sets of smooth *PDMS2* substrates were cut into 1 cm² specimens, sent to an offsite vendor laboratory (PVA Tepla America, Inc., Corona, CA) for exposure to an oxygen plasma treatment process using an *M4L* asher (Model # 4055, Metroline Industries, Corona, CA) at 600 Watts, 1000 mTorr, with 98% purity Oxygen flowing at 500 mL/min for 15 min. These process parameters were recommended by the vendor as conditions to enhance surface hydrophilicity. Immediately after oxygen plasma treatment, samples were immersed in DI water to preserve the effect of surface treatment (McDonald and Whitesides, 2002) and shipped back to our laboratory for goniometry measurements. Prior to static contact angle measurements (>24 hr after the oxygen plasma treatment), both sets of samples were removed from the water and dried in air; one set was dried for 5 min, while the other was dried for 35 min.

Sterilization. Sterilization is critical for most biomedical applications (Kowalski and Morrissey, 1996). PDMS substrates from formulations *PDMS1*, *PDMS2*, *PDMS3*, *PDMS4*, and *PDMS5* were processed by three sterilization procedures normally used for biomedical devices: (a) Ethanol (ETH)—samples were immersed in 70% ethanol (Aaper Alcohol and Chemical Co., Shelbyville, KY) for 30 min and dried in air at room temperature; (b) ultraviolet light (UV)—samples were irradiated with UV light (254 nm, 100 μW/cm² for 30 min) inside a laboratory hood (~50 cm from light source); and (c) steam autoclave (AS)—samples were placed inside an *SI-120* autoclave system (Amsco Scientific, Apex, NC) at 121°C for 20 min. All samples were stored at room temperature for at least 24 hr before goniometry. The effects of sterilization

Table 2. Chemical and PDMS2 substrate characterization after immersion

Chemical	Concentration (wt.%)	Time (min)	No	Mild	Medium	Total	Weight gain (%)
Buffered hydrofluoric acid	49.0	10	x				-0.97
Hydrochloric acid	37.9	10	x				-0.34
Potassium hydroxide ^a	86.9	10	x				-0.27
Hydrogen peroxide (H ₂ O ₂)	31.8	10	x				2.01
Piranha	3(H ₂ O ₂) : 1(H ₂ SO ₄)	10, 30	x				0.64
Photoresist developer ^b	100.0	10	x				-0.97
Water (deionized)	100.0	10, 30	x				-0.33
Hexane	99.9	10	x				4.67
Toluene	99.9	10	x				45.51
Acetone	99.7	10, 30	x				2.78
Methanol	100.0	10	x				-0.34
Isopropanol	100.0	10	x				-0.97
Potassium hydroxide ^a	86.9	60		x			0.75
Buffered hydrofluoric acid	49.0	30			x		1.39
Nitric acid	69.8	10			x		4.13
Hydrofluoric acid	49.0	10				x	-1.38
Sulfuric acid (H ₂ SO ₄)	96.0	10				x	-14.00
Potassium hydroxide ^a	86.9	1620				x	-0.90

Note. Chemicals were obtained from Mallinckrodt Baker Inc., Phillipsburg, NJ, except potassium hydroxide which was obtained from Fisher Scientific (Fairlawn, NJ) and photoresist developer (Shipley 351), which was obtained from Rohm and Hass Electronic Materials, Sunnyvale, CA.

^a800 g of Potassium hydroxide were diluted in 4 L of deionized water. Immersion was done at 55°C.

^bPhotoresist developer was combined with deionized water at a ratio of 1:4 (developer:water).

were analyzed using SEM to assess micro-texture degradation; goniometry and XPS to evaluate surface effects; and nanoindentation, tensile testing, and FTIR to assess changes in mechanical properties.

Culture media. Culture media consists of a number of nutrients that are used to provide an appropriate biochemical environment in cell and tissue culture applications, where PDMS is increasingly used as a substrate material (Leclerc et al., 2003; Mata et al., 2002b). Therefore, the effect of tissue culture media on the surface chemical composition of PDMS was examined using XPS. Two sets of smooth PDMS1, PDMS2, PDMS3, PDMS4, and PDMS5 substrates, were prepared and cut into 1 cm² specimens. One set was immersed for 4 days in α -MEM Minimum Essential Medium (Gibco, Grand Island, NY) containing amino acids, vitamins, inorganic salts, ribonucleosides, deoxyribonucleosides, and 10% Fetal Bovine Serum (Whittaker, Walkersville, MD). Substrates were removed from the media, dipped twice in DI water to remove excess media, and dried in air for 5 min prior to XPS analysis. The other set (control) was not immersed in media; instead it was dipped twice in DI water and dried in air for 5 min prior to XPS analysis.

2.3. Analysis tools

Scanning electron microscopy. A JSM-5310 SEM (JEOL USA, Peabody, MA) was used to measure the PDMS thickness after spin coating, and qualitatively char-

acterize PDMS pattern degradation after chemical immersion and sterilization. Samples were gold coated with a ~20 nm thick layer via sputtering prior to SEM examination. Pattern degradation on the samples was categorized according to their appearance as: *no change* (similar to original), *mild change* (rounding of sharp edges), *medium change* (surface distortion), or *total change* (complete pattern loss).

Gravimetry. Gravimetry was used to quantify changes in PDMS sample weight due to immersion in the different chemicals. PDMS substrates were weighed prior and subsequent to chemical immersion on a AG 204 precision digital scale (Mettler Toledo, Columbus, OH), to determine weight change. After chemical immersion, substrates were immersed in water for 10 min followed by air-drying for 5 min.

Goniometry. Goniometry was used to measure the surface contact angles of the various PDMS formulations prior and subsequent to sterilization and oxygen plasma treatment. This technique provides information on surface hydrophilicity, by assessing the material's wetting characteristics (Khorasani et al., 1996). Surface wettability with water was measured in triplicate with an NRL-100 Goniometer (Rame-Hart, Inc., Mountain Lakes, NJ) on five different locations of the PDMS substrate. A 6 μ L droplet of DI water was placed on the substrate surface

and the static contact angle was measured immediately thereafter.

Nanoindentation. Nanoindentation measurements were performed using a *Nano DCM*[®] indentation head and a *Nano Indenter XP*[®] system (MTS Systems Corporation, Oak Ridge, TN) and the Continuous Stiffness Measurement (CSM) technique (U.S. Patent No. 4,848,141). Storage modulus (σ) and tangent delta ($\text{Tan } \delta$) were monitored as a continuous function of both the indenter's displacement into the sample and the vibration frequency. Sterilized and untreated substrates were sent to MTS Systems Corporation (Oak Ridge, TN) where the experiments were conducted. Each sample was tested five times with a Berkovich tip moving down to 20 μm in depth at 4, 8, 16, 32, 64, 128, and 256 Hz. Loading was controlled by maintaining the ratio of loading rate over the load at 0.05/sec. Results were analyzed for the data recorded between 30 and 90% of the maximum load applied to *PDMS1*, *PDMS2*, *PDMS3*, and *PDMS4* substrates.

Tensile testing. Ultimate tensile stress (UTS) of *PDMS1*, *PDMS2*, *PDMS3*, *PDMS4*, and *PDMS5* substrates subjected to sterilization was investigated by using an *Instron 5543* electromechanical materials testing system (Instron Corporation, Canton, MA). Substrates were cut to a dumbbell shape with a die (Die Cut Products, Cleveland, OH), sterilized, and tested in triplicate. Testing was carried out according to the ASTM D 412 standard for rubber and thermoplastic elastomers with the modification that the dumbbell-shaped test specimens were made one-fourth the standard size. Figure 1 presents a schematic illustration of the sample geometry prior to testing. All specimens were clamped in custom grips with a reducing amplitude sinusoidal wave profile, under uniform torque of 14.12 N-cm. The design of the custom grips was selected because it allows for maximum contact surface area with the specimen, while reducing the stress concentration on the specimen near the edges of the grip. Load and crosshead

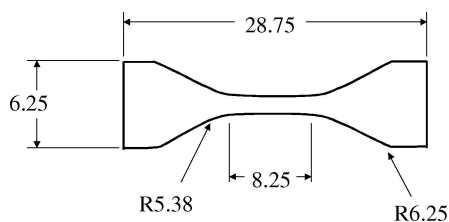


Fig. 1. Schematic illustration of the 220 μm thick sample geometry used for tensile testing. Dimensions are in millimeters (mm), and are one-fourth the standard ASTM D 412 size.

position were computer-controlled and digitally acquired at 200 Hz using *Merlin* software V. 22043 (Instron Corporation).

X-Ray photoelectron spectroscopy. XPS was performed on the substrates with a *PHI 5600 ESCA* system (Physical Electronics Co., Chanhassen, MN) to examine possible changes in surface composition of the different PDMS formulations due to sterilization and culture media exposure. The XPS analysis was performed using monochromated aluminum $K\alpha$ 945 radiation, at 250 W, 45° angle, and 93.9 eV band pass. These conditions produced a sampling depth of ~ 10 nm, with the predominant signal originating from the top 3 nm. A 16 channel Multi-Channel detector was used to accelerate the data acquisition at 16 different energy locations on every sweep, while signal-averaging algorithms were used to enhance signal-to-noise ratio (S/N). The instrument band pass and data point energy interval were selected near the middle of the possible choices, representing a compromise between energy resolution and signal levels (S/N ratios and limits of detectability).

Fourier transform infrared spectroscopy. FTIR was performed on 50 μm thick *PDMS2* substrates to examine the effect of sterilization on the cross-linking of PDMS. The FTIR analysis was performed using an *Equinox 55* FTIR Spectrometer (Bruker Optics, Billerica, MA) equipped with a KBr beam splitter. Each PDMS sample was scanned 32 times at room temperature and atmospheric pressure with a resolution of 4 cm^{-1} under constant nitrogen flux to remove water vapor. The data was collected in the range of 4000–400 cm^{-1} and analyzed using Bruker Optics OPUS (Bruker Optics) 4.0 software.

3. Results and Discussion

3.1. Spin coating

PDMS2 decreased in thickness as the spin coating speed increased from 50 rpm (1085 μm) to 1000 rpm (55 μm) (Figure 2), which is generally consistent with a previous report (Linderholm and Asberg, 2000). PDMS curing is time and temperature dependent; the thicker the spin coated PDMS films, the longer they take to cure and the more sensitive the uncured PDMS is to flow due to gravity if the wafer is not perfectly horizontal. Consequently, films produced at lower spin speeds exhibit higher standard deviations. At 200 rpm, the spin coated PDMS films decreased in thickness as the cross-linking agent in the formulation increased, ranging from 308 μm for *PDMS1* to 171 μm for *PDMS5*. Surface tension, material viscosity, and interfacial energy of the coating surface

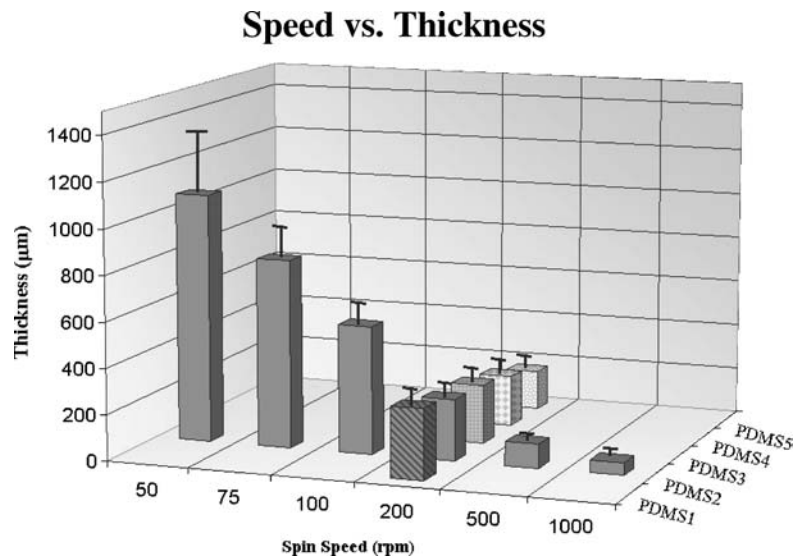


Fig. 2. Speed-thickness correlation for *PDMS1*, *PDMS2*, *PDMS3*, *PDMS4*, and *PDMS5* spin coated at 200 rpm, as well as *PDMS2* spin coated at 50, 75, 100, 200, 500, and 1000 rpm. PDMS thickness decreased considerably from 50 rpm (~1100 µm) to 1000 rpm (~50 µm) as shown by the solid gray bars, while increasing the cross-linking agent decreased the thickness from *PDMS1* (~308 µm) to *PDMS5* (~171 µm) as shown by the patterned bars.

are spin coating parameters that affect the thickness of spin coated films (Tiffany, 1998); their interplay results in the thickness decrease observed from *PDMS1* to *PDMS5*. The viscosity of the cross-linker ($0.0011 \text{ m}^2/\text{s}$) is considerably less than that of the pre-polymer ($0.0050 \text{ m}^2/\text{s}$). Therefore, an increase in cross-linker from *PDMS1* to *PDMS5* would tend to decrease the effective viscosity of the uncured PDMS mixture. The lower viscosity would, in turn, allow the uncured PDMS to flow

more readily over and off the wafer during the spin coat procedure.

3.2. Chemical immersion

Table 2 summarizes the chemicals used for immersion and their respective effects on micro-texture degradation of PDMS Channels. The majority of chemical immersions did not alter the structure of *PDMS2* Channels (Table 2, Figure 3(a)). These results are generally consistent

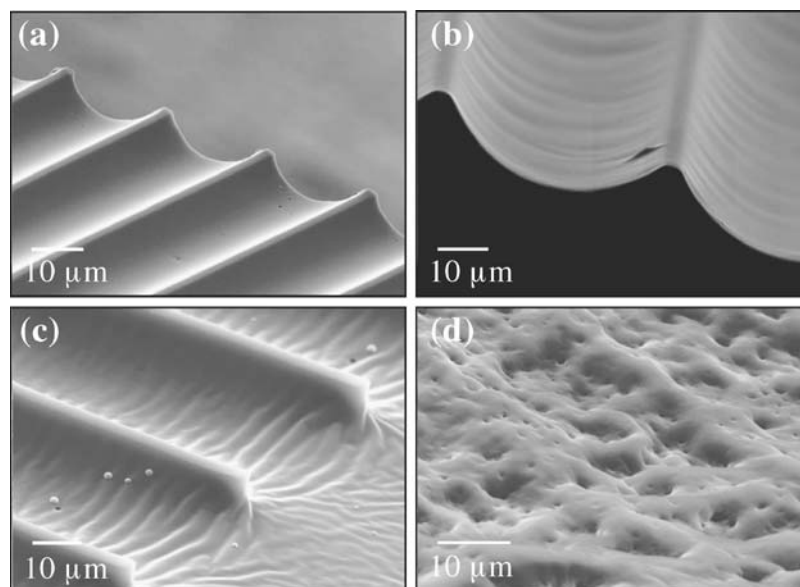


Fig. 3. Scanning electron microscope (SEM) images showing the condition of *PDMS2* Channels after chemical immersion: (a) no change, (b) mild change, (c) medium change, and (d) total change.

Table 3. Contact angle (in degrees) of PDMS substrates

Treatment	PDMS1	PDMS2	PDMS3	PDMS4
Untreated PDMS	113.5 ± 2.0	113.5 ± 2.0 ^a	112.6 ± 2.6	114.8 ± 1.0
Autoclave	106.9 ± 3.9	112.6 ± 2.8	109.8 ± 4.9	115.0 ± 2.8
Ethanol	114.6 ± 1.8	117.5 ± 1.9	120.0 ± 1.1	115.7 ± 1.6
UV	118.2 ± 4.0	119.0 ± 1.4 ^c	119.6 ± 2.1	114.6 ± 2.0
Hydrochloric acid-10 min	113.3 ± 1.2	109.7 ± 3.1	111.0 ± 1.1	113.2 ± 1.6
Hydrogen peroxide-10 min	118.7 ± 0.9	114.1 ± 1.6	114.0 ± 3.2	116.5 ± 0.9
Photoresist developer-10 min ^b	104.2 ± 3.7	102.0 ± 3.5	100.9 ± 4.9 ^c	122.2 ± 3.9 ^c
Water-10 min	116.1 ± 0.7	115.1 ± 1.0	113.5 ± 1.7	113.6 ± 0.8
Water-30 min	116.2 ± 1.8	115.1 ± 2.8	114.5 ± 1.8	116.4 ± 1.4
Hexane-10 min	104.0 ± 5.2	117.4 ± 1.1	106.4 ± 5.3	113.8 ± 0.6
Toluene-10 min	115.1 ± 0.2	114.3 ± 2.3	101.2 ± 10.8	113.2 ± 1.3
Acetone-10 min	114.2 ± 1.0	114.1 ± 1.0	113.2 ± 0.5	113.3 ± 1.0
Acetone-30 min	120.2 ± 0.8 ^c	114.5 ± 1.0	114.0 ± 1.8	114.0 ± 0.8
Methanol-10 min	114.9 ± 1.7	114.1 ± 1.2	112.4 ± 2.4	112.5 ± 0.8
Isopropanol-10 min	118.3 ± 1.0	113.4 ± 2.0	111.9 ± 0.7	114.4 ± 1.3
Oxygen plasma-5 min in air		60.0 ± 7.0 ^c		
Oxygen plasma-30 min in air		84.0 ± 6.0 ^c		

^aContact angle for untreated PDMS2 during oxygen plasma experiment was 108.9°.

^bContact angles for untreated PDMS after photoresist developer immersion were: PDMS1 = 103.6° ± 3.0, PDMS2 = 104.8° ± 2.2, PDMS3 = 106.6° ± 2.2, and PDMS4 = 108.5° ± 1.3.

^cDenotes statistical significance ($p < 0.05$).

with another report for PDMS2 (Lee et al., 2003). Rounding of micro-channel edges was observed for the 60 min immersion in potassium hydroxide (KOH) (Figure 3(b)). Little pattern distortion was exhibited by PDMS specimens immersed for 30 min in buffered hydrofluoric acid (BHF) as well as those for 10 min in nitric acid (Figure 3(c)). The minimal effect on PDMS when immersed in KOH and BHF for ≥ 4 hr has been previously reported (Brugger et al., 1998). Complete pattern degradation was observed for PDMS specimens that were immersed for 10 min in hydrofluoric acid, 10 min in sulfuric acid, and 27 hr (1620 min) in KOH (Figure 3(d)). Immersion of the PDMS specimens in the various chemical solutions did not result in major changes in weight except for two cases. The 10 min immersion in sulfuric acid resulted in a weight decrease, probably due to degradation of the PDMS. In contrast, a marked increase (+46%) was observed after 10 min immersion in toluene, which was absorbed into the PDMS (Oh et al., 2001).

The surface contact angles of water on PDMS after chemical immersion are summarized in Table 3. There was no statistically significant difference in contact angles among the four PDMS formulations before immersion. Furthermore, exposure to the chemical solutions did not affect the long-term (>24 hr) hydrophilicity of the PDMS specimens. However, there were slight, but statistically significant ($p < 0.05$), contact angle changes in three cases: PDMS1—from 113.5° to 120.2° after immersion in acetone for 30 min; PDMS3—from 106.6° to 100.9° after immersion in Shipley 351 photoresist developer (Rohm and Haas Electronic Materials, Sunny-

vale, CA) for 10 min; and PDMS4 - from 108.5° to 122.2° after immersion in Shipley 351 photoresist developer (Rohm and Haas Electronic Materials, Sunnyvale, CA) for 10 min.

3.3. Oxygen plasma exposure

Surface treatment was preserved by immersion of the PDMS2 specimens in water immediately after the oxygen plasma treatment (McDonald and Whitesides, 2002; Ng et al., 2002). The lowest contact angle was exhibited by PDMS2 specimens that were exposed to air for only 5 min prior to measurement (60°), while those exposed to air for 30 min recovered significant hydrophobicity (84°) as shown in Table 3. The untreated PDMS specimens exhibited highest contact angle (109°), which is consistent with previous studies (Duffy et al., 1998; Lee et al., 2003; Murakami et al., 1998). The decrease in contact angle upon exposure to oxygen plasma results from the introduction of hydrophilic silanol (Si—OH) groups and destruction of methyl groups (Si—CH₃) on the surface of PDMS (McDonald et al., 2000). The recovery of the hydrophobicity of oxygen plasma treated PDMS after exposure to air has also been reported (Berdichevsky et al., 2004; Fritz and Owen, 1995; Hillborg and Gedde, 1998). Although the exact mechanism is not established, it has been proposed that the recovery of hydrophobicity results from the diffusion of low molecular weight PDMS chains from the bulk to the surface and/or overturning of the surface polar hydrophilic groups (SiOH or SiCH₂OH) (Berdichevsky et al., 2004; Hillborg and Gedde, 1998).

Previous reports have attempted to correlate surface oxygenation of PDMS by exposure to oxygen plasma with increased hydrophilicity and improved bonding quality of PDMS to other surfaces (Duffy et al., 1998; Jo et al., 2000). For example, one report showed that optimum PDMS bonding conditions were achieved with exposure at 120–180 W for 10 sec; higher power and/or longer periods decreased bond quality (Jo et al., 2000). In contrast, the present work did not experimentally investigate bond quality, but surface oxygenation with higher exposure parameters (600 W for 15 min) did not decrease PDMS hydrophilicity.

3.4. Sterilization

Scanning electron microscope. The surfaces of PDMS Channel specimens were examined using SEM to determine how the patterned features might be affected by sterilization. Assessment of channel micro-texture degradation was based on variations in micro-channel geometry (dimensions and angles) and surface roughness. Examination of the post-sterilization specimens from all five PDMS formulations did not reveal any discernable pattern degradation or surface distortion. The compatibility of PDMS with AS and ETH has been previously mentioned (Leclerc et al., 2003) and confirm the utility of the different PDMS formulations for biomedical applications.

Goniometry. The long-term hydrophilicity of *PDMS4* did not change significantly after any of the sterilization procedures. In contrast, *PDMS1* (113.5°), *PDMS2* (113.5°), and *PDMS3* (112.6°) tended to become more hydrophobic after ETH (114.6°, 117.5°, and 120.1°, respectively) and UV (118.2°, 119.0°, and 119.6°, respectively) sterilization (Table 3). A previous report presented a slight increase (~105° to ~90°) in surface hydrophilicity after UV irradiation (Efimenko et al., 2002). However, that research group used more powerful irradiation parameters (185 nm, 28 mW/cm², 5 mm from light source) compared to those in the present work (254 nm, 100 μW/cm², 50 cm from light source). Furthermore, the contact angles of PDMS in the present work were measured ≥24 hr after the sterilization treatments, which suggest recovery of hydrophobicity with time. The radicals and chain scissions that occur on the main backbone and side groups of the PDMS as a result of UV irradiation can recombine (Efimenko et al., 2002), which will, in turn, increase contact angle and decrease hydrophilicity of the PDMS surface. Nevertheless, the four PDMS formulations did not exhibit statistically significant changes in contact angle after the sterilization procedures, except for an increase on *PDMS2* from 113.5° to 119.0° after UV ($p = 0.003$).

Nanoindentation. Nanoindentation offers the possibility of studying mechanical properties of the outermost layer of a polymer, which is susceptible to destruction due to different treatments such as UV irradiation (Nowicki et al., 2003). The four PDMS formulations were evaluated prior and subsequent to sterilization using nano-indentation. UV and ETH did not have major effects on storage modulus (σ) or tangent delta (Tan δ) for all the tested PDMS samples. In contrast, AS had an effect on the mechanical properties of the outer most layer of the PDMS (Figure 4). For the untreated samples, σ increased from 0.96 MPa (*PDMS1*) to 1.54 MPa (*PDMS2*) to 1.94 MPa (*PDMS3*), and decreased to 1.89 MPa (*PDMS4*). Previous studies have reported comparable σ values for PDMS (Lee et al., 2004; Rau et al., 2002; White et al., 2005). Another investigation reported σ values ranging from 0.36 MPa (6.7%) to 0.87 MPa (20.0%) for various amounts of cross-linker in the formulation (Armani et al., 1999). Although this group also reported an increase in σ with increasing amount of cross-linker in the PDMS formulation, their values are lower than our measurements. This discrepancy might result from their shorter curing times (15 min) and different measurement technique (single side clamped cantilever beam) for σ .

Like typical viscoelastic materials, σ increased with indentation frequency (4 to 256 Hz) for all PDMS formulations and sterilization procedures. However, higher increase as a function of frequency was observed for Tan δ , with higher values for the PDMS formulation with least amount of cross-linker (*PDMS1*). The increase in Tan δ (defined as the ratio of loss modulus (ϵ) over σ) as a function of frequency corresponds to a higher increase in ϵ (~120%) compared to σ (~22%) for all PDMS formulations. This higher increase in ϵ corresponds to the material becoming more viscoelastic when loaded at higher frequencies, which, in turn, could result in higher stress relaxation and heat generation (Mata, 1999).

Tensile testing. Figure 5 presents the ultimate tensile stress (UTS) sustained by the PDMS specimens. UTS increased with the amount of cross-linker ranging from 3.9 MPa (*PDMS1*) to 10.8 MPa (*PDMS3*). However, further increase in the amount of cross-linker decreased the UTS to 8.1 MPa (*PDMS4*) and down to 4.0 MPa (*PDMS5*). This UTS decrease correlates with the decrease in σ determined via nano-indentation. For all formulations, no statistically significant differences were observed between the untreated samples and those treated by UV and ETH sterilization. However, there was a statistically significant increase (except for *PDMS3*) in the UTS after AS, with the highest increase on *PDMS5* (from 4.0 to 8.7 MPa). The formulation that resulted in the highest tensile strength was *PDMS3*, where none of the sterilization procedures

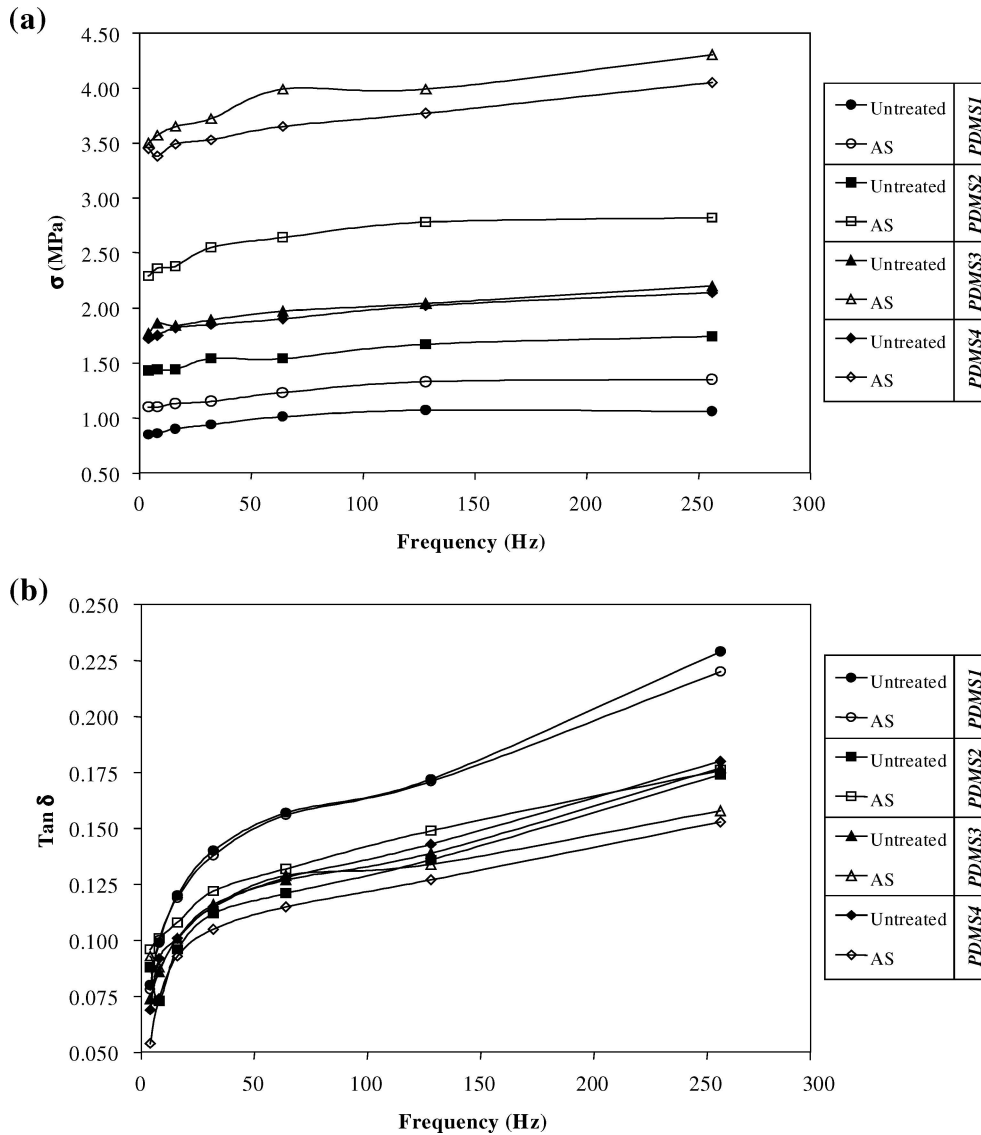


Fig. 4. Graphs of: (a) storage modulus (σ); and (b) tangent delta ($\tan \delta$). Data is obtained from nano-indentation tests on PDMS1, PDMS2, PDMS3, and PDMS4 before and after autoclave sterilization (AS). Style of the line markers refers to PDMS formulation, while solid markers correspond to untreated samples, and open markers correspond to AS treated samples. Note an increase in σ after AS, while little change was observed for $\tan \delta$, and a marked increase in $\tan \delta$ as a function of frequency, while little increase was observed for σ .

had a significant effect. In contrast to the manufacturer's recommendation that PDMS2 is the optimum formulation, our observation suggests that the curing conditions were optimum to achieve an efficient reaction between cross-linking agent and pre-polymer in PDMS3. This suggestion is also supported by the minimal effect of AS on PDMS3 as compared to PDMS4 and PDMS5. It is possible that higher curing temperatures and/or longer time periods could result in comparable or higher UTS for PDMS4 and PDMS5 relative to PDMS3. This possibility is suggested by the effect of AS on PDMS4, which results in the highest UTS.

X-Ray photoelectron spectroscopy. The three major chemical elements on the PDMS surface prior and subsequent to sterilizations were Carbon (C), Oxygen (O), and Silicon (Si). C was the most abundant with surface concentrations from 41.2% (UV treated PDMS4) to 70.1% (untreated PDMS5). Although there was no trend in changes in surface element concentration as a function of the amount of cross-linker, PDMS samples from all four formulations exhibit similar distribution (Figure 6). Higher O and Si concentrations were observed on PDMS1 and PDMS4, and lower on PDMS2, while higher C concentration was observed on PDMS2 and PDMS5,

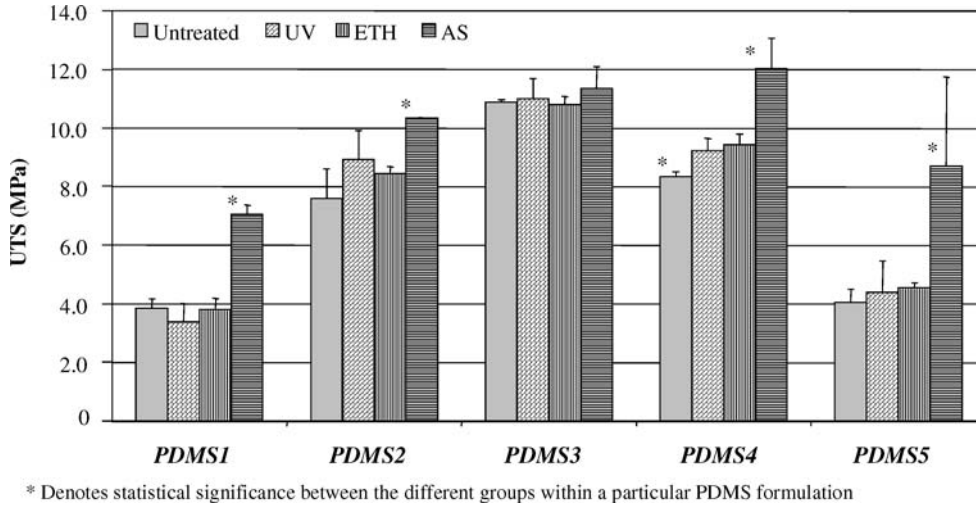


Fig. 5. Graph showing the ultimate tensile stress (UTS) of PDMS1, PDMS2, PDMS3, and PDMS4 samples. UTS is PDMS formulation dependent, as it significantly increased with amount of cross-linker up to PDMS3 (similar to σ from the nano-indentation test). Statistically significant increase was also observed after AS treatment (except for PDMS3), which suggests a stronger material after AS.

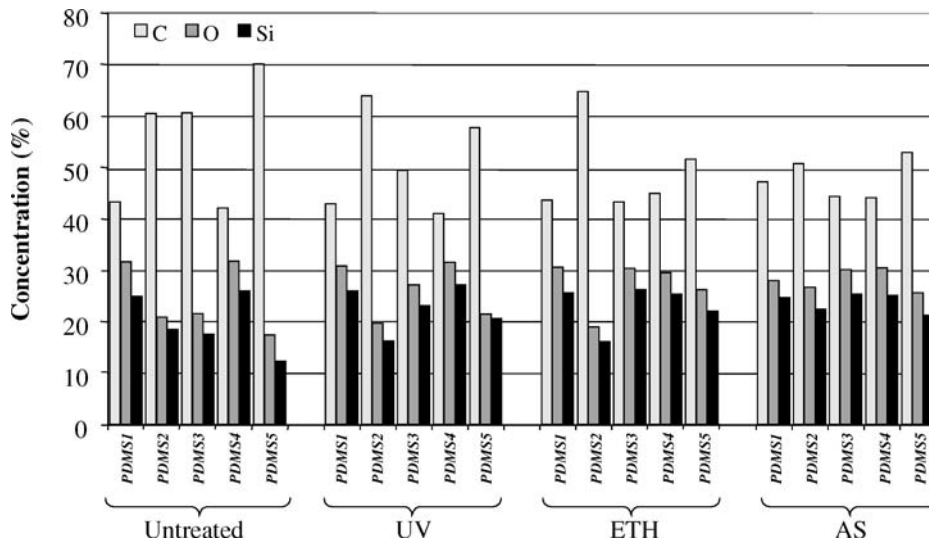


Fig. 6. Graph showing the surface concentrations of C, O, and Si for PDMS1, PDMS2, PDMS3, PDMS4, and PDMS5 before and after sterilization. No relationship is observed between amount of cross-linker and element concentration. AS decreased the variation in surface element concentration between the different PDMS formulations.

and lower on PDMS1. In addition, AS decreased the variation in surface element concentration between the different PDMS formulations. No major effects were observed after UV or ETH. This stability correlates with the goniometry data, which revealed the absence of any significant effect of sterilization on static contact angles. In contrast, another investigation reported an increase in O concentration and decrease in C concentration after UV irradiation (Schnyder et al., 2003). The reason for this apparent discrepancy with our results is likely due to their powerful irradiation parameters (172 nm, 30 mW/cm², 5 mm

from light source) compared to the present work (254 nm, 100 μ W/cm², 50 cm from light source).

Fourier transform infrared spectroscopy. The infrared (IR) spectra from the various PDMS2 substrates exhibited characteristic IR bands (Efimenko et al., 2002; Khorasani et al., 1996). Possible effects of sterilization and cross-linking are indicated by -CH₂ and -CH₃ stretching modes in the 3000–2950 cm⁻¹ region. Sterilization resulted in increased absorbance at 2970 cm⁻¹ compared to untreated

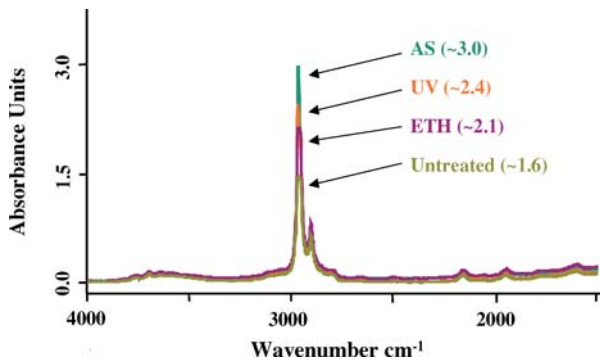


Fig. 7. Graph showing overlays of infrared (IR) spectra from the untreated and sterilized PDMS2 substrates. AS treated PDMS exhibited maximum absorbance in the $3000\text{--}2950\text{ cm}^{-1}$ region, which indicates increased PDMS cross-linking relative to other PDMS2 substrates. (Courtesy: Dr. Lily Ng, Department of Chemistry, Cleveland State University).

PDMS, which exhibited 1.6 absorbance units (a.u.) and increased to 2.1, 2.4, and 3.0 a.u. for ETH, UV, and AS treatments, respectively (Figure 7). The maximum absorbance by PDMS treated by AS suggests increased cross-linking relative to substrates treated by UV and ETH. This information is consistent with the trends in the tensile strength of PDMS2 specimens (Figure 5) due to the various sterilization treatments.

3.5. Culture media exposure

Similar to the sterilization experiment, XPS revealed highest surface element concentrations before media immer-

sion for C (from 46.2% on PDMS5 to 47.3% on PDMS3), followed by O (27.2% on PDMS3 to 28.0% on PDMS2) and Si (25.2% on PDMS2 to 26.0% on PDMS4). Media immersion did not generally have major effects on the surface element concentration of the PDMS samples, except for presence of nitrogen (N) (2.0% on PDMS3 to 6.0% on PDMS1), and an increase in the O/Si ratio (Figure 8). The increased presence of N and O is likely due to ingredients present on the α -MEM Minimum Essential Medium such as amino acids and proteins. Amino acids such as Arginine, Glutamine, Histidine, and Threonine possess amino (NH_2) and carboxyl groups (CO) rich in N and O, which deposit on the surface of the PDMS upon exposure to culture media (Horbertt et al., 1996).

4. Conclusions

The compatibility of Polydimethylsiloxane (PDMS) with various biomedical, microfabrication, and micromachining processes has been investigated. The resulting insight into the structural and surface properties of PDMS Sylgard® 184 will be relevant to the design, fabrication, and development of PDMS micro- and nanostructures for BioMEMS applications.

Spin coating of PDMS was formulation dependent; increased amounts of cross-linker agent in the formulation decreased film thickness from $308\ \mu\text{m}$ on PDMS1 to $171\ \mu\text{m}$ on PDMS5 at 200 rpm. Immersion in buffered hydrofluoric and nitric acids resulted in little microtexture distortion, while potassium hydroxide, sulfuric, and hydrofluoric acids caused total destruction of

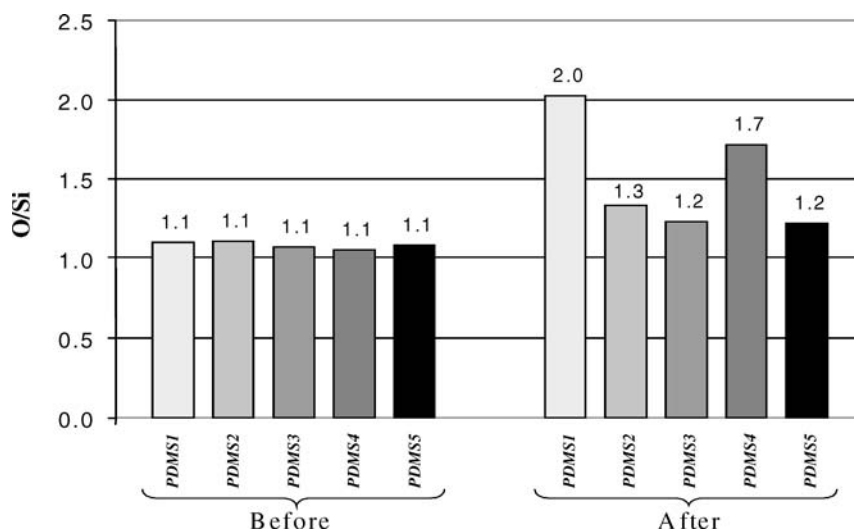


Fig. 8. Graph showing the effect of culture media immersion on the Oxygen (O) to Silicon (Si) surface concentration ratio of PDMS1, PDMS2, PDMS3, PDMS4, and PDMS5. The increase in O along with the increase in Nitrogen (not shown) suggests the surface deposition of a variety of ingredients present in the α -MEM Minimum Essential Medium such as amino acids.

micro-textures. However, chemical immersion did not result in major changes in PDMS surface hydrophilicity. Oxygen plasma exposure rendered an increase in PDMS2 surface hydrophilicity, while subsequent exposure to air induced hydrophobic recovery. Sterilization did not affect the PDMS surface micro-textures, element concentration, or hydrophilicity, except for an increase in contact angle of PDMS2 from 113.5° to 119.0° after UV sterilization. UV and ETH did not have an effect on the mechanical properties of PDMS, while AS increased the storage modulus (σ) and ultimate tensile stress (UTS). σ and UTS were also formulation dependent, increasing from PDMS1 (UTS of 3.9 MPa) up to PDMS3 (UTS of 10.8 MPa), and then decreasing with additional cross-linker agent. AS also decreased the variation in surface element concentration for all PDMS formulations. Immersion in tissue culture media induced an increase in surface concentration of oxygen relative to silicon.

The recommended PDMS formulation by the manufacturer corresponds to our notation PDMS2. This formulation was resistant to the majority of chemicals tested and behaved similarly to the other formulations (PDMS1, PDMS3, and PDMS4) in terms of contact angles, surface chemistry, and culture media exposure. Nonetheless, it was the PDMS3 formulation that exhibited the highest tensile strength and storage modulus. Therefore, the mechanical properties of PDMS could be altered (by changing the polymer to cross-linker ratio) without variations in surface chemistry.

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