

# Polymethylhydrosiloxane (PMHS) as a functional material for microfluidic chips

S J Lee<sup>1</sup>, M Goedert<sup>1</sup>, M T Matyska<sup>2</sup>, E M Ghandehari<sup>3</sup>, M Vijay<sup>1</sup>  
and J J Pesek<sup>2</sup>

<sup>1</sup> Mechanical and Aerospace Engineering, San José State University, San José, CA, USA

<sup>2</sup> Department of Chemistry, San José State University, San José, CA, USA

<sup>3</sup> Chemical and Materials Engineering, San José State University, San José, CA, USA

E-mail: [sjlee@sjsu.edu](mailto:sjlee@sjsu.edu)

Received 15 October 2007, in final form 6 December 2007

Published 9 January 2008

Online at [stacks.iop.org/JMM/18/025026](http://stacks.iop.org/JMM/18/025026)

## Abstract

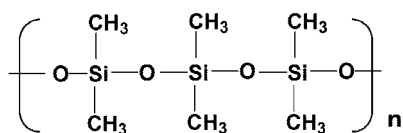
Polymethylhydrosiloxane (PMHS) has been investigated as a candidate material for microfluidic chips. The ability to modify the surface of PMHS by hydrosilation is particularly advantageous for separation processes. The chemical modification of PMHS is verified by diffuse reflectance infrared Fourier transform (DRIFT) analysis, and the modified PMHS is shown to be stable when exposed to extreme pH conditions between 2 and 9. Spectrophotometer measurements show that PMHS exhibits over 40% transmittance for ultraviolet (UV) wavelength as low as 220 nm, indicating viability for sensor applications based on UV absorption. The UV transmittance is furthermore observed to be insensitive to thickness for specimens tested between 1.6 mm and 6.4 mm thick. Full curing of PMHS liquid resin occurs between 48 and 72 h at 110 °C with no secondary additives. Casting of microscale features is achieved by using soft lithography methods similar to established techniques for fabrication based on polydimethylsiloxane (PDMS). Microchannels approximately 100  $\mu\text{m}$  wide and 50  $\mu\text{m}$  deep are also demonstrated by carbon dioxide laser ablation, with uniform channels produced using an energy dose of 0.2 mJ mm<sup>-1</sup> with respect to line length. Other basic functional requirements for microfluidic chips are discussed, including the ability to bond PMHS substrates by plasma treatment.

## 1. Introduction

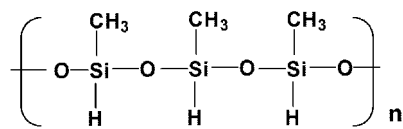
Research activity in microfluidics and lab-on-chip technologies has produced an extremely wide variety of devices for fluid manipulation and sample analysis [1]. Microfluidic chips made of polymer materials in particular are drawing greater attention than materials such as silicon, fused silica and borosilicate glass because of advantages in cost and high-volume manufacturability [2]. Common materials for microfluidic chips include polydimethylsiloxane (PDMS), polymethyl methacrylate (PMMA), polyimide and cyclic olefin copolymer (COC). PDMS in particular is used very extensively in devices such as microvalves [3], micropumps [4] and mixers [5]. PDMS devices have been applied to a wide variety of applications including electrophoresis [6, 7], hydrodynamic focusing [8], cell sorting [9] and fluidic logic [10]. It is a frequent material of choice for 'soft lithography', which encompasses a wide variety of techniques for pattern

transfer in microscale and nanoscale dimensions, well beyond microfluidic applications alone [11]. PMMA and COC have also been demonstrated in fine-resolution microfluidic devices, with the added advantage of thermoplastic behavior for low-cost manufacturing by embossing and injection molding methods [12, 13]. Microfluidic chips made of polyimide have excellent dimensional stability, and have been successfully fabricated by laser ablation [14].

While these materials have been extensively investigated, polymethylhydrosiloxane (PMHS) is a far less explored alternative that offers a unique benefit in terms of chemically modifiable surface characteristics, in particular for microchannel-based separation processes. PMHS is optically transparent, and (as discussed later in this paper) it exhibits UV transmittance similar to or better than other polymers that have been successfully implemented in microfluidic devices. PMHS is readily synthesized with straightforward techniques common to polymethyl-polysiloxanes [15], and the cured



**Figure 1.** Structure of polydimethylsiloxane (PDMS). Each silicon atom along the siloxane backbone is bonded to two methyl groups.



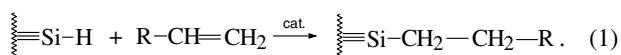
**Figure 2.** Structure of polymethylhydrosiloxane (PMHS). In contrast to PDMS, a surface hydride is present instead of one of the methyl groups.

material is inert to water and moisture. PMHS is also commercially available in a liquid resin form, and has been shown to be an effective reducing agent in support of organic synthesis [16]. However, to the best knowledge of the authors, until this recent work [17] PMHS has not yet been investigated as a direct substrate material for microfluidic applications.

The present study investigates process development and characterization of PMHS as a new candidate material for microfluidic chip applications. First experimental results are discussed, which demonstrate the ability to chemically modify the surface of PMHS by hydrosilation. Next an examination of the optical properties in terms of UV transmittance is given. The curing behavior and ability to form channel features are addressed subsequently, followed by a discussion of substrate bonding for assembly into practical devices. Although there are some unique fabrication challenges (discussed later in this paper), PMHS can be processed with techniques similar to PDMS-based soft lithography [11], and the material has been successfully patterned with features in the 10–100  $\mu\text{m}$  size range that is common to microfluidic devices.

PDMS, which has been extensively used in microfluidic applications, has two methyl groups along a siloxane backbone, as illustrated in figure 1. In contrast, as shown in figure 2, PMHS has a surface hydride instead of one of the methyl groups, making it favorable for modification by hydrosilation.

The hydrosilation process attaches an organic moiety to the hydride intermediate, and thus can be used to create a product that has desired surface properties for electrophoresis, such as resistance to accumulated adsorption of proteins on microchannel walls [18]. Reaction (1) attaches an organic moiety to the surface with a stable Si–C bond:



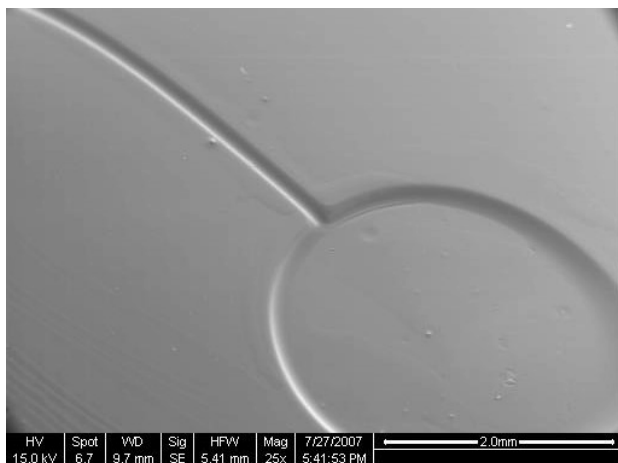
The Si–C bond leads to high stability observed in both chromatographic and electrophoretic experiments [19, 20]. A typical catalyst for the hydrosilation reaction is hexachloroplatinic acid, but catalysts such as other metal ion complexes and free radical initiators [21] have also been shown to be effective in the hydrosilation reaction. Modification of microchannel surfaces by hydrosilation would make PMHS

an effective material for electrochromatographic processes, in a way similar to that already developed for particulate silica and etched capillary surfaces [22, 23]. As in high-performance liquid chromatography (HPLC), a variety of compounds such as 1-octadecene, 1-octene, 1-octadecyne and 1-octyne may be added through hydrosilation. With respect to other materials like COC, polyimide and PMMA, PMHS can be more easily modified because the hydrosilation reaction is a more straightforward and versatile means of attaching organic groups to the surface.

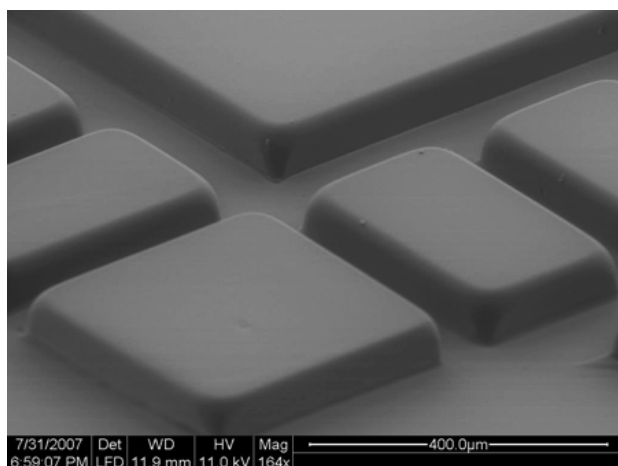
A number of methods have been developed to modify the more ubiquitous PDMS, in order to diminish some of its hydrophobic properties or to create a surface amenable to certain types of separations. A common process starts out with an oxidation process such as plasma discharge that serves to create silanol groups on the surface [24, 25]. This treatment results in a functionality (Si–OH) that can be modified by standard organosilane chemistry, the same protocol that is used for the chemical modification of ordinary silica [26–28]. Another approach after oxidation has been atom transfer radical polymerization when compounds such as polyacrylamide or poly(ethylene glycol) are attached to the surface [29–32]. Surface oxidation can also be produced with reagents such as Ce(IV) or nitric acid [33, 34]. The sol–gel process can be used to generate silica and titania particles in PDMS polymers [35, 36]. These particles with the PDMS are then modified in the same manner as silica or titania. All of these methods are rather complex, often involving at least two major steps and resulting in a very limited number of sites for modification in comparison to the overall surface area. This is in contrast to the process proposed here for PMHS. Each polymer unit of PMHS has a point of attachment for a chemical species, the Si–H group. The process of modification requires only a single step, hydrosilation. The reaction is very versatile allowing for the attachment of a broad range of moieties from small organic groups to polymer precursors and even biopolymers. In addition, the reaction can be catalyzed by a variety of transition metal complexes, numerous free radical initiators and even by UV initiation [22]. The case of UV initiation is possible because of the UV transparency of the PMHS material, demonstrated in this investigation.

## 2. Fabrication and experimental methods

PMHS liquid resin (Product HMS-993 from Gelest, Inc., Morrisville, PA) cures to solid form at elevated temperature without additives. In an atmospheric oven at a temperature of 110  $^{\circ}\text{C}$ , complete curing typically occurs between 48 and 72 h, depending on the liquid volume and container geometry. The extent of full curing into solid form is inspected by checking for shearing of the liquid when the container is tilted at an incline, and then confirmed by puncture with a pin to confirm that no uncured liquid remains at the bottom of the mold. Metal catalysts are known to accelerate curing of methylhydrosiloxanes [37], but the observations reported in this paper are based on curing PMHS by temperature and time alone.



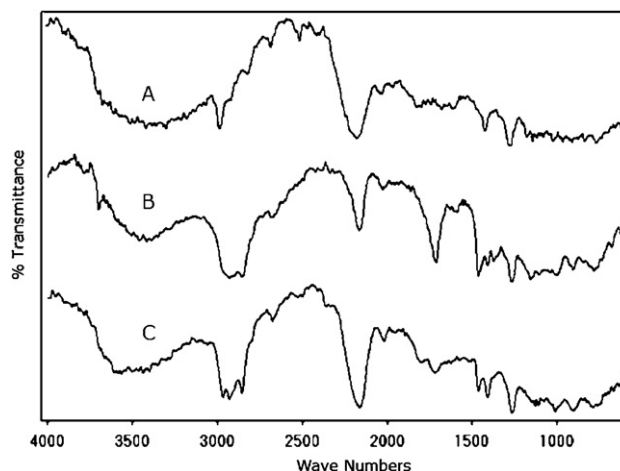
**Figure 3.** Microchannel and circular well fabricated in a flexible PMHS substrate by casting over a photo-patterned SU-8 master.



**Figure 4.** Pattern in PMHS, demonstrating the ability to fabricate complex passages with characteristic dimensions less than 100  $\mu\text{m}$ , typical of microfluidic channel structures.

PMHS can be patterned with microscale features of almost arbitrary complexity by casting over a patterned master substrate. The technique follows methods already established in rapid prototyping of PDMS by soft lithography [24]. Figure 3 shows an example of an open fluid microchannel connected to a circular well. This sample was fabricated by casting over photo-patterned SU-8 (MicroChem, Newton, MA) on a 100 mm silicon wafer. The master was pre-treated with tridecafluorooctyl-trichlorosilane vapor (Product T2492 from United Chemical Technologies, Inc., Bristol, PA) to facilitate separation after curing. Figure 4 shows a more intricate pattern of mosaic tiles that demonstrate narrow gaps that are 60  $\mu\text{m}$  wide and 400  $\mu\text{m}$  long. The height of the features is approximately 50  $\mu\text{m}$ .

Vacuum degassing is applied to the liquid resin before curing immediately after it is poured over the SU-8 master. However, unlike PDMS which is typically cured in a two-part reaction mixture, the PMHS curing is conducted with single-part thermal curing only. Apart from the evacuation of



**Figure 5.** Diffuse reflectance infrared Fourier transform (DRIFT) spectra of PMHS before (A) and after hydrosilation with 1-octadecene by Pt catalyst (B) and by free radical catalyst (C). The characteristic carbon–hydrogen stretching near 2900  $\text{cm}^{-1}$  provides evidence that hydrosilation treatment was successful.

pockets in the patterned topology of the SU-8 master, no bubble formation is observed in the liquid PMHS when placed in a vacuum chamber below  $-70$  kPa ( $-20$  in. Hg). Furthermore, by either optical or scanning electron microscope inspection trapped bubbles are not observed in the solid PMHS even without vacuum degassing.

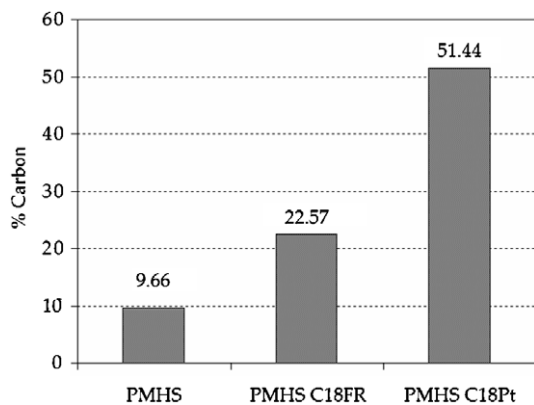
For experiments involving DRIFT spectroscopy to examine chemical modification, cured PMHS is ground and then modified by hydrosilation with 1-octadecene. DRIFT spectra are obtained using an ATI Mattson Infinity Series spectrophotometer (Madison, WI). Spectral analysis is performed on a Hewlett-Packard Venturis FX-2 computer using Mattson WinFIRST software. For experiments involving optical characterization by spectrophotometry, samples are cast with appropriately measured volume into a fluoropolymer tray to establish prescribed thickness, and then sectioned into square specimens, typically 10 mm  $\times$  10 mm. Spectrophotometer measurements are made by using a Lambda 35 UV/VIS instrument from Perkin-Elmer, Inc. (Waltham, MA).

### 3. Results and discussion

#### 3.1. Chemical modification

The PMHS polymer was ground with a mortar and pestle to an approximate particle size of 20  $\mu\text{m}$ . A 5 g sample of PMHS powder was modified according to the procedure for particulate silica hydride [20] using a 100 h reaction time for the hydrosilation process. The modified material was washed with three 20 ml portions of toluene and diethyl ether. This protocol has been shown to be effective in removing all residual octadecene and catalyst in the case of silica particle modification.

Figure 5(a) presents the DRIFT spectrum of the ground PMHS material before modification. The Si–H stretch near 2250  $\text{cm}^{-1}$  and the C–H stretching of the methyl group



**Figure 6.** Carbon analysis of unmodified PMHS, PMHS modified by C18 with free radical (FR) catalyst and PMHS modified by C18 with Pt catalyst. The increase in carbon content provides evidence that the hydrosilation reaction was effective in modifying the PMHS surface.

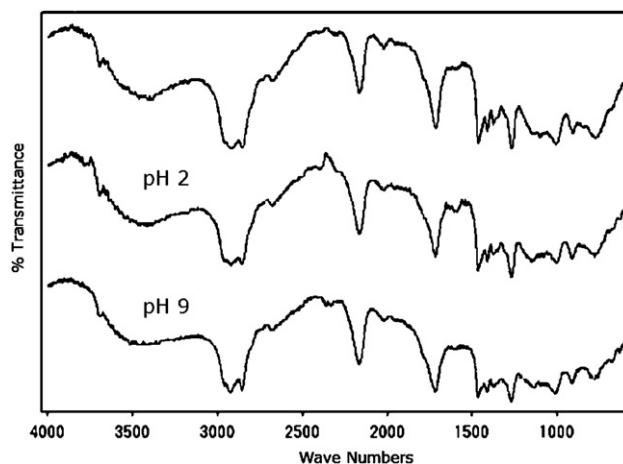
between 2800 and 3000  $\text{cm}^{-1}$  are evident. Figure 5(b) is a spectrum that shows the result of chemical modification using hexachloroplatinic acid in the hydrosilation reaction, and figure 5(c) is a spectrum that shows the result of hydrosilation with a free radical catalyst (*t*-butyl peroxide). In both cases there is a substantial increase in the carbon–hydrogen stretching bands indicating successful chemical modification of the PMHS material.

Elemental analysis for carbon (contracted through Desert Analytics, Inc., Tucson, AZ) further confirms the effectiveness of the modification. As shown in figure 6, unmodified PMHS has a carbon content of 9.66%. However, PMHS subject to hydrosilation with free radical catalyst exhibited an increase in carbon content to 22.6%, and PMHS modified using platinum catalyst showed an even greater increase to 51.4%.

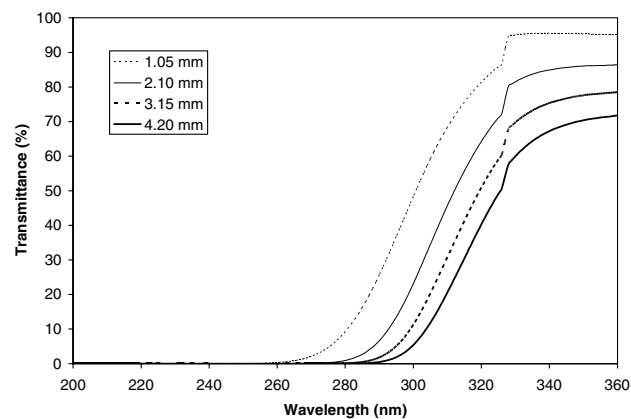
Many applications of silane reagents on oxide surfaces, such as fused silica, borosilicate glass and alumina, are known to produce unstable siloxane linkages when subjected to pH extremes. As such, micro-devices that are based on silicon dioxide or aluminum oxide suffer from lack of stability once modified by a siloxane substituent. Since surface modification to alter surface energy or activate the surface for the bonding of chemical and biological moieties is essential to micro-device function, lack of pH stability is a serious drawback for micro-devices that are based on inorganic oxides. Figure 7 shows the DRIFT spectra for samples of PMHS in which the chemical stability of modified PMHS is demonstrated. Samples of the polymer modified with 1-octadecene using hydrosilation were placed in solutions at pH 2 and pH 9 and stirred continuously for 48 h. In both cases no appreciable decrease in the Si–H stretching band at 2250  $\text{cm}^{-1}$  was observed. These results indicate good stability of the base polymeric material and no decrease in the carbon–hydrogen stretching bands in the range of 2800–3000  $\text{cm}^{-1}$ , indicating that not only the polymer itself but also the bonded organic moiety is stable.

### 3.2. Optical characteristics

Capillary electrophoresis (CE) is a method of sample identification based on differences in the electrophoretic



**Figure 7.** DRIFT spectra of PMHS subject to pH 2 and pH 9. The starting sample (top) is PMHS modified by hexachloroplatinic acid in the hydrosilation reaction, identical to figure 5(b). The results indicate that modified PMHS is stable and resilient to extreme pH conditions.

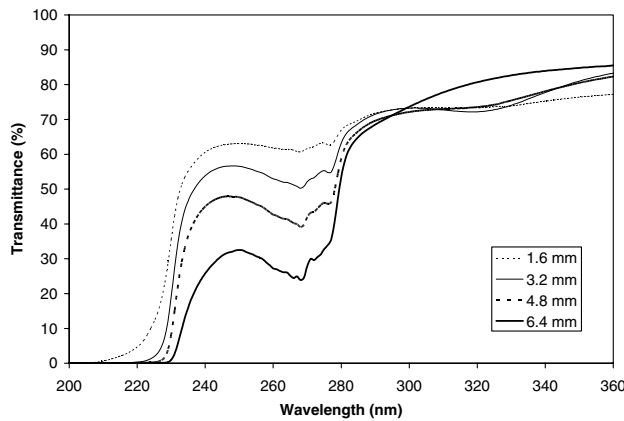


**Figure 8.** Transmittance of glass through sample thicknesses 1.05, 2.10, 3.15 and 4.20 mm. There is a sharp decline below 300 nm wavelength.

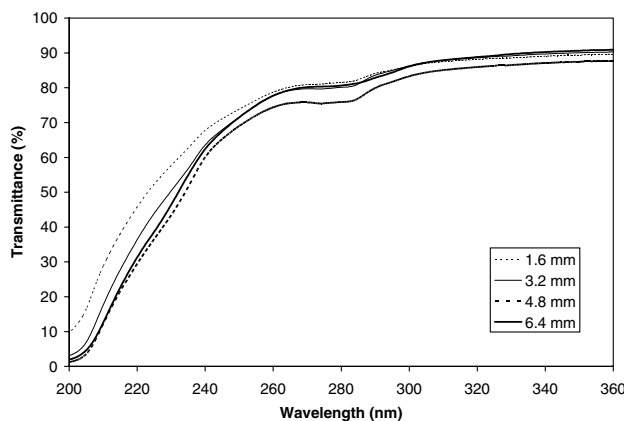
mobility of ions and the effects of electroosmotic flow on both ions and neutral particles, as they are driven by an electric field along a long narrow channel [38]. A very common method of distinguishing species in CE is by UV absorption [39]. Therefore, microfluidic chips used in CE and other UV-based detection applications should exhibit UV transparency. The performance of PMHS was compared to PDMS (Sylgard 184 from Dow Corning, Midland, MI), and conventional microscope glass slides (Corning 2947 from Corning, Inc., Corning, NY). Figures 8–10 plot per cent (%) transmittance for the different materials as a function of wavelength. Different thickness values are compared by stacking up to four identical specimens. The glass samples were 1.05 mm thick, and the PMHS and PDMS samples were 1.6 mm thick. The PMHS specimens were tested as cast, with no chemical modification.

The glass exhibits a characteristically sharp decline in transmittance below 300 nm, while the polymers continue to





**Figure 9.** Transmittance of PDMS through sample thicknesses 1.6, 3.2, 4.8 and 6.4 mm. Although there is transmission exhibited even below 250 nm, the signal is attenuated by thickness.

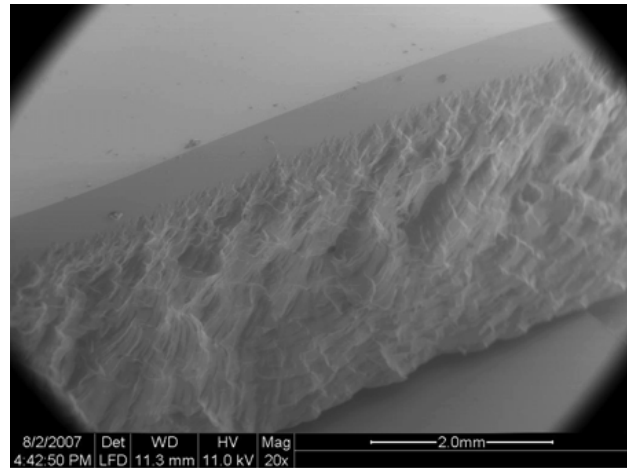


**Figure 10.** Transmittance of PMHS through sample thicknesses 1.6, 3.2, 4.8 and 6.4 mm. There is transmission exhibited below 250 nm, and very little thickness-dependent attenuation.

have substantial transmittance below 250 nm. While both glass and PDMS exhibit approximately linear attenuation with respect to thickness, PMHS is observed to be far more insensitive to sample thickness. In contrast, transmittance through PDMS becomes substantially attenuated as the specimen thickness increases. For direct application in sensor devices, it may be possible simply to use extremely thin substrates to avoid this signal attenuation problem, but in the case of PDMS there is still extremely little transmittance below 220 nm even for the thinnest sample. PMHS, however, has measurable transmission below 220 nm at all thickness values. The unique UV transparency of PMHS not only makes it favorable for through-chip sensing, but further opens up the possibility of performing UV-initiated chemical modifications even along the walls of sealed fluidic channels.

### 3.3. Mechanical behavior

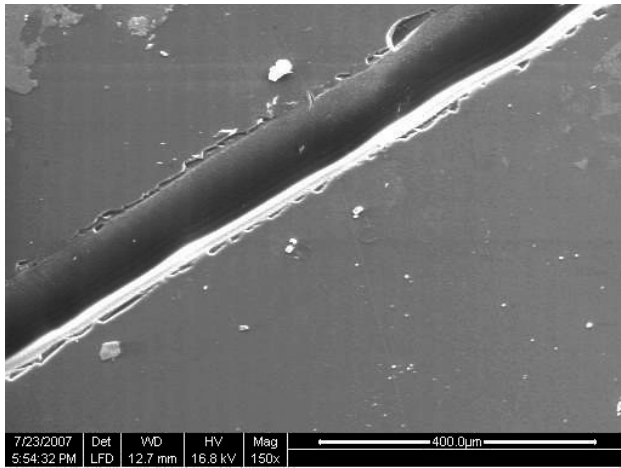
Although PMHS exhibits some pliability similar to PDMS, its mechanical toughness and ease of handling are limited by brittle failure as increasing strain is applied. PDMS is well



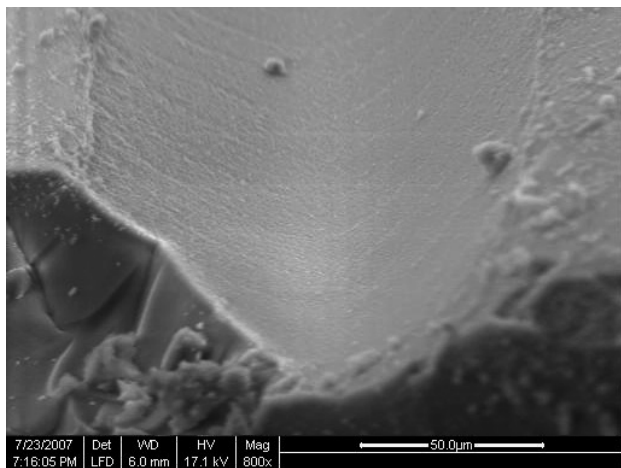
**Figure 11.** Cross-section view of a fracture surface for a PMHS sample, showing two-phase composition. The hard upper layer has a smooth fracture surface while the softer bulk material fractures with a highly textured surface.

documented in terms of its exceptional mechanical resilience even under very large strains [40]. Formulations of PDMS are known to tolerate static strain even in excess of 100% elongation [41]. The PMHS specimens as prepared, however, have two distinct limitations. One limiting aspect is a rigid crust layer that forms at the exposed (top) surface of PMHS during curing [42]. This surface layer is not as pliable as the bulk material and fails in a brittle mode resembling the fracture of thin glass. The second limiting aspect is fracture of the softer bulk material underneath the surface. Even this bulk phase is unable to sustain linear strains beyond approximately 10% elongation. A typical fracture surface is shown in figure 11. The sample is approximately 3 mm thick, and has a rigid upper layer approximately 50  $\mu\text{m}$  thick. The lower bulk region is pliable, yet also fractures in brittle separation when subjected to increasing strain. The thickness of the brittle layer has been observed qualitatively to be reduced with longer curing time at lower temperature. Preparations for quantitative measurements using a combination of nanoindentation and atomic force microscopy [43, 44] are in progress and will be reported via subsequent publication.

Despite its inability to sustain large strain magnitudes, at low strain PMHS is still compliant, and sufficiently so for feature patterning by soft lithography. Under durometer testing, the overall bulk PMHS was found to have a Shore A hardness value of 46.2 compared to PDMS measured with Shore A hardness of 55.6. Measurements were conducted based on the ASTM D2240 test standard using a dial durometer (Model 1600, Rex Gauge Company, Inc., Buffalo Grove, IL). Lack of resilience at high strain limits the breadth of applications for PMHS, but the pliability at low strain is still beneficial for practical requirements such as mold separation and substrate-to-substrate bonding [45]. If particular applications or device configurations require greater mechanical resilience, additives or co-polymers may be investigated in future development.



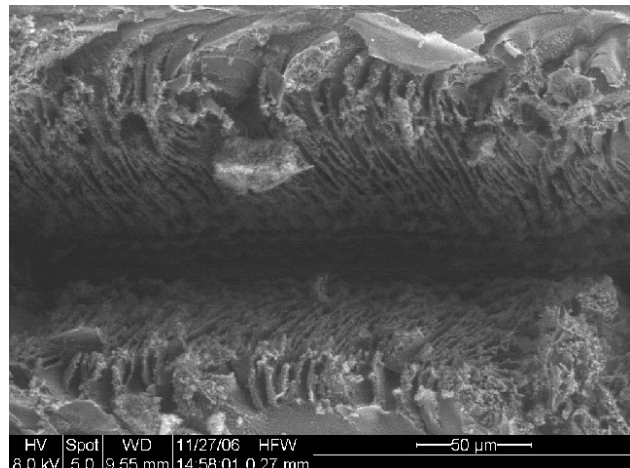
**Figure 12.** Top view of a microchannel formed in PMHS by laser ablation. The channel is straight and has consistent width, but some brittle fracture is observed at the surface edges.



**Figure 13.** End view of a microchannel formed in PMHS by laser ablation, revealing a contoured cross-section and a maximum depth-to-width ratio of approximately 1:2.

### 3.4. Laser ablation

Laser ablation is an alternative method for defining channels and other geometric features. Compared to casting over relief topology as discussed above, direct-write laser methods offer additional flexibility and rapid iteration for arbitrary spatial addressing, which is especially beneficial for low-volume custom designs. An example of a laser-scribed channel is shown in figure 12. The channel was cut with a low-power carbon dioxide laser (Model 48-1 from Synrad, Inc., Mukilteo, WA). The maximum laser power of 10 W was reduced to 100 mW by running at 1% duty cycle controlled by pulse width modulation. The energy dose delivered to the substrate was set by traversing the scan head across the surface at  $500 \text{ mm s}^{-1}$ . This resulted in an energy dose per unit length of  $0.2 \text{ mJ mm}^{-1}$ . Figure 13 shows the end view of a channel formed by laser ablation. It reveals the cross-section as a hyperbolically-shaped trough. The channel is wider than it is deep with a depth-to-width aspect ratio of approximately 1:2.



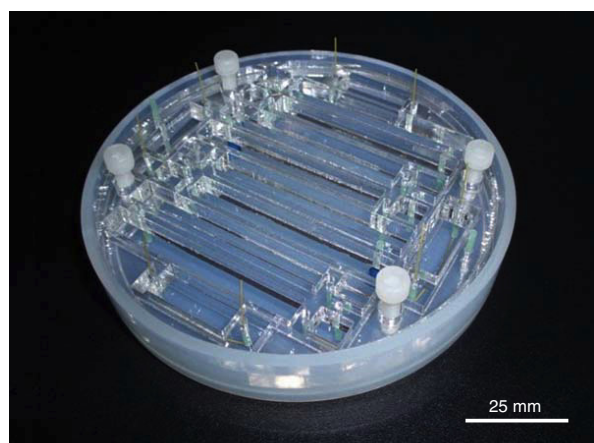
**Figure 14.** Top view of a laser-ablated microchannel in PMHS, with a regular pattern of surface ripple features that are a few microns thick. Laser pulse frequency and scan speed combine to determine the ripple conditions.

In addition to the design flexibility associated with direct-write fabrication, another benefit of laser ablation is the fact that channel geometry and roughness can be varied by adjusting the energy dose delivered to any given region [46]. A particularly extreme example is illustrated in figure 14, in which the combination of laser pulse frequency and scan speed was such that the periodicity of energy pulses was directly manifested in the PMHS sample. The observed ripples are spaced at an approximate distance of  $5 \mu\text{m}$ . This particular channel was scribed with  $25 \text{ mm s}^{-1}$  scanning speed and the laser pulses occurred with a frequency of 5 kHz (a period of  $200 \mu\text{s}$ ). The corresponding periodic separation of pulses is  $5 \mu\text{m}$  along the PMHS substrate, consistent with microscope observation. The power delivered was  $500 \text{ mW}$  for an energy dose of  $20 \text{ mJ mm}^{-1}$ . Adjusting the pulse frequency, scan speed and energy dose provides an effective means of locally manipulating the surface geometry for applications such as open tubular capillary electrokinetic chromatography [23], which benefit from having a very large surface-to-volume ratio. Other examples of applications that demand high surface area include catalytic conversion, particle filtering and convective heat transfer.

### 3.5. Chip fabrication and fluid interfacing

In addition to curing PMHS and forming channels (by casting or laser ablation), three other conditions are important for the application of PMHS in functional microfluidic chips: (1) it should be possible to bond PMHS substrates to form sealed channels, (2) it must be possible to interface inlet and outlet ports with external connections and (3) the material must support electroosmotic flow.

The feasibility of substrate bonding has been tested both by liquid-interface bonding [47] with uncured PMHS as the interfacial material, and plasma-assisted bonding [48]. Two PMHS substrates can be bonded to each other with a secondary curing operation using a thin film of liquid PMHS between



**Figure 15.** Frame assembly in a 100 mm fluoropolymer dish. This particular frame facilitates alignment of multiple inlet and outlet ports for four 64 mm × 16 mm chips and four 31 mm × 8 mm test chips.

substrates. However, the dry (plasma) method is preferred because no special measures are required to prevent clogging of channels. PMHS substrates have been successfully bonded to borosilicate glass and to each other with plasma treatment using a bench-top plasma chamber (Product PDC-001 from Harrick Plasma, Ithaca, NY). Typical plasma conditions of 10 W for 60 s result in bonds that exceeded the material strength of the polymer itself. When mechanically forced apart, the bulk material tears before separation occurs at the bonded interface. Results are similar whether the vacuum chamber was fed with pure oxygen or simply left with residual air. Quantitative investigation of optimal bonding conditions is underway and results will be reported via future publication.

Macro-to-micro interfacing is a non-trivial problem for microfluidic chips, and numerous strategies have been developed [49]. The brittle nature of PMHS (figure 11) makes it especially challenging, and methods of coring the solid material after curing have resulted in poor yield. For producing devices with multiple ports that need to be aligned in specific locations, a supplementary acrylic frame as shown in figure 15 is used during casting. The frame fixes tubing inserts at prescribed locations across the container, and casting the inserts in place eliminates the need for subsequent drilling or coring operations that may lead to brittle fracture of the material.

Finally, an important requirement for any material used in separation processes by electrophoresis is that the channel walls be capable of supporting electroosmotic flow. Wu *et al* have demonstrated that when coated with PMHS, the electroosmotic flow velocity in fused silica capillary columns is enhanced from 1.8 mm s<sup>-1</sup> to 2.4 mm s<sup>-1</sup> [50]. This suggests that PMHS is viable as a material to support electroosmotic flow, and its functionality as such is the topic of current study to be reported in future publications.

#### 4. Conclusions and future work

Polymethylhydrosiloxane has been presented as a candidate material for microfluidic chips. A unique feature of this

material is the ability to modify its surface by hydrosilation, which is advantageous especially for microfluidic separation applications. The chemical modification has been shown to be stable against extreme pH levels. PMHS exhibits UV transparency that is relatively insensitive to sample thickness, indicating good potential for sensor applications based on UV absorption. Complex, high-resolution patterns can be produced in PMHS using soft lithography casting techniques, and features can also be patterned in PMHS by laser ablation. Furthermore, PMHS substrates can be bonded by plasma treatment and arrayed with fluidic interface ports using alignment frames during casting. PMHS meets basic functional requirements for microfluidic electrophoresis chips, and its chemical modifiability justifies further investigation of its performance in CE and related applications.

Preliminary experiments with both hydrosilation treatment and plasma roughening on flat PMHS samples have already been initiated and each of these will be reported via subsequent publications. Next steps in chip development include quantitative characterization of bond strength and seal integrity, followed by demonstration and characterization of electrokinetic flow. Additional future work focuses on selectively modifying PMHS with spatial control confined to the inside surfaces of microchannels without compromising structural or sealing integrity. Thereafter, the chips will be tested for effectiveness in protein separation.

#### Acknowledgments

Part of this work has been supported by the Defense Microelectronics Activity (DMEA) grant H94003-06-2-0605 for Nanoscale Materials and Device Characterization. Scanning electron microscope images were possible thanks to National Science Foundation grant 0421562 for Major Research Instrumentation. The authors acknowledge the California State University Program for Education and Research in Biotechnology (CSUPERB) for partial support during the initial stages of the investigation, and also thank Dr Claire Komives for access to spectrophotometry measurements.

#### References

- [1] Abgrall P and Gué A M 2007 Lab-on-chip technologies: making a microfluidic network and coupling it into a complete microsystem—a review *J. Micromech. Microeng.* **17** R15–49
- [2] Becker H and Locascio L E 2002 Polymer microfluidic devices *Talanta* **56** 267–87
- [3] Lee S J, Chan J C Y, Maung K J, Rezler E and Sundararajan N 2007 Characterization of laterally deformable elastomer membranes for microfluidics *J. Micromech. Microeng.* **17** 843–51
- [4] Jeong O C and Konishi S 2007 Fabrication and drive test of pneumatic PDMS micro pump *Sensors Actuators A* **135** 849–56
- [5] Hsiung S-K, Lee C-H, Lin J-L and Lee G-B 2007 Active micro-mixers utilizing moving wall structures activated pneumatically by buried side chambers *J. Micromech. Microeng.* **17** 129–38



- [6] Duffy D C, Schueller O J A, Brittain S T and Whitesides G M 1999 Rapid prototyping of microfluidic switches in poly(dimethyl siloxane) and their actuation by electro-osmotic flow *J. Micromech. Microeng.* **9** 211–7
- [7] Das C, Fredrickson C K, Xia Z and Fan Z H 2007 Device fabrication and integration with photodefinable microvalves for protein separation *Sensors Actuators A* **134** 271–7
- [8] Sundararajan N, Pio M S, Lee L P and Berlin A A 2004 Three-dimensional hydrodynamic focusing in polydimethylsiloxane (PDMS) microchannels *J. Microelectromech. Syst.* **13** 559–67
- [9] Sun Y, Lim C S, Liu A Q, Ayi T C and Yap P H 2007 Design, simulation and experiment of electroosmotic microfluidic chip for cell sorting *Sensors Actuators A* **133** 340–8
- [10] Thorsen T, Maerkl S J and Quake S R 2002 Microfluidic large-scale integration *Science* **298** 580–4
- [11] Xia Y and Whitesides G M 1998 Soft lithography *Annu. Rev. Mater. Sci.* **28** 153–84
- [12] Horng R-H, Han P, Chen H-Y, Lin K-W, Tsa T-M and Zen J-M 2005 PMMA-based capillary electrophoresis electrochemical detection microchip fabrication *J. Micromech. Microeng.* **15** 6–10
- [13] Steigert J et al 2007 Rapid prototyping of microfluidic chips in COC *J. Micromech. Microeng.* **17** 333–41
- [14] Yin H, Killeen K, Brennen R, Sobek D, Werlich M and vandeGoor T 2005 Microfluidic chip for peptide analysis with an integrated HPLC column, sample enrichment column, and nanoelectrospray tip *Anal. Chem.* **77** 527–33
- [15] Sauer R O, Scheiber W J and Brewer S D 1946 Derivatives of the methylchlorosilanes: V. Polysiloxanes from methylchlorosilane *J. Am. Chem. Soc.* **68** 962–3
- [16] Lawrence N J, Drew M D and Bushell S M 1999 Polymethylhydrosiloxane: a versatile reducing agent for organic synthesis *Perkin Trans. 1* **23** 3381–91
- [17] Pesek J J, Matyska M T, Lee S J and Goedert M 2007 Microfluidic separation devices for biological and pharmaceutical analyses based on a modifiable, optically transparent and nonadsorbent polymeric material *MSB 2007: 21st Int. Symp. on Microscale Bioseparations (Vancouver, British Columbia, Canada, 17 January 2007)*.
- [18] Liu J and Lee M L 2006 Permanent surface modification of polymeric capillary electrophoresis microchips for protein and peptide analysis *Electrophoresis* **27** 3533–46
- [19] Pesek J J, Matyska M T, Sandoval J E and Williamsen E J 1996 Synthesis, characterization and applications of hydride-based surface materials for HPLC, HPCE and electrochromatography *J. Liq. Chromatogr. Relat. Technol.* **19** 2843–65
- [20] Chu C H, Jonsson E, Auvinen M, Pesek J J and Sandoval J E 1993 A new approach for the preparation of a hydride-modified substrate used as an intermediate in the synthesis of surface-bonded materials *Anal. Chem.* **65** 808–16
- [21] Pesek J J, Matyska M T, Williamsen E J, Evanchic M, Hazari V, Konjuh K, Takhar S and Tranchina R 1997 Synthesis and characterization of alkyl bonded phases from a silica hydride via hydrosilation with free radical initiation *J. Chromatogr. A* **786** 219–28
- [22] Pullen P E, Pesek J J, Matyska M T and Frommer J 2000 Characterization by atomic force microscopy of fused-silica capillaries chemically modified for capillary electrokinetic chromatography *Anal. Chem.* **72** 2751–7
- [23] Pesek J J and Matyska M T 2000 Open tubular capillary electrokinetic chromatography in etched fused-silica tubes *J. Chromatogr. A* **887** 31–41
- [24] Duffy D C, McDonald J C, Schueller O J A and Whitesides G M 1998 Rapid prototyping of microfluidic systems in poly(dimethylsiloxane) *Anal. Chem.* **70** 4974–84
- [25] McDonald J C, Duffy D C, Anderson J R, Chiu D T, Wu H, Schueller O J A and Whitesides G M 2000 Fabrication of microfluidic systems in poly(dimethylsiloxane) *Electrophoresis* **21** 27–40
- [26] Wang B, Oleschuk R D and Horton J H 2005 Chemical force titrations of amine- and sulfonic acid-modified poly(dimethylsiloxane) *Langmuir* **21** 1290–8
- [27] Makamba H, Kim J H, Lim K, Park N and Hahn J H 2003 Surface modification of poly(dimethylsiloxane) microchannels *Electrophoresis* **24** 3607–19
- [28] Wang B, Chen L, Abdulali-Kanji Z, Horton J H and Oleschuk R D 2003 Aging effects on oxidized and amine-modified poly(dimethylsiloxane) surfaces studied with chemical force titrations: effects on electroosmotic flow rate in microfluidic channels *Langmuir* **19** 9792–8
- [29] Chen L, Ren J, Bi R and Chen D 2004 Ultraviolet sealing and poly(dimethylacrylamide) modification for poly(dimethylsiloxane)/glass microchips *Electrophoresis* **25** 914–21
- [30] Hu S, Ren X, Bachman M, Sims C E, Li G P and Allbritton N 2003 Cross-linked coatings for electrophoretic separations in poly(dimethylsiloxane) microchannels *Electrophoresis* **24** 3679–88
- [31] Xiao D, Le T V and Wirth M J 2004 Surface modification of the channels of poly(dimethylsiloxane) microfluidic chips with polyacrylamide for fast electrophoretic separations of proteins *Anal. Chem.* **76** 2055–61
- [32] Xiao D, Zhang H and Wirth M J 2002 Chemical modification of the surface of poly(dimethylsiloxane) by atom-transfer radical polymerization of acrylamide *Langmuir* **18** 9971–6
- [33] Slentz B E, Penner N A and Regnier F E 2002 Capillary electrochromatography of peptides on microfabricated poly(dimethylsiloxane) chips modified by cerium(IV)-catalyzed polymerization *J. Chromatogr. A* **948** 225–33
- [34] Sung W-C, Huang S-Y, Liao P-C, Lee G-B, Li C-W and Chen S-H 2003 Poly(dimethylsiloxane)-based microfluidic device with electrospray ionization-mass spectrometry interface for protein identification *Electrophoresis* **24** 3648–54
- [35] Mark J E 1989 Generate reinforcing particles in place *CHEMTECH* **19** 230–3
- [36] Roman G T and Culbertson C T 2006 Surface engineering of poly(dimethylsiloxane) microfluidic devices using transition metal sol–gel chemistry *Langmuir* **22** 4445–51
- [37] Revis A 1990 Process of curing methylhydrosiloxanes *US Patent* 4,954,401
- [38] Altria K 2000 Capillary electrophoresis *Chem. Br* **36** 38–41
- [39] Elder D and Altria K D 2004 Overview of the status and applications of capillary electrophoresis to the analysis of small molecules *J. Chromatogr. A* **1023** 1–14
- [40] Lotters J C, Olthuis W, Veltink P H and Bergveld P 1997 The mechanical properties of the rubber elastic polymer polydimethylsiloxane for sensor applications *J. Micromech. Microeng.* **7** 145–7
- [41] Choi K M and Rogers J A 2003 A photocurable poly(dimethylsiloxane) chemistry designed for soft lithographic molding and printing in the nanometer regime *J. Am. Chem. Soc.* **125** 4060–1
- [42] Vijay M, Ghandehari E, Goedert M, Manickam S K and Lee S J 2007 Fabrication process development and characterization of polymethylhydrosiloxane (PMHS) for surface-modified microfluidic chips *Proc. of the ASME Int. Mechanical Engineering Congress and Exposition (Washington, USA) Paper I M ECE2007-42575*
- [43] Tranchida D, Piccarolo S and Soliman M 2006 Nanoscale mechanical characterization of polymers by AFM nanoindentations: critical approach to the elastic characterization *Macromolecules* **39** 4547–56



- [44] Xu W-H, Xiao Z-Y and Zhang T-Y 2005 Mechanical properties of silicone elastomer on temperature in biomaterial application *Mater. Lett.* **59** 2153–5
- [45] Jo B H, Van Lerberghe L M, Motsegood K M and Beebe D J 2000 Three-dimensional micro-channel fabrication in polydimethylsiloxane (PDMS) elastomer *J. Microelectromech. Syst.* **9** 76–81
- [46] Heng Q, Tao C and Tie-chuan Z 2006 Surface roughness analysis and improvement of micro-fluidic channel with excimer laser *Microfluidics Nanofluidics* **2** 357–60
- [47] Chow W W Y, Lei K F, Shi G, Li W J and Huang Q 2006 Microfluidic channel fabrication by PDMS-interface bonding *Smart Mater. Struct.* **15** 112–16
- [48] Bhattacharya S, Datta A, Berg J M and Gangopadhyay S 2005 Studies on surface wettability of poly(dimethyl) siloxane (PDMS) and glass under oxygen–plasma treatment and correlation with bond strength *J. Microelectromech. Syst.* **14** 590–7
- [49] Fredrickson C K and Fan Z H 2004 Macro-to-micro interfaces for microfluidic devices *Lab-on-a-Chip* **4** 526–33
- [50] Wu Q, Claessens H and Cramers C 1992 The influence of surface treatments on the electroosmotic flow in micellar electrokinetic capillary chromatography *Chromatographia* **33** 303–8