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FABRICATION PROCESS DEVELOPMENT AND CHARACTERIZATION OF POLYMETHYLHYDROSILOXANE (PMHS) FOR SURFACE-MODIFIED MICROFLUIDIC CHIPS

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ABSTRACT

Microfluidic chips made of polymer materials such as polydimethylsiloxane (PDMS), polyimide, and cyclic olefin co-polymer have cost and manufacturing advantages over materials such as fused silica and borosilicate glass. While these materials have been extensively investigated, polymethylhydrosiloxane (PMHS) is an alternative that has a unique combination of properties in terms of UV transparency and potential for chemical surface modification. The present study investigates process development and characterization of PMHS as a new candidate material for microfluidic chip applications, in particular separation processes that would benefit from the ability to custom-engineer its surface conditions. This paper compares different approaches for fabricating microchannel features as well as options for enhancing the surface area of the channel walls. The fabrication methods include replication by casting over patterned molds, soft lithography casting, and material removal by laser ablation. Casting into solid form is achieved in 48-hours at 110 ºC. Laser ablation is studied with energy dose varying from 2 mJ to 160 mJ per millimeter scanned, with channels approximately 100 microns wide occurring at 0.2 mJ/mm. Mechanical characterization is applied to quantify the hardness of cast PMHS, because fine-resolution features are limited by mold removal. PMHS samples have been measured to have a Shore A hardness of 46.2, similar to PDMS that is well-established in polymer microfluidic devices. Surface enhancement techniques including laser and plasma treatment are investigated for the prospective benefit of separation processes that require high surface-to-volume ratio. Spectrophotometry shows that PMHS exhibits transmittance even below 250 nm, which is favorable for sample analysis by UV absorption methods.

INTRODUCTION

Microfluidic technology has the potential to provide rapid, target-specific, and very low-cost analysis for environmental, biological and clinical applications [1]. Early approaches implemented in capillary electrophoresis devices used glass or quartz capillaries, while polymer devices have been increasingly investigated since 1990 [2]. The use of polymers is attractive due to reasons such as low cost, ease of fabrication, and greater flexibility in geometric design. Polymers have been used for a variety of microfluidic applications such as bio-sensing [3, 4], as microchannels [5, 6], lab-on-chip systems [7], and also as coatings [8] on compliant microfluidic structures.

The choice of polymer to be used as a substrate material depends on its mechanical, chemical, and optical properties. Polydimethylsiloxane (PDMS) has been widely investigated in microfluidics [9], but its surface is not readily modifiable for separation processes. Polymethyl methacrylate (PMMA) can be rapidly manufactured by embossing [10], but its thermoplastic nature compromises dimensional stability. Some polyimide microfluidic devices are fabricated by laser ablation [11], but polyimide is opaque to ultraviolet (UV) light, limiting its options for applications involving UV detection methods. Polymethylhydrosiloxane (PMHS) adds a unique combination of optical and chemical properties which motivates the work presented in this paper. In particular, the potential for chemical modification combined with its UV transparency make PMHS a favorable option for bioseparation process [12].

The long-range objective is to fabricate a microfluidic device that is capable of electrokinetically separating biological samples such as proteins and peptides. Prior work using fused silica capillaries has shown enhanced resolution performance with roughened, chemically-modified channels [13]. To transfer the benefits to polymer chips, a non-conventional material, PMHS, is being explored because of its unique combination of chemical and optical properties. The chemical modifiability of PMHS over other polymers is one of the primary motivations for further study on its viability as the substrate material for microfluidic devices. The surface of PMHS has been proven to be modifiable by hydrosilation, as evidenced by Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra [12].

EXPERIMENTATION

Investigations on optical properties and physical behavior of PMHS are reported in this section. Soft lithography methods for microchannel fabrication and feature replication on the polymer have been incorporated with good reproducibility. Laser ablation shows great promise of surface enhancement of the microchannel as well as surface roughening of the PMHS surface.

UV Transmission

Spectrophotometry measurements were performed using a Lambda 35 spectrophotometer from Perkin-Elmer, Inc. (Waltham, Massachusetts, USA). This was used to quantify the performance of PMHS compared to more conventional materials such as PDMS. Quartz was used as a reference material for its known outstanding transmission properties, although its cost makes it impractical for high-volume manufacturing. The results in Figure 1 show that the optical transmittance of PMHS is greater than that of PDMS especially at lower wavelengths, 200 nm to 300 nm. Thus PMHS is confirmed as a superior candidate over PDMS for sample detection methods based on UV absorption, particularly below 230 nm.

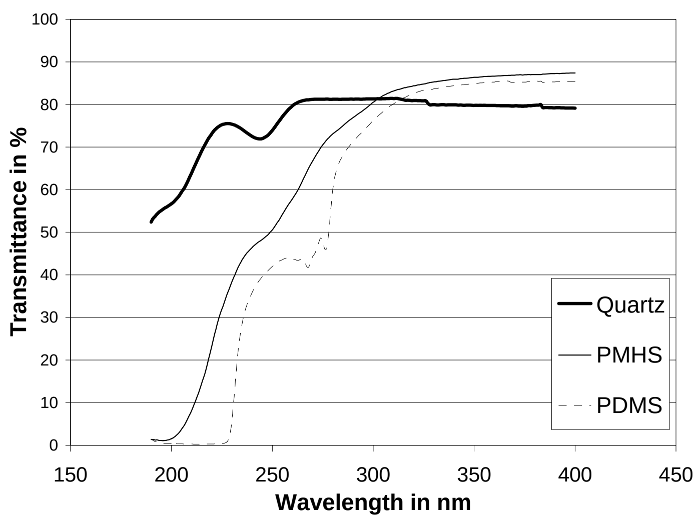

Figure 1. Spectrophotometry results among PDMS, PMHS, and quartz. PMHS transmits substantially in the range below 230 nm, and is thus superior to PDMS.

Casting

Consistent sample preparation is an important requirement for the study of surface modification techniques such as plasma treatment or laser ablation. Individual samples are cast in PTFE or similar perfluoroalkoxy (PFA) dishes. PMHS samples can be batch processed with the implementation of sleeves as shown in figure 2. This method consists of using hollow PTFE cylinders to isolate disc-shaped regions in a wide, flat PFA dish. Thickness is determined by calculating the appropriate volume to dispense, taking into account the volume displaced by the PTFE sleeves.

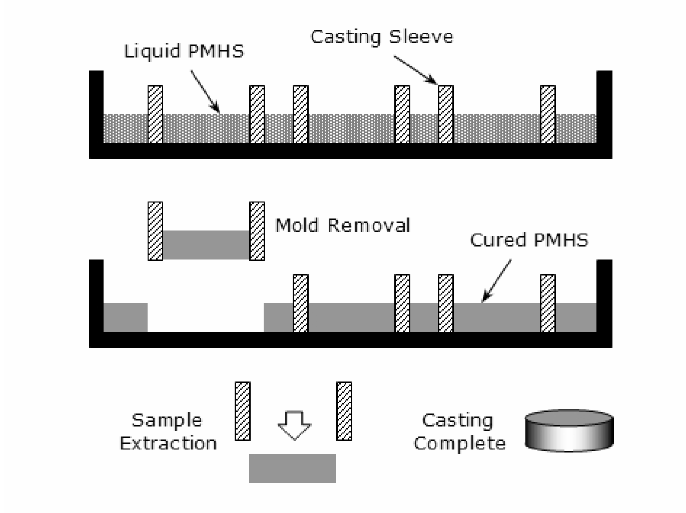

Figure 2. Apparatus for casting PMHS samples. Sample thickness is determined by calculating the net volume of liquid resin that is dispensed.

SU-8 Soft Lithography

The soft lithography method for the fabrication and manufacture of microstructures has been widely used for PDMS processing in microfluidics [9]. This molding technique finds its application with PMHS as well and has been successfully implemented for channel formation and surface feature replication. This method was used to generate patterns with critical dimensions in the order of 10 to 100 µm. The master pattern is prepared by SU-8 photolithography on 100 mm silicon wafers. PMHS casting using patterned silicon wafers was implemented to produce channels of different sizes for microfluidic applications. Adapted from [14], the schematic diagram depicting the PMHS casting process is shown in figure 3.

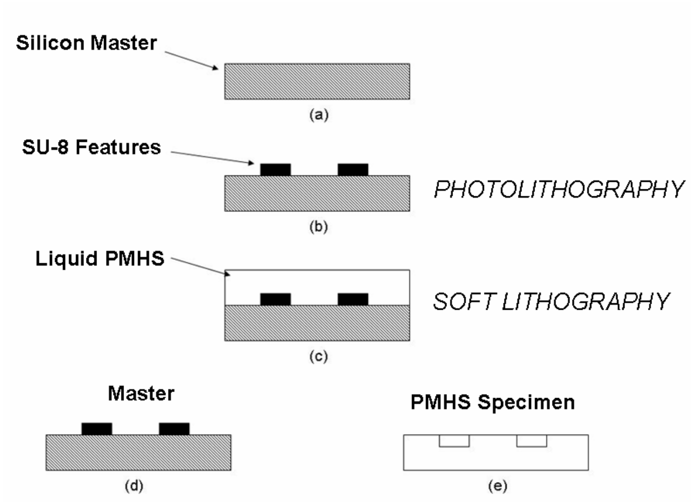

Figure 3. PMHS Casting procedure [14]. (a) Silicon wafer, (b) SU-8 patterns on silicon wafer by photolithography, (c) Liquid PMHS casted over chlorosilane treated silicon master, (d) Silicon master removed from PMHS specimen, (e) Patterned PMHS specimen released from silicon master.

A FEI Quanta 200 Environmental Scanning Electron Microscope with Energy Dispersive X-Ray Analysis (EDAX) was utilized for surface characterization, and the acquired images to demonstrate proof-of-concept are shown in figures 4 and 5. This soft lithographic technique enables duplication of complex structures from the master onto the polymer material with high resolution. This is a simple and inexpensive way to produce structures with higher aspect-ratio as compared to photolithography techniques.

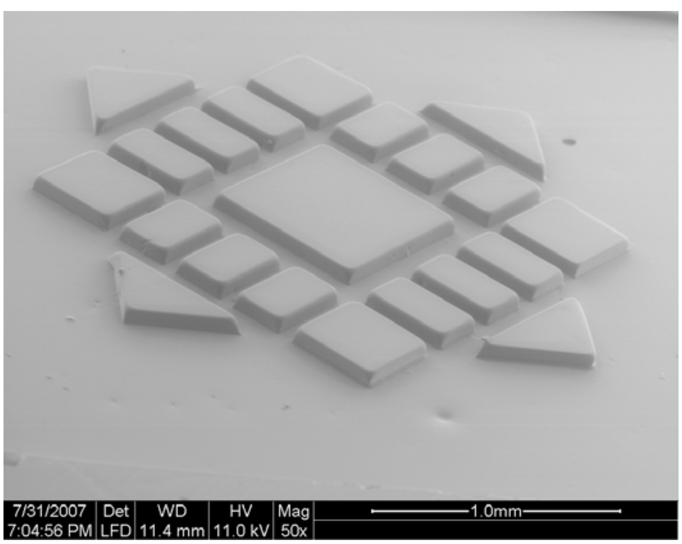

Figure 4. San Jose State University (SJSU) logo patterned on PMHS specimen

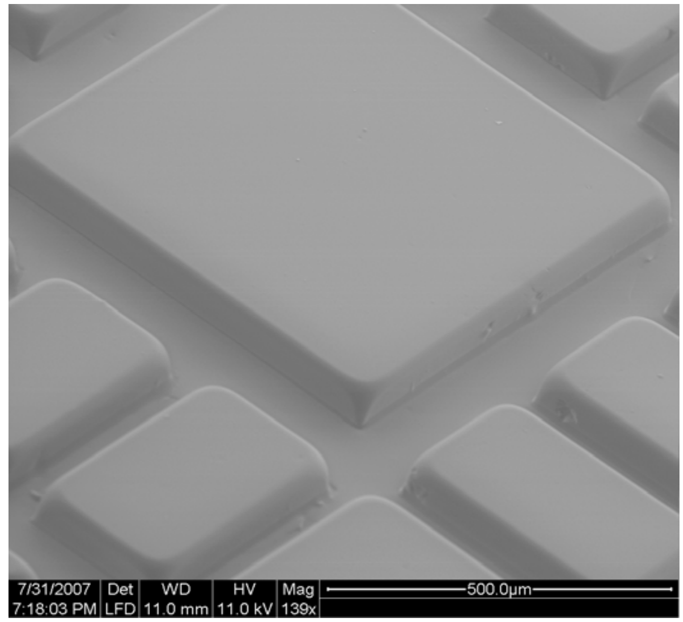

Figure 5. PMHS relief features produced by quick, cost-effective replica molding soft lithography technique.

PDMS has been extensively used as a resin in various soft lithography techniques such as replica molding, imprint molding, and finds its application for flow delivery in microfluidics chips. Unlike PDMS which has uniform curing behavior, PMHS specimens cure in a different manner. The presence of two layers after polymerization is evident as shown in figure 6. While atmospheric exposure during cross-linking leads to the formation of a rigid upper layer, the enclosed lower region turns out to be a soft, pliable layer.

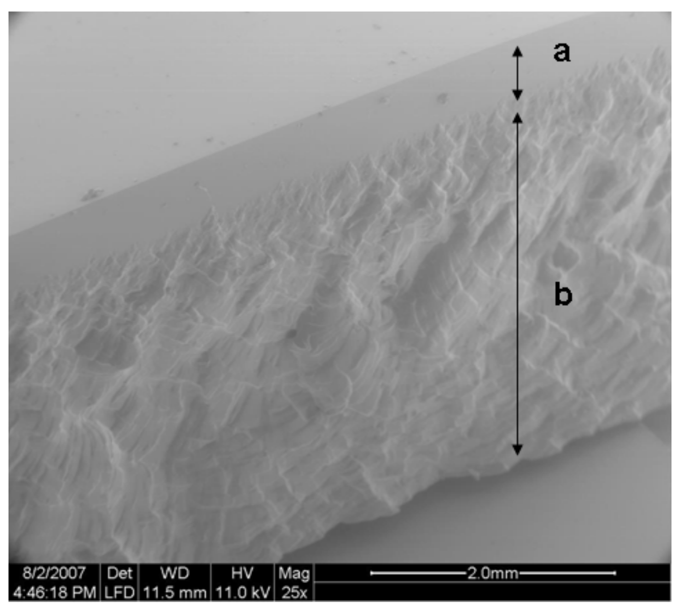

Figure 6. Cross-sectional view of a 100 mm diameter, 3 mm thick PMHS sample confirming the presence of two layers, (a) upper rigid layer and (b) lower pliable layer.

Another discovery was the rigid nature of the top layer (figure 6) and a lip formation along the periphery at the end of the polymerization process (figure 7). On trying to penetrate the PMHS specimen which is essential for port-interfacing of the microfluidic chip, crack propagation was detected across the rigid surface (figure 8). On the other hand, figure 9 shows much less disturbance on the pliable surface. The objective of cleaner and more localized penetration was achieved on the pliable side.

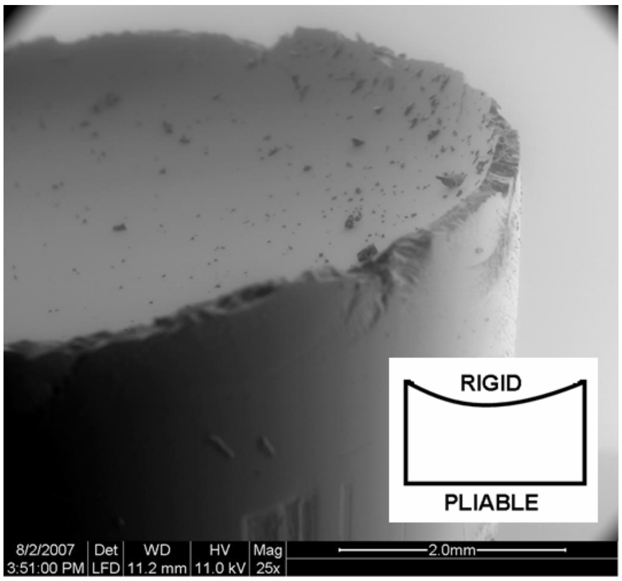

Figure 7. Isometric view of the lip formation along the periphery on the rigid surface of a 50 mm diameter, 4 mm thick PMHS sample. Inset: Schematic diagram showing the lip formation on the top rigid surface of the PMHS specimen.

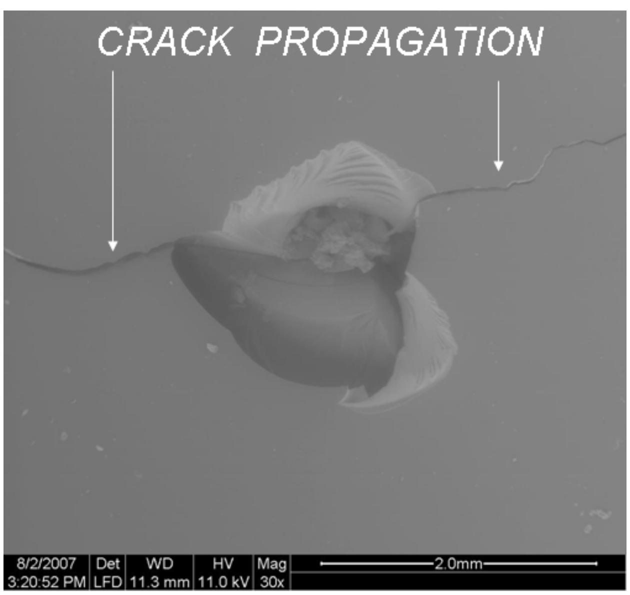

Figure 8. Top view of a hole through the rigid side of a PMHS specimen.

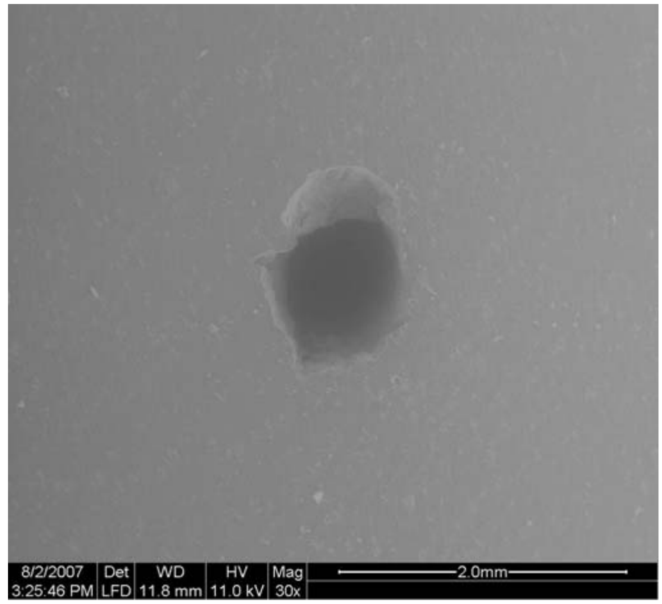

Figure 9. Top view of a hole through the pliable side of a PMHS specimen.

Laser Ablation

The surface of a typical cast PMHS sample has been measured by atomic force microscopy (AFM) to be smooth with a root mean square (RMS) roughness of approximately 30 nm. Figure 10 shows a 30 µm x 30 µm scan field, wherein the PMHS furthermore shows flatness of about 200 nm, except for the small number of isolated particles on the surface.

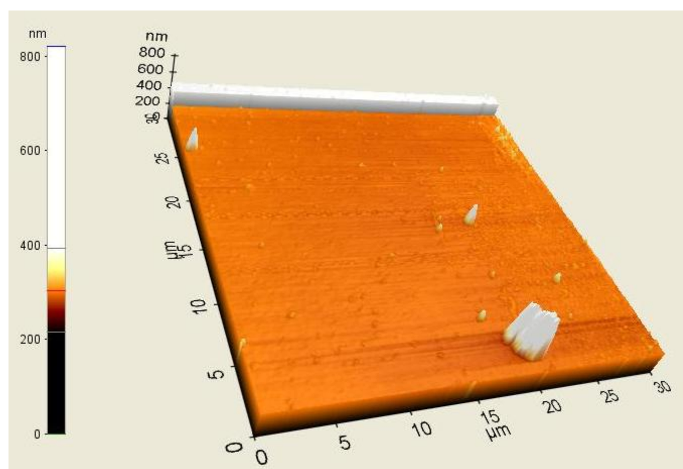

Figure 10. A non-contact mode AFM scan showing the top surface of a cast PMHS sample. Scan courtesy of Park Systems, Inc. (Santa Clara, CA).

A smooth surface is favorable for such considerations as substrate bonding and optical transparency, but in some applications a very rough surface may be preferred. For example, rough side-walls would contribute increased surface area for attachment of a bonded stationary phase for higher sensitivity in chemical and biological separation processes [13].

As an alternative method to channel formation by casting over photo-patterned molds, microchannels have also been fabricated in PMHS substrates by CO_2 laser ablation. The dimensions are suitable for the intended channel width of approximately 100 µm. An additional benefit as shown in figures 11 and 12 is the ability to roughen the surfaces, and to do so on a spatially selective basis. A range of input power was investigated from 100-10,000 mW, and the speed was varied from 120-500 mm/sec.

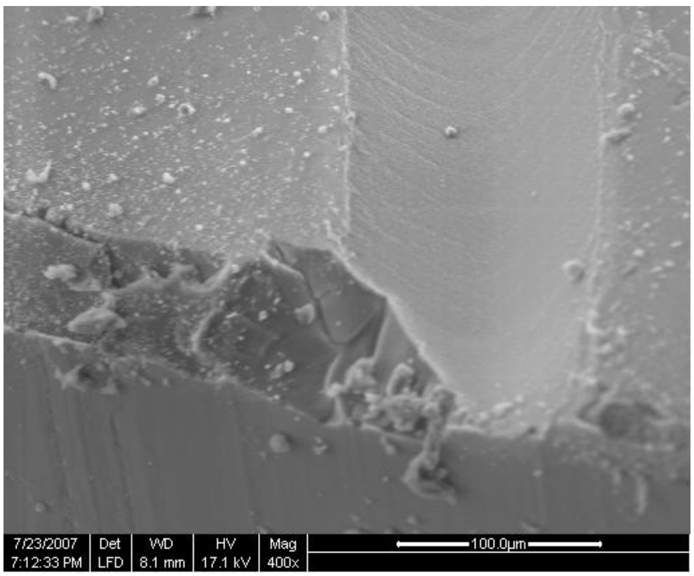

Figure 11. Laser-ablated channel on a PMHS substrate with energy dose of 0.20 mJ/mm.

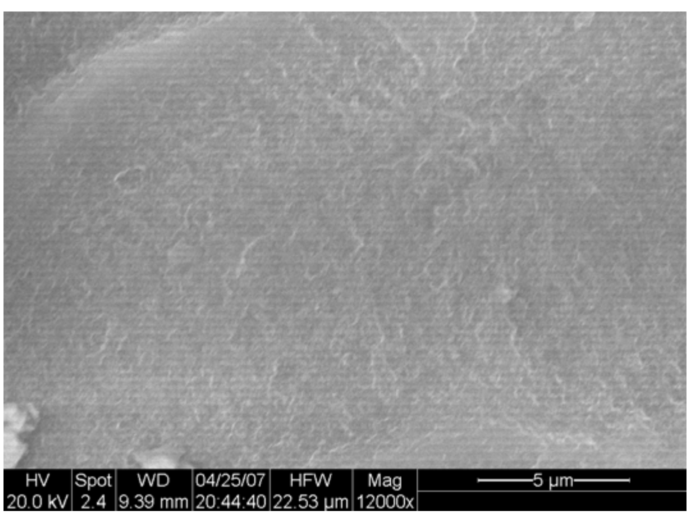

Figure 12. Close-up view of a laser-ablated channel on a PMHS substrate. This highlights the ability to increase channel surface area.

As an extension to this principle of surface roughening by energy impingement, plasma treatments [15] are under investigation and results will be reported in future work.

Mechanical Characterization

Thermal curing has been considered an easier mode of curing as compared to electron-beam radiation, UV curing, or microwave radiation [16]. Varied curing conditions affect the mechanical properties of PMHS, hardness in particular. Durometer testing has been used to quantify the hardness of PMHS and compare it to PDMS, which is far more routinely used in microfluidics.

The sample size chosen was 50 mm diameter, with a thickness of 3 mm. Five measurements were taken per sample, at the center and at four evenly spaced locations along an orthogonal cross pattern. The average Shore A hardness for PDMS was measured to be 55.6 with a standard deviation among location measurements being 0.55. On the other hand, the Shore A hardness of PMHS was found to be lower with a value 46.2 with a standard deviation of 0.84. Although durometer results are similar, PDMS elastically restores its shape even under large strains whereas PMHS does not. PMHS has been found to have poor resilience and suffers from brittle fracture. While the lower durometer values would help in easier channel fabrication in PMHS, use of additives in future experiments could help improve its elastic recovery.

CONCLUSION

PMHS has been presented as a new candidate material for microfluidic chip applications. Prior work has shown that it is chemically modifiable by hydrosilation, and spectrophotometry results show that PMHS exhibits better UV transmission than common materials used in microfluidic applications. Soft lithography casting has been demonstrated for making channels approximately 100 µm in lateral width and relief features ranging from 10 to 100 µm. Casting PMHS resin in smooth PFA containers produces repeatable samples with trouble-free mold release. Multiple options for roughening the surface exist, and these include laser ablation, plasma treatment, and direct casting onto rough molds. The durometer of PMHS has been measured to be similar to PDMS, but PMHS is subject to brittle fracture. Future and ongoing work involves optimization of processing conditions for higher resilience, fine feature resolution, and repeatable control of surface roughness.

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