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ABSTRACT

The use of three-dimensional (3D) printing for fabrication of master molds for microfluidic devices is very attractive due to its availability and simplicity and replaces the standard methods of soft lithography. However, the commercially available photopolymer resins inhibit the curing of polydimethylsiloxane (PDMS), preventing reliable replication of 3D printed master mold structures. Here, we present a simple and safe method to post-process 3D printed photopolymer master molds for PDMS microfluidic devices. This approach expands the possibilities of prototyping microfluidic PDMS devices for a wider research community without complex post-processing tools currently required for fabrication of 3D photopolymer master molds.

I. INTRODUCTION

Fabrication of master molds for microfluidic devices from polydimethylsiloxane (PDMS) requires clean rooms, specialized equipment for lithography, and expensive consumables.[1–4] The manufacturing process includes several stages,[5–9] which, in turn, are laborious and time-consuming. To date, three-dimensional (3D) technologies[10–14] allow the production of master molds in one step using low-cost materials. 3D printed photopolymer master molds are more durable compared to molds made of other materials. In this case, the print resolution depends entirely on printing technology and the printer model.[15] For most 3D printer models, print quality is lower than that of the lithography method with the exception of specialized 3D printers designed for microfluidic applications.[16,17] Another disadvantage of photopolymer resin master molds is that many of the available photopolymers inhibit the curing process of polydimethylsiloxane (PDMS), which hampers replica casting from such 3D printed structures.[18–21] The reason is, after they are printed, such master molds still contain residual monomeric units, which prevent the polymerization of PDMS.[22] Special resins developed for microfluidics overcome this limitation,[23] but their cost is several times higher than that of the commonly available ones. To solve the inhibition problem, silanization of the master mold can be performed. This post-processing procedure involves coating the mold with a monolayer of organosilane by vapor deposition.[24,25] The silanization method is effective, but it requires aggressive chemicals that are pyrophoric[26] and require extreme caution as well as additional permits for laboratory work and trained personnel to prevent accidents.

The presented method will be useful for a wide research community for prototyping of microfluidic PDMS devices without the need to use hazardous chemicals in the post-processing of three-dimensional photopolymer master molds.

II. MASTER MOLD FABRICATION

A. 3D printed master mold

We fabricated master molds using a Phrozen Sonic Mini 4K 3D printer (Taiwan) with a light-emitting diode matrix (LED) with a wavelength of 405 nm and a pixel size of $35 \times 35\ \mu m^2$. We developed a 3D model of the master mold using SOLIDWORKS design software. Then, the files were saved in the STereoLithography (STL) format and prepared for printing using CHITUBOX v1.8.1 software (CBD-Tech) with a layer thickness of 50 μm. As a mold material, we used different resins: (i) TR250LV Resin (Phrozen Standard Resin), (ii) HT100, (iii) G217 (RESIONE, China), and (iv) Eryone White Water Washable (ERYONE, China). After printing, each master mold was washed with isopropyl alcohol in an ultrasonic bath for 3–4 min, blown with clean air, and post-polymerized under UV light at a wavelength of 405 nm for 10 min at ambient temperature (21 °C) (Fig. 1). For Eryone resin, instead of isopropanol, distilled water was used.

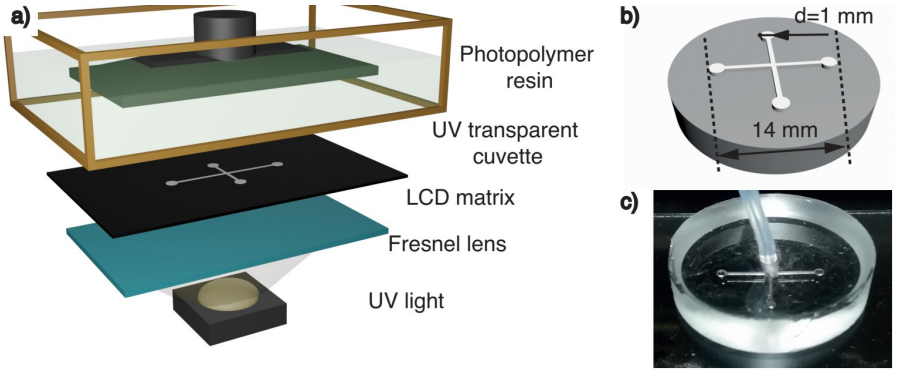

FIG. 1. (a) Scheme of the used liquid crystal display (LCD) printing device, (b) 3D model of the master mold, and (c) PDMS chip assembly. PDMS chip has a diameter of 26 mm and a thickness of 5 mm. The channels' width is 300 μm, and their height is 200 μm.

B. Post-treatment of a 3D printed master mold

After we 3D printed master molds, we investigated a simple and reliable master mold post-processing method that would provide the best PDMS adhesion after microfluidic chip sealing as an alternative to the master mold silanization method. Polytetrafluoroethylene (PTFE) is a commonly used coating, because of its good chemical resistance, low permittivity, low dielectric loss, and low coefficient of friction.[27] However, it is almost impossible to use PTFE dissolved with commercially available solvents and liquid adhesives[28,29] with the exception of 3M^{TM} FC series halogenated solvents,[30] but these 3M solvents are toxic. Applying a uniform layer on a master mold with a 3D microstructure is a separate problem. The use of low-temperature plasmas promotes the formation of active fluorine-containing elements as a by-product of etching the PTFE material,[31–34] and these by-products are left on the surface of the master mold. Due to the fact that resin manufacturers do not indicate the exact composition of their products, the formation mechanism of a fluorine-containing film on the master mold is speculative. To empirically verify whether the use of a PTFE target in cold plasma is efficient, after we fabricated the master molds on a 3D printer, they were subjected to subsequent post-processing. In total, we developed five post-processing protocols (Fig. 2). These procedures were carried out before pouring PDMS into the master molds. We used the following post-processing protocols:

(1) A 3D printed master mold was heat treated at 100 °C for 6 h to eliminate unreacted additives and monomers inside the mold [Fig. 2(I)].
(2) A 3D printed master mold was heat treated at 100 °C for 6 h and further treated with oxygen plasma Femto A (Diener electronic GmbH + Co. KG) for 20 min [Fig. 2(II)].
(3) A 3D printed master mold was heat treated at 100 °C for 6 h and further treated with nitrogen plasma Femto A (Diener electronic GmbH + Co. KG) for 20 min [Fig. 2(III)].
(4) A 3D printed master mold was heat treated at 100 °C for 6 h and further treated with oxygen plasma Femto A (Diener

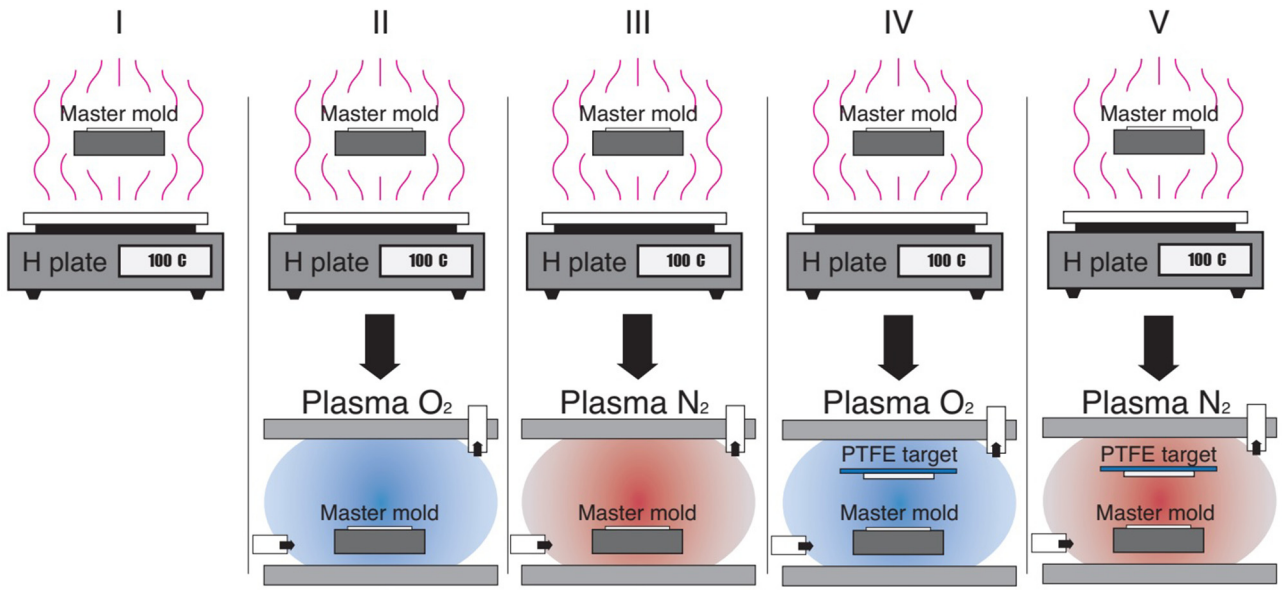

FIG. 2. Schematic illustration of the I–V post-processing protocols for the 3D printed master molds.

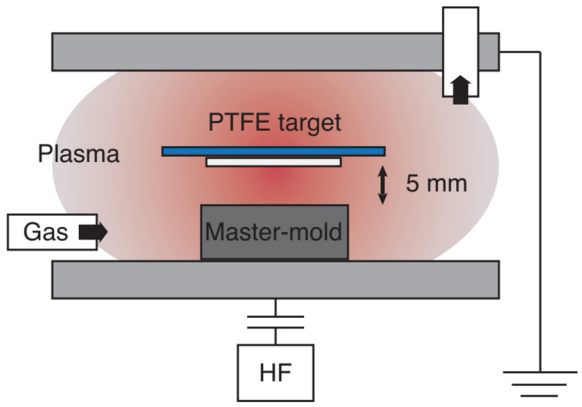

FIG. 3. Scheme of the master mold processing in plasma with a fluoroplastic target.

electronic GmbH + Co. KG) for 20 min with a fluoroplastic target near the master mold [Fig. 2(IV)].

(5) A 3D printed master mold was heat treated at 100 °C for 6 h and further treated with nitrogen plasma Femto A (Diener electronic GmbH + Co. KG) for 20 min with a fluoroplastic target near the master mold [Fig. 2(V)].

The fluoroplastic target has a sandwich structure: it consists of a glass substrate and a polytetrafluoroethylene (PTFE) layer, which is also known as "Ftuoroplast-4" and can be found under the brand name "Teflon," "Halon," or "Fluon"; it is produced according to GOST 10007–80.[35] PTFE was deposited on a glass substrate using PDMS prepared in a mass ratio of 1:10 of the initiator to the monomer. After polymerization, PDMS acted as an adhesive holding the PTFE to the glass substrate (Fig. 3). We chose PDMS as a binder because no organic or other compounds are released into the plasma atmosphere during plasma treatment.

III. PDMS CHIPS FABRICATION

Microfluidic chips were fabricated from PDMS by mixing a PDMS base and initiator in a mass ratio of 10:1. Before thermal curing, PDMS was degassed in a vacuum chamber for 10 min to remove air bubbles formed during the filling of the prepared master molds with liquid PDMS according to protocols I–V. After that, the master molds were placed in an oven set at 60 °C for 3 h. After polymerization, each replica was peeled off from the master mold; then, holes were pierced to connect tubes, and the samples were blown with nitrogen. The PDMS replicas were sealed with glass (SP-7107, 76 × 26 mm^2, thickness 1.0 mm, Menimed LLC) by activating the surface with oxygen plasma for 22 s, at a power of 80% in the Femto A installation. After plasma activation, the replicas were connected to a glass substrate and placed on a 100 °C plate for 1 h to strengthen the bonds formed between PDMS and glass. In total, 48 replicas were prepared for further investigation and assembled into microfluidic chips: three samples made of each of the three resins were treated with five post-processing methods with one control sample for each material, i.e., without post-processing.

IV. TESTING THE MICROFLUIDIC CHIPS

We performed adhesion tests for the fabricated microfluidic chips (MFCs). To test PDMS–glass surface bonding, we supplied de-ionized water to the MFCs and gradually increased the pressure in the channels until the integrity between PDMS and glass was broken (Fig. 4). All the tests were carried out at room temperature (22 °C).

Table I reports the values of the maximum pressure before the destruction of the MFC (in MPa units). As mentioned, the replicas were cast from the master molds post-processed according to protocols I–V, Sec. II B. As control replicas, we used the casts from the master molds printed without post-processing.

The strongest adhesion was shown by the PDMS replicas cast from master molds according to the post-processing protocols IV and V, in which a fluoroplastic target in oxygen or nitrogen plasma was applied for all the presented materials. It is worth noting that for protocols IV and V, at an applied pressure above 0.6 MPa, PDMS was ruptured in the area of the connection between PDMS and tubes. In protocols I–III, there was a rupture in the PDMS replicas along the PDMS–glass contact, which indicates weak adhesion or complete lack of it. According to the performed studies, it can be concluded that the increased adhesion cannot be attributed to the heating or processing master mold with nitrogen\oxygen plasma (protocols I–III), but directly to the treatment of PTFE with nitrogen\oxygen plasma (protocols IV–V).

V. CONCLUSION

This work demonstrates a simple and reliable method to post-process 3D printed master molds in oxygen or nitrogen plasma in the presence of a fluoroplastic target. This strategy have shown excellent results for the four resins randomly selected for testing, which have different characteristics. We expect that this post-treatment approach will be successful for other types of polymer resins as well. The illustrated method solves the problems associated with the inhibition of the PDMS polymerization process as a result of replica casting.

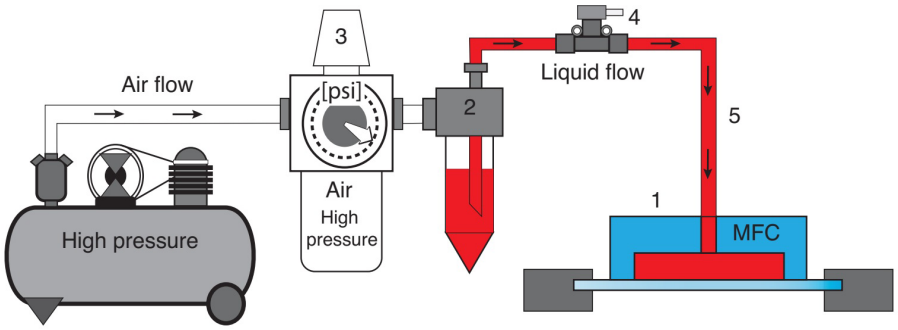

FIG. 4. Scheme of MFC testing: 1—MFC, the master mold; 2—a tank with de-ionized tinted water for a better visualization of the MFC leakage; 3—pressure regulator, AR10-60 (SMC Corporation), maximum pressure 7 bar; 4—stopcock, Tefzel® (ETFE), for pressure up to 34.5 bar (IDEX Health & Science, LLC); 5—connecting tubes, PFA Nat 1/16 × 0.02 × 50 ft. (IDEX Health & Science, LLC). Purified air is supplied from the eight-bar line to the pressure regulator AR10-60.

TABLE I. MFC tests data for the maximum pressure in the channels, expressed in MPa units (mean ± standard deviation), for protocols I–V, Sec. II B.

	Post-processing method					
Material	I	II	III	IV	V	No post-processing
TR250LV	[a]	0.1 ± 0.1	0.1 ± 0.2	0.7 ± 0.1	0.7 ± 0.1	[b]
HT100	[a]	0.2 ± 0.2	0.2 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	[b]
G217	[a]	0.2 ± 0.1	0.1 ± 0.2	0.7 ± 0.1	0.7 ± 0.1	[b]
Eryone white	[b]	0.1 ± 0.1	0.1 ± 0.1	0.7 ± 0.1	0.6 ± 0.1	[b]

[a]Partial adhesion of PDMS to glass or lack of complete tightness of the channels.
[b]The absence of PDMS polymerization.

Moreover, this method does not require the use of aggressive chemicals with pyrophoric properties. The proposed approach was confirmed to be effective with maximum pressure tests performed for the fabricated MFCs made of four different materials. We have shown that the replicas cast from master molds processed by this method show a higher PDMS–glass adhesion than those cast from the non-treated molds. As a result, the MFCs fabricated using such processed molds withstand a much higher pressure, up to 0.7 MPa. The proposed simple and safe strategy for the post-processing of photopolymer resin master molds will facilitate the production of ready-to-use PDMS chips using a 3D printer.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Anatolii Otroshchenko: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Software (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Mikhail Zyuzin:** Investigation (equal); Validation (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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