Enhancement of the thermo-mechanical properties of PDMS molds for the hot embossing of PMMA microfluidic devices

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Enhancement of the thermo-mechanical properties of PDMS molds for the hot embossing of PMMA microfluidic devices

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Abstract

We present a cost-efficient and rapid prototyping technique for polymethylmethacrylate (PMMA) microfluidic devices using a polydimethylsiloxane (PDMS)-based hot embossing process. Compared to conventional hot embossing methods, this technique uses PDMS molds with enhanced thermo-mechanical properties. To improve the replication performance, increases in both PDMS stiffness and hardness were achieved through several processing and curing means. First, the amount of curing agent was increased from 1/10 to 1/5 with respect to the amount of prepolymer. Second, the cured PDMS was thermally aged either over three days at 85 °C or for 30 min at 250 °C. Those combined steps led to increases in stiffness and hardness of up to 150% and 32%, respectively, as compared to standard PDMS molds. Using these enhanced molds, structures with features of the order of 100 μm in PMMA are successfully embossed using a standard laboratory press at 150 °C. The PDMS molds and process produce identical structures through multiple embossing cycles ($\geqslant$10) without any mold damage or deterioration. A Y-shaped microfluidic mixer was fabricated with this technique. The successful demonstration of this enhanced PDMS-based hot embossing technique introduces a new approach for the rapid prototyping of polymer-based microfluidic devices at low-cost.

(Some figures may appear in colour only in the online journal)

1. Introduction

Microfluidics is now an ubiquitous field that offers a wide range of applications in portable chemical and biological analyses such as electrophoresis, polymerase chain reactions and protein analysis [1]. Accordingly, the fabrication of microfluidic devices has attracted tremendous attention due to their portability, reduced amount of sample and chemical reagent use, low cost, high performance and high degree of integration [2–4]. The first generation of microfluidic chips was fabricated using a planar glass processes, chosen in the early stages of chip production due to its surface properties and development of compatible microfabrication technologies [5, 6]. However, the fabrication of glass chips

presents numerous challenges since it is time-consuming, involves hazardous and dangerous chemicals, and is limited in terms of geometrical modifications [7, 8]. Over the last few decades, there has been a strong demand for the development of polymer-based microfluidic devices.

Polymeric microfluidic devices have many advantages since they (1) have a wide availability in terms of material properties and surface chemistries, (2) are chemically and biologically compatible, (3) are suitable for fabrication in various geometries including high aspect ratios, (4) are relatively inexpensive and easy to fabricate, and (5) make mass manufacturing possible [7, 8]. Commonly-used polymers include polydimethylsiloxane (PDMS), polymethylmethacrylate (PMMA), polycarbonate, and cyclic

olefin copolymer (COC). Among them, PMMA has been one of the most popular polymers for microfluidics since it is cheap, has excellent transparency to visible light, has good electrical and mechanical properties, and is biocompatible [4, 9]. To fabricate PMMA devices, injection molding [10], hot embossing [11], room-temperature imprinting [12], laser ablation [13], *in situ* polymerization [14, 15] and solvent etching [16] have been used. Hot embossing is well-suited for the rapid fabrication of PMMA chips and therefore for mass production [11, 17]. This method uses the behavior of PMMA at temperatures above the glass transition temperature (T_g), where it becomes soft and flexible.

A variety of techniques have been developed for the fabrication of PMMA chips by this hot embossing method. In many cases, the embossing master is engraved in silicon [12, 18]. Wet chemical and deep dry etching techniques are able to accommodate decent structures on silicon. However, etched silicon typically suffers from size mismatch between photomask and etched features [19]. Metal molds by electroplating [17, 19] are also employed since they have better mechanical durability than silicon and are suitable for mass production, but the electroplating process is time-consuming [20, 21]. Poor adhesion to seed layers on the metal, and non-uniform deposition, are other challenges [22]. Furthermore, a special mold design is typically required in both silicon and metal for the demoulding process. To overcome these issues, soft molds made of PDMS have been employed [22–28], which lowers fabrication costs, reduces processing times, and allows for higher complexity.

Hot embossing techniques using soft PDMS molds have been developed by several groups. Narasimhan *et al* [22] demonstrated that PMMA-based microstructures, with a feature size of the order of 40 μm and an aspect ratio of two, were fabricated using a PDMS mold. Russo *et al* [28] used PDMS molds to fabricate polystyrene (PS) micro-pillars, 1.1 μm in diameter spaced 0.9 μm apart and 6.2 μm high. The PS replica was embossed by four binder clips with a compression force of 350 N/cm^2 in a vacuum oven at 210 °C for 20–60 min. Recently Goral *et al* [27] showed a similar method to Russo *et al*'s work in that a PDMS mold was used to emboss PS in a standard laboratory oven using two 3/4 inch wide binder clips. Compared to the work of Russo *et al*, they improved the pattern transfer and obtained a replication of 5 μm $\times$ 7.5 μm rectangular and 15 μm tall micro-pillars. Although microstructures in these studies can be fabricated by hot embossing with PDMS molds, no comprehensive studies have investigated the embossing performance, which indicates the degree of the fidelity of the embossed structures to the original mold, expected to be low since the mold masters are soft [27].

The embossing performance can be improved by various factors such as the embossing conditions (e.g., temperature, pressure, time) and the properties of the molds (e.g., stiffness, hardness, thermal conductivity). Among them, the stiffness and hardness of the mold master play important roles in the hot embossing process in that stiffer molds offer a higher quality of embossed structures [29]. All previous techniques for the hot embossing of polymer chips used PDMS at a mixing ratio of 10:1 (PDMS prepolymer to curing agent ratio). It is known that increased amounts of the curing agent reduces uncrosslinked prepolymers and hence increases the stiffness of PDMS [30]. Stiffness increase is also possible by thermally ageing PDMS at 100 °C for few hours or days [31]. Combining these methods, which enhance PDMS properties, gives an opportunity to improve the replication performance of embossed structures.

In this technical note, we present a hot embossing technique which allows rapid, low-cost and mass-produced fabrication of PMMA microfluidic chips with soft PDMS molds. To reinforce the mechanical and thermal properties of PDMS, we combine previously isolated approaches into an integrated process. First, the PDMS stiffness and hardness are improved by changing the mixing ratio from 10:1 to 5:1. Second, the increases in curing agent makes the PDMS molds thermally stable up to 300 °C, allowing the hot embossing process to take place at higher temperatures that facilitate the reproduction step. Third, the stiffness and hardness are further increased by two different thermal ageing methods; either fast but with less of an increase in stiffness and hardness, or slow but with more of an increase in stiffness and hardness. For the fast method, the PDMS molds were thermally aged at 250 °C for 30 min, resulting in 78% and 28% increases in stiffness and hardness, respectively. For the slow method, the PDMS molds were thermally aged at 85 °C for three days, leading to 150% and 32% increases in stiffness and hardness, respectively. The enhanced thermo-mechanical properties of the PDMS molds made it possible to emboss PMMA chips with a low-cost regular laboratory press without the need for an expensive hot embossing system. The feasibility of this enhanced technique to create microfluidics systems was demonstrated by employing the fabricated PMMA chip in a fluid mixing application.

2. Experimental details

2.1. Fabrication of the Si master

The silicon master was fabricated using photolithography as described in previous literature [32, 33]. Briefly, a plain polished 3 inch silicon wafer (University Wafer, MA, USA) was cleaned with acetone and isopropanol (IPA) subsequently, and was treated by plasma (PDC-32G, Harrick Plasma, USA) for 6 min. A negative photoresist SU-8 2075 (Microchem, MA, USA) was coated at 2000 rpm for 40 s in a spin coater (Specialty Coating Systems, Inc., USA), as shown in figure 1(*a*). The coated silicon wafer was softbaked at 65 °C for 5 min and subsequently at 95 °C for 25 min on hot plates. After leaving it at 65 °C for 1 min and then at room temperature for 10 min, the wafer was exposed to UV at 13 mJ cm^{-2} for 23 s by using a transparent photomask containing a printed design (figure 1(*b*)). Following exposure, the wafer was hardbaked at 65 °C for 3 min and at 95 °C for 15 min. It was then cooled down to 65 °C for 1 min and room temperature for 15 min, respectively. The baked silicon wafer was then developed (Microchem, USA) for 10 min, as shown in figure 1(*c*). After rinsing with IPA and DI water, the wafer was baked in a laboratory oven for 3 h.
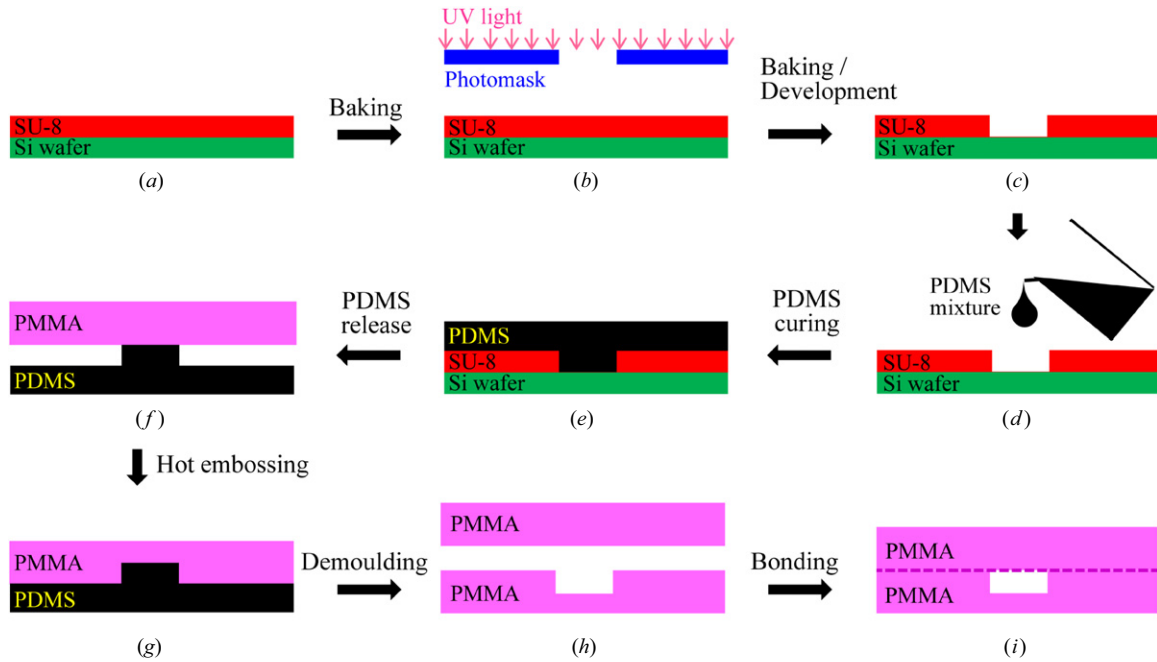
Figure 1. A schematic of the PDMS-based hot embossing process for PMMA microfluidic devices. (*a*) SU-8 2075 is deposited on the Si wafer. (*b*) UV light is used to bake SU-8 layer through a photomask containing the device patterns. (*c*) An SU-8 developer removes unexposed patterns. (*d*) A mixed PDMS solution is poured onto the Si substrate. (*e*) The PDMS is cured in the oven and carefully peeled off the Si substrate. (*f*) A plain PMMA substrate is prepared and brought into conformal contact with the PDMS mold. (*g*) The assembly of PMMA and PDMS is compressed in the hydraulic press. (*h*) After removing the embossed PMMA, another plain PMMA substrate is prepared. (*i*) Two PMMA substrates are bonded together.

2.2. PDMS mold fabrication

The PDMS mold was prepared by standard softlithography [34]. The PDMS prepolymer and the curing agent were well mixed in a plastic cup at a ratio of 5:1 (w/w) or 10:1. The mixture was poured on the patterned silicon wafer in a petri dish to generate a negative replica of the microstructures and was degassed for 20 min to remove air bubbles formed during mixing, as shown in figure 1(*d*). The PDMS with a mixing ratio of 5:1 (5:1 PDMS) was then cured on the hot plate at 85 °C for 30 min, whereas the PDMS with a 10:1 mixing ratio (10:1 PDMS) was cured at 85 °C for 1 h (figure 1(*e*)). Once cured, the PDMS mold was carefully peeled off the silicon master. The 10:1 PDMS mold was used for hot embossing without further treatment. In contrast, the 5:1 PDMS was peeled off and put on the glass microscope slide (Fisher Scientific, USA) to thermally age the PDMS at 250 °C for 1 h. The thermally-aged 5:1 PDMS was then used as a mold for hot embossing.

2.3. Hot embossing of PMMA

Figure 1 shows the fabrication process of PMMA chips with the PDMS-based hot embossing technique. As previously described, the positive PDMS mold was prepared by standard softlithography (figures 1(*a*)–(*e*)). The cured PDMS was transferred onto the glass slide with the microstructures facing up. The PMMA substrate (40 mm × 50 mm × 3 mm) was cut by a CO_2 laser (M360, Universal Laser Systems, USA). The substrate was then cleaned with IPA and dried with compressed air. In the meantime, a laboratory hydraulic press with heating platens was set to the embossing temperature of 145 °C. The press (Carver Inc., model 4358, USA) used in
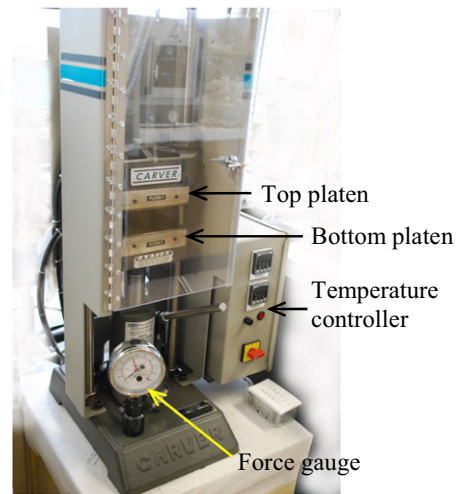
Figure 2. A laboratory hydraulic press system composed of top and bottom platens equipped with a temperature controller. The attached force gauge shows the mounting forces between the two platens.

this work is shown in figure 2. The PMMA piece was brought into conformal contact with the top of PDMS on the glass slide, as shown in figure 1(*f*). Another glass slide was used to sandwich the PDMS mold and the PMMA piece. Once the temperature reached the set point, the assembly was carried onto the bottom heating platen in the press. After waiting for 1 min, approximately 2 kN of force were applied with the press to the assembly for 3 min (figure 1(*g*)). After 3 min, the press was released and the embossed assembly was removed from the press, as shown in figure 1(*h*). The assembly was allowed to cool down to room temperature for 10 min and

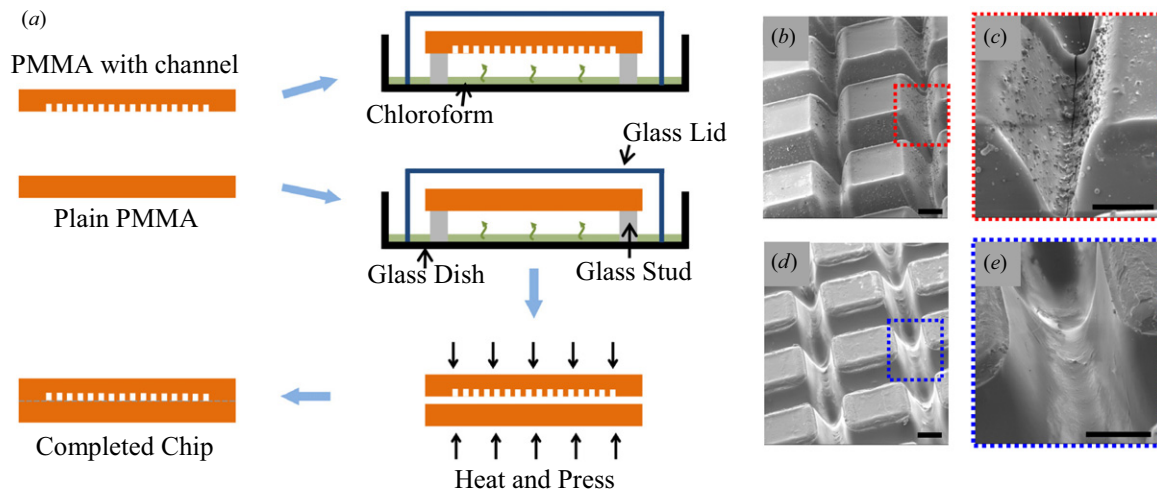**Figure 3.** (*a*) Schematic of the PMMA–PMMA bonding procedure with chloroform exposure for 70 s. (*b*) and (*c*) SEM images of PMMA chips after CO_2 laser ablation at different magnifications without chloroform treatment. (*d*) and (*e*) SEM images after 70 s of chloroform exposure. It can be seen that surface roughness is significantly reduced after the chloroform exposure. The scale bars show 100 μm.

then the embossed PMMA piece was carefully peeled off the PDMS mold. The demoulding process was straightforward, performed manually without any assistance. The embossed PMMA piece was cleaned with IPA and dried with compressed air for further use.

2.4. Bonding of PMMA chips

A detail bonding procedure is shown in figure 3. A plain PMMA substrate was prepared at the same size as the embossed piece, cleaned and dried by IPA and compressed air, respectively. Inlet and outlet holes with 1 mm diameter were created on the embossed PMMA piece by CO_2 laser ablation. Afterward, both the embossed and plain PMMA were exposed to chloroform (Anachemia, Canada) for 70 s inside glass petri dishes. As shown in figures 3(*b*)–(*e*), while providing strong bonding, the exposure of the PMMA chip to chloroform also made the surface smooth. Two PMMA substrates were then brought into conformal contact between two aluminum plates holding PDMS pads. Next, the whole assembly was placed in the press to provide 1.3 kN of clamping force at 76 °C for 10 min. The assembly was then removed from the press and finally both inlet and outlet ports (P–881, IDEX Health & Science) were connected to the bonded chip.

2.5. Scanning electron microscopy (SEM)

The microstructure features of PDMS molds and embossed PMMA substrate were imaged using an SEM (Hitachi S-250, Japan). All samples were sonicated in an ultrasonic bath for 1 h and subsequently cleaned using compressed nitrogen to remove dust particles. The samples were then mounted onto the SEM stubs using a carbon tape, and were coated with 50 Å of gold in argon plasma under a vacuum. Finally, images were captured at different magnifications.

2.6. Visualization of fluid mixing

The working solution used in the fluid mixing experiments was a 50 μmol L^{-1} fluorescein (Sigma, Canada) in DI water.

Two syringes, containing the 10 mL of fluorescein solution and plain DI water respectively, were installed in syringe pumps. Each solution was connected to the inlet ports of the microfluidic chip, while the outlet port was open to atmospheric pressure. While the injection flow rate in both syringes was set to the same value of 5 μL min^{-1}, images were taken through an inverted optical microscope (DMI 6000B, Leica). A built-in 100 W mercury lamp was used to excite the fluorescein by adjusting the illumination intensity. A filter cube was used to cut out wavelengths from the illumination source outside of the narrow 460–500 nm band and to pass fluorescein's emission within the 510–560 nm range (mainly green in color). Individual images were taken by a CCD camera (Orca-ER, 1344 × 1024 pixels, Hamamatsu) with a 5 × or a 10 × microscope objective (N Plan, Leica) and a 0.5 × camera adaptor.

3. Results and discussion

The crucial physical parameters controlling the quality of the embossed structures include embossing temperature, compression force and embossing time. These parameters vary depending on the type of material being embossed. The embossing temperature (T_E) is typically in-between two temperatures: the glass transition temperature T_g and the melting temperature T_m of the material. To characterize the fidelity of the microstructures replicated by hot embossing with the hydraulic press, a square array of circular posts was created on the 10:1 PDMS mold. Figure 4(*a*) shows a photograph of the cured 10:1 PDMS mold containing three hundred circular posts. The surface area of the PDMS is 3 cm × 4 cm and the thickness is 3 mm. The same size of the PMMA substrate is on the top of the PDMS mold to perform hot embossing in the hydraulic press. Figure 4(*b*) shows a magnified microscope image of the PDMS mold with nine circular pillars of 200 μm diameter. For the temperature effect, figure 4(*c*) shows a micrograph image of the embossed PMMA structures at 155 °C for 3 min. Since it is well known that exposure of the
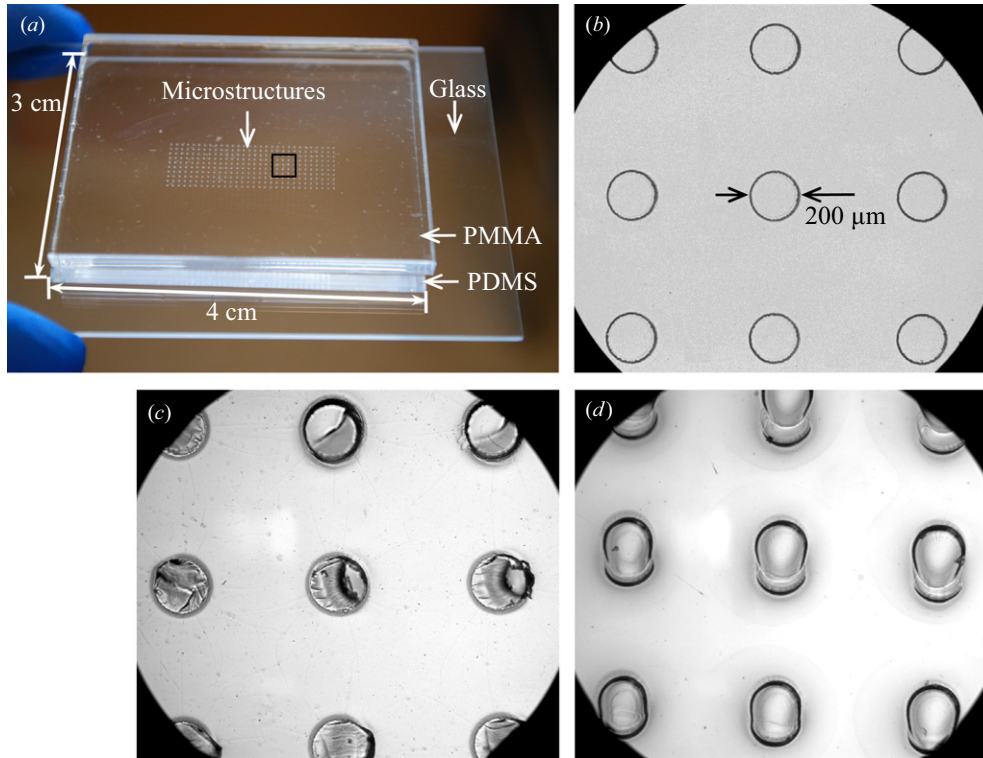
Figure 4. (*a*) A photograph of the assembly of the 10:1 PDMS mold and PMMA substrate on the glass slide. The thickness of the PDMS mold is 3 mm. The black rectangle indicates the image area, as shown in (*b*)–(*d*). (*b*) A microscope image of the 10:1 PDMS mold composed of nine circular pillars. (*c*) Circular pillars embossed by the PDMS mold (*b*) with a 2 kN force at 155 °C for 3 min. (*d*) Nine pillars squeezed due to the over-exertion of the embossing force.

PMMA substrate to extreme embossing temperatures results in deficient structures, it is apparent from this figure that the bottom surface of the structure was crushed due to an excessive temperature exposure during embossing. Note that the T_g and T_m of PMMA are 106 °C and 160 °C, respectively. It was also noticed that lower embossing temperatures in the range of 120–135 °C produced incomplete structures, and therefore in this study the embossing temperature T_E was chosen to be 145 °C.

Pressure plays another important role in producing faithful embossed structures. It was observed that the quality of the embossed structures remained the same when the embossing pressure varied within 10% of its optimum value. However, the replication performance of the PMMA substrate with the PDMS mold became worse when the embossing pressure was out of range by more than 10%. Figure 4(*d*) shows the embossed structures when the embossing pressure was 20% more than the most suitable condition, resulting in the production of poor elliptical pillars. We found that the application of a 2kN force at 145 °C for 3 min ensured the highest embossing fidelity with PMMA substrates using a PDMS soft mold.

Other factors affecting the replication performance of the hot embossing technique are the shape of the PDMS mold and the surface property of the PMMA substrate. The flatness and proper leveling the of PDMS mixture while curing also determine the quality of the embossed structures since a uniform thickness of the PDMS mold ensures evenly distributed embossing force on the PMMA substrate. To
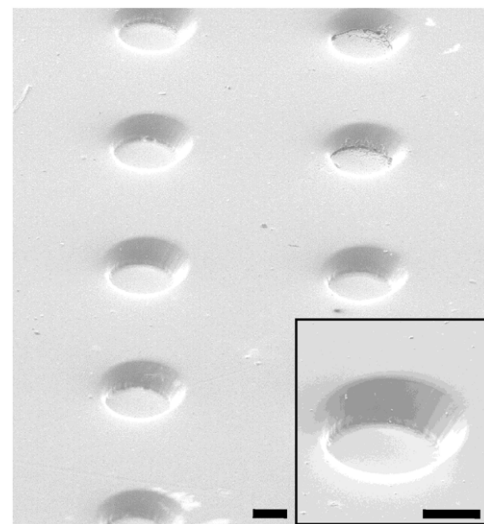
Figure 5. An SEM image of embossed circular pillars in a PMMA substrate using the 10:1 PDMS mold with a 2 kN force at 145 °C for 3 min. Scale bars indicate 100 μm.

ensure flat PDMS molds, the hot plate was carefully balanced during curing. The PMMA substrates prepared from laser ablation frequently have sharp edges which make the entire surface unbalanced. To get a flat surface, ultrafine sandpaper (McMaster Carr, USA) was used to smooth the surfaces of the PMMA substrate before embossing.

Figure 5 shows an SEM image of representative circular pillars in the PMMA fabricated using the hot embossing

technique by a hydraulic press with the 10:1 PDMS mold. During the hot embossing process, a force of 2 kN was applied for 3 min while the embossing temperature was maintained at 145 °C. In the figure, the diameters of the top and bottom surfaces of each pillar are approximately 250 μm and 210 μm, respectively. Considering the diameter of the PDMS mold is 200 μm, the embossed geometry has a 25% and 5% increased diameter at the top and bottom surfaces. The expanded structures are due partially to the thermal expansion of the PDMS mold during the embossing process [35]. Skewed structures are observed in figure 5 due to the relatively low stiffness of the PDMS mold. Since the thermal expansion coefficient is inversely proportional to the Young's modulus [36], the stiffer mold produces microstructures with less expansion. Collectively, although the pressure, temperature and time are all matched to the best embossing conditions, these results suggest that there is a likelihood of improving the quality of the embossed structures through enhancing the material properties of the PDMS molds.

Stiffer molds would enable less thermal expansion of the PDMS and hence it is expected that they would produce more reliable structures. It is known that the stiffness of PDMS can be increased by increasing the ratio of the curing agent to the prepolymer [30, 37]. Although there are numerous conditions of the mixing ratio available to increase the stiffness, in this study we used 10:1 and 5:1 ratios for comparison, which are the most common mixing conditions [1–3, 30, 37], in consideration of the embossing performance of a single PDMS mold. Rather than using a single mold with a higher mixing ratio (for example, 2:1) for multiple embossing runs, we used a new mold before the total number of embossing cycles reached ∼10 cycles. The 10 embossing cycles were chosen for the following reasons. First of all, the 10 embossing cycles are relevant to available studies [22, 26, 27] that reported embossed structures after 4, 7 and 20 cycles. Second, the 10 cycles are chosen under the consideration of two thresholds: (1) the embossing performance of the single mold and (2) the easiness and cost of PDMS mold fabrication. Third, more importantly, the focus of this study was on the investigation of the performance of PDMS molds with enhanced thermo-mechanical properties for a hot embossing process and we assumed that 10 cycles for a single mold is acceptable range. The maximum number of cycles is known to be around 20 times in the literature [22].

The Young's moduli of PDMS at fabrication and post-curing conditions were measured through a tensile test. A PDMS specimen (8 cm × 0.6 cm × 0.1 cm) was prepared and tested in a universal tensile tester (Model 840 LEZ, Test Resources, USA). Each test was set to 10% elongation from the initial specimen length. Figure 6 shows the resulting stress–strain curves at different mixing ratios. For the 5:1 PDMS, the stress reached more than 0.26 MPa, compared to 0.12 MPa for the 10:1 PDMS. In both tests, the stress was not exactly linear with the strain since PDMS is not a purely elastic material [38]. The Young's modulus is estimated by the slope of the curves at the intersection between the curve itself and a line passing through a midpoint of the strain, corresponding to 5% in these tests (as shown in the inset). The estimated Young's moduli
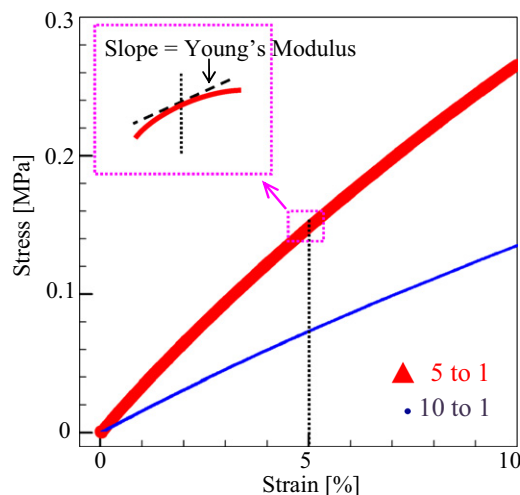

Figure 6. Tests for a stress–strain relationship at different mixing ratios (prepolymer: curing agent) of PDMS. Inset: Young's modulus was estimated by the slope of the curve at the midpoint of the elongation.

for both 5:1 and 10:1 PDMS are 1.61 MPa and 1.35 MPa, respectively. A 20% increase in curing agent makes the cured PDMS much stiffer (∼20%), and this behavior is in agreement with results reported previously [30, 37].

Improvement in the stiffness of PDMS is also possible by thermal ageing [39]. Eddington *et al* showed that the Young's modulus of the cured 10:1 PDMS increased by more than 80% when aged at 100 °C for seven days. The increase of the Young's modulus is most likely due to the displacement of volatile polymer chains with lower molecular weight and non-polymerized prepolymer to the PDMS surfaces [39, 40]. In addition to thermal ageing, it was found that post baking of PDMS at 250 °C after curing provides the opportunity to significantly increase its stiffness further. Although the highest viable temperature of the 10:1 PDMS for thermal molding without forming a gas bubble in the mold is known to be approximately 150 °C, the 5:1 PDMS, cured at 85 °C for 30 min and subsequently postbaked at 250 °C, can be usable at temperatures up to 250 °C without failure. The maximum reliable temperature for 5:1 PDMS is known to be 350 °C [41], but it was damaged during the hot embossing process after thermal ageing it for 2 h at 300 °C. Therefore, the postbaking temperature of the PDMS was chosen to be 250 °C, which rapidly increased its stiffness in a short time.

Table 1 summarizes the Young's modulus of the cured PDMS molds under different conditions: the mixing ratio, curing time, and thermal ageing temperature and time. In agreement with a previous study [37], a higher amount of curing agent make the PDMS stiffer. When the PDMS is thermally-aged at 85 °C for 72 h, its Young's modulus remarkably increases regardless of the mixing ratio (a 150% increase for the 5:1 ratio and a 44% increase for the 10:1 ratio). More importantly, the modulus of the 5:1 PDMS increases more than 78% with post-baking at 250 °C for only 30 min, while a longer baking time has no effect on further increasing the stiffness. Accordingly, the thermally-aged 5:1 PDMS was used in the embossing process.
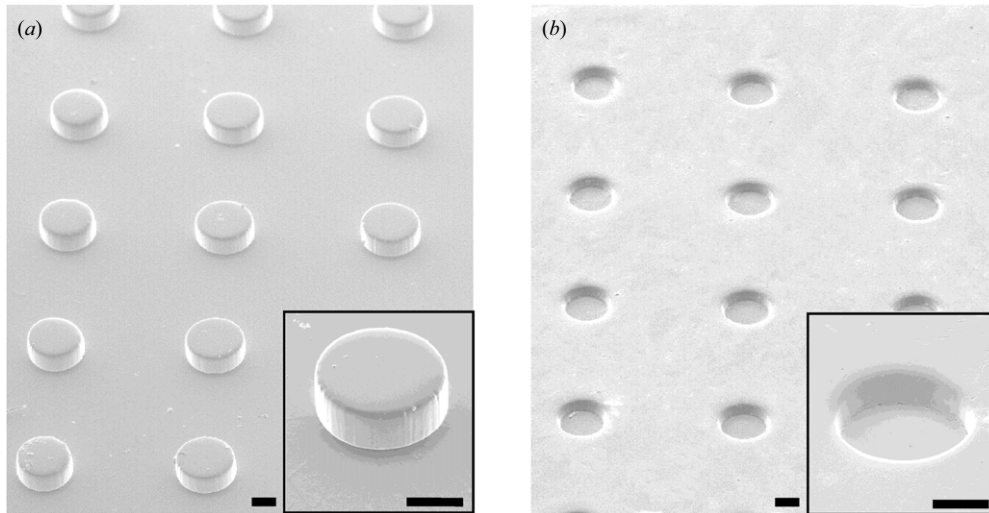
Figure 7. SEM images of (*a*) the 5:1 PDMS mold and (*b*) the embossed PMMA. Each scale bar represents 100 μm.

Table 1. Young's modulus of PDMS at different curing conditions.

Mixing ratio	Curing T (°C)	Curing time (h)	Thermal ageing		E (MPa)
			T (°C)	Time (h)	
5:1	85	0.5	–	–	1.61
		1	–	–	1.57
			85	18	1.93
				72	3.29
		0.5	250	0.5	2.39
				1	2.56
				2	2.46
10:1	85	0.5	–	–	1.35
		1	–	–	1.39
			85	18	1.72
				72	2.01

Table 2. Hardness scale of PDMS at different curing conditions.

Mixing ratio	Curing T (°C)	Curing time (h)	Thermal ageing		Hardness[a] (Shore A)(–)
			T (°C)	Time (h)	
5:1	85	0.5	–	–	48
		1	85	18	56
				72	61
		0.5	250	0.5	59
10:1	85	0.5	–	–	46
			85	18	54
				72	58

[a] Shore A scale: 1–100.

To evaluate the replication performance of the thermally-aged 5:1 PDMS, the hot embossing process was performed using the hydraulic press. Figure 7(*a*) shows SEM images of the 5:1 PDMS mold, consisting of a series of circular pillars with a height of 30 μm. The PDMS mold was cured at 85 °C for 30 min and thermally aged at 250 °C for 1 h. After thermal ageing, the mold was used to emboss PMMA, as shown in figure 7(*b*). The diameter and height of the embossed circular pillars are measured to be 205 μm and 31 μm, respectively, resulting in 2.5% and 3.3% larger structures. The center-to-center spacing in the replica shows less than 1% difference with the mold. Compared to the results in figure 5, the replication performance was improved by an order of magnitude.

The higher replication performance with the 5:1 PDMS mold is due to four complementary factors. First, a higher percentage of the curing agent makes the mold stiffer, such that microstructures maintain their shape appropriately during the embossing process, as described previously. Second, compared to the 10:1 PDMS, the 5:1 PDMS is thermally stable when it is embossed at 145 °C because the higher amount of curing agent provides a much wider range of suitable temperature [41]. Third, the 5:1 PDMS mold swells less since the thermal expansion coefficient is much less than that of the 10:1 PDMS. Lastly, the harder PDMS molds allow

higher replication fidelity. Table 2 shows the hardness scale of the PDMS molds at different mixing ratios measured by the Shore A durometer (PTC Instruments, USA) following the ASTM D2240. Consistent with the stiffness data in table 1, the hardness increases as the mixing ratio and the time of thermal ageing increase. The repeatability of the replication performance of the 5:1 PDMS was investigated through multiple embossing processes and the results showed that the thermally-aged 5:1 PDMS molds could consistently emboss microstructures at an improved quality.

An SEM image of the PDMS mold after multiple embossing runs was taken to investigate the reliability to produce good replications. Figure 8 compares two SEM images for PDMS molds, between the intact mold and one after ten embossing cycles. The image shows that the mold remains undamaged after multiple embossing processes, suggesting that it has a reasonable durability to produce identical structures. This repeatability is possible due to the elasto-mechanical property of PDMS and its thermal stability at the embossing temperature [27]. These unique properties of PDMS make it possible to emboss PMMA channels as small as 5–40 μm [22, 27].

Figure 9 shows microscope images of the PMMA channels embossed by the technique described here. The width of the single channel is 100 μm. As shown in figures 9(*a*) and (*b*), the embossing performance with the 10:1 PDMS
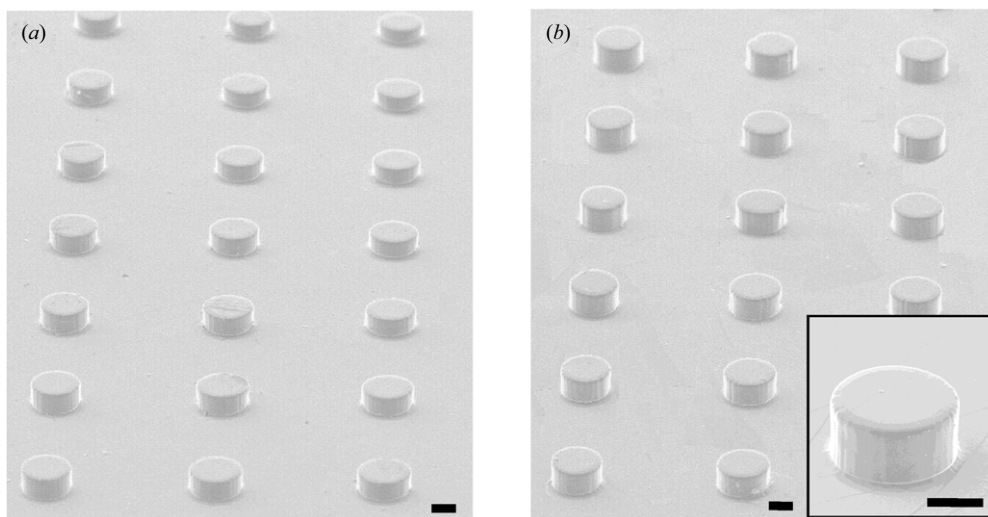
Figure 8. SEM images of two PDMS molds. (*a*) A fresh PDMS mold. (*b*) A PDMS mold after the tenth hot embossing process. Note that the height of pillars in both images are the same at different viewing angles and sample positions during the SEM imaging. Each scale bar represents 100 μm.
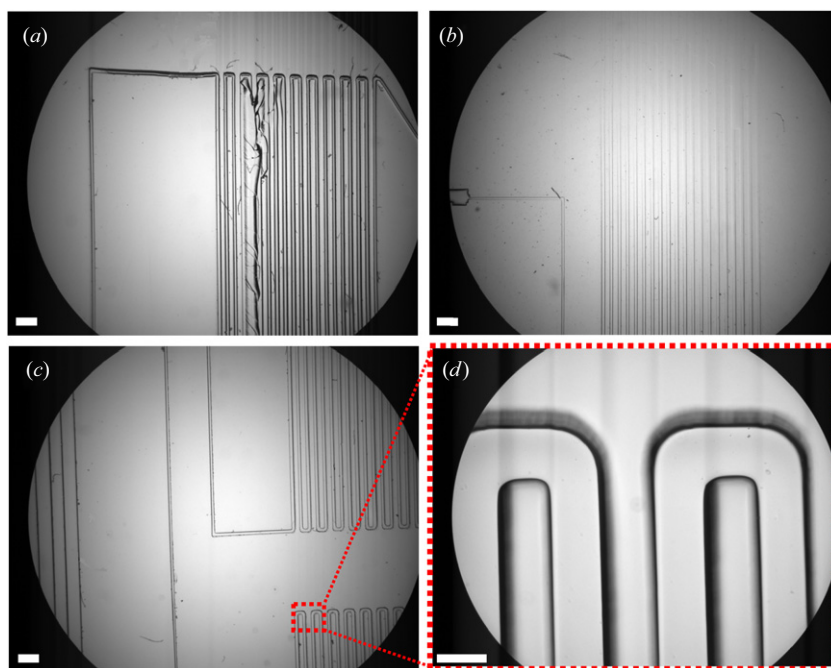

Figure 9. Microscope images of the hot embossed PMMA channels with the PDMS molds at the mixing ratio (*a*) and (*b*) 10:1, (*c*) and (*d*) 5:1. The scale bars in (*a*)–(*c*) represent 500 μm and the one in (*d*) indicates 100 μm.

molds is insufficient to employ the embossed structures in microfluidics. In figure 9(*a*), it is apparent that four channels are collapsed into each other which has caused the features to be damaged. Figure 9(*b*) shows that the properties of the PDMS mold do not produce embossed structures with high efficiency. On the other hand, figures 9(*c*) and (*d*) show that the 5:1 PDMS molds offer a high fidelity of PMMA structures, well-suited for microfluidic channels.

The feasibility of PDMS-based hot embossed PMMA microstructures for microfluidic applications was demonstrated by visualizing fluid mixing in a Y-shaped channel. Figure 10(*a*) shows the channel configuration for the hot embossed PMMA device. The two branches are 100 μm wide and 100 μm deep.

They are joined from the Y-junction channel of 200 μm width and 100 μm depth. A 50 μM fluorescein solution was introduced to one inlet while aqueous solution was provided to another inlet. The two fluids met and mixed in the main channel, finally draining out of the outlet port. The flow rate was set at 5 μL min^{-1} in each channel. The captured fluorescence microscopy images in the beginning and end of the main channel are shown in figures 10(*b*) and (*c*), respectively. In figure 10(*b*), the fluorescently-tagged solution flows through the upper branch and meets the pure water from the bottom channel. There is a sharp discontinuity of the fluorescence emission at the center of the main channel, suggesting that no mixing of the two streams has occurred. The fluorescence
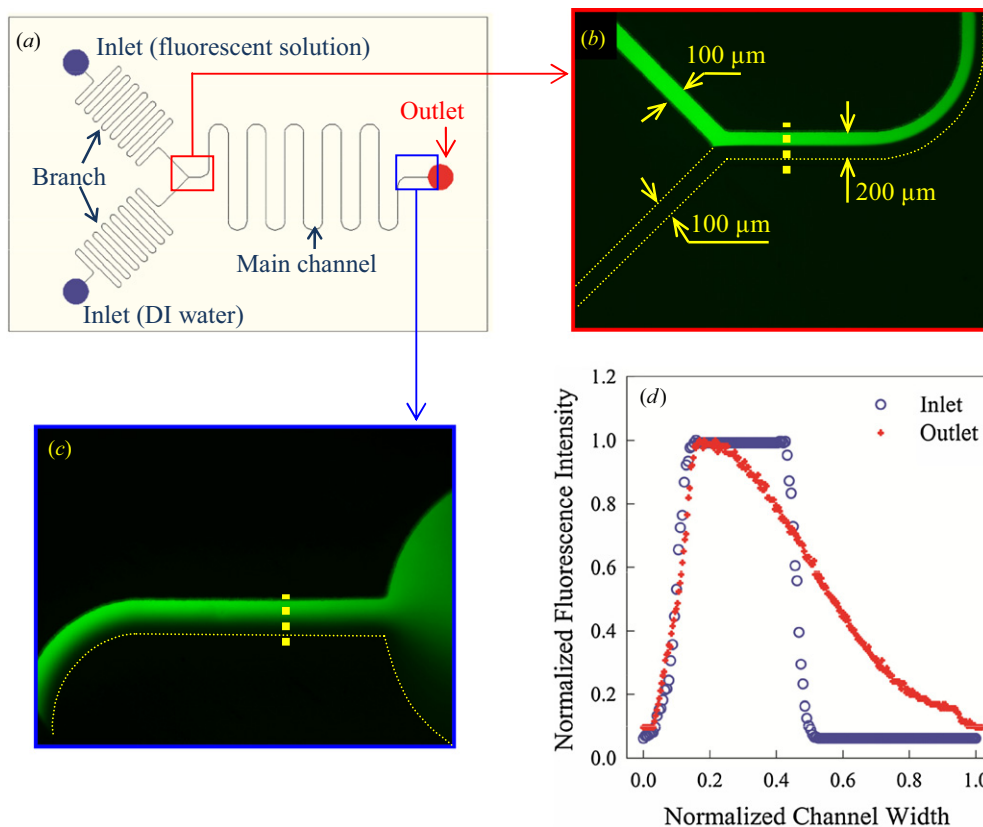
Figure 10. Visualization of fluid mixing between fluorescently-tagged DI water and pure DI water in PMMA channels embossed by the PDMS-based method. (*a*) A representative photomask design of Y-shaped microchannels composed of branches of 100 μm wide and a main channel of 200 μm wide. The depth of all channels was 100 μm. (*b*) Fluorescence image of fluid flow from the Y-junction at a total flow rate of 10 μL min^{-1} with a 1:1 flow rate ratio of fluorescein solution and DI water. (*c*) Fluorescence image of the mixed flow at the end of the main channel. The bold yellow dotted lines in (*b*) and (*c*) represent the location where the fluorescence intensity was measured in (*d*). (*d*) Normalized intensity profiles across the main channel at the inlet and outlet along the dotted lines.

image also show that the boundary between the fluorescent solution and its surrounding is sharp and straight, indicating that the channel edges of the fabricated PMMA device are straight and in good shape. Figure 10(*c*) shows the fluorescence image at the flow in the end of the main channel. Compared to the upstream image in figure 10(*b*), the intensity gradient across the channel at the downstream location is much more gradual and diffuse, portraying fluid mixing along the stream-wise direction. Figure 10(*d*) shows the normalized intensity profiles across the main channel from the top to the bottom (yellow dotted lines in figures 10(*b*) and (*c*)). Once the flows meet at the inlet, the contact interface between the fluorescein solution and the DI water is clearly visible. This interface is shown as a rapid drop of the emission intensity, as shown in figure 10(*d*). As the fluids flow downstream, the mixing zone grows bigger through diffusion. The enhanced mixing of the two streams is signified by the gradual decrease of the intensity, as shown in figure 10(*d*). The current results are similar to those reported previously [42], and this implies that the embossed PMMA chips present a good alternative to other microfluidic devices.

4. Conclusion

In this study, we present a cost-effective hot embossing method using a PDMS-based soft mold to fabricate PMMA microflu-idic devices. The described technique significantly reduces the device fabrication time. The demolding process is also straightforward compared to existing embossing processes with hard molds such as silicon and nickel. The increase in the amount of curing agent makes the PDMS molds 20% stiffer and also makes the molds thermally stable at temperatures of up to 300 °C, as compared to standard 10:1 PMDS molds. The thermal ageing and postbaking at 250 °C of the cured PDMS further enhance its mechanical properties resulting in an increase in the replication performance. We found that there is no damage to the PDMS mold after multiple embossing runs ($\geqslant$10 cycles), which suggests that the replication performance is good enough to fabricate identical chip assemblies. Fluid mixing in the PMMA microfluidic chip was demonstrated to present the feasibility of the developed technique. The embossed PMMA chips present a strong, reliable alternative to PDMS for polymer-based microfluidic devices.

Acknowledgments

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