TECHNICAL PAPER

Impact of oxygen‑permeable mold on fabrication of microchannels with ultraviolet curable materials

Jafar Alvankarian1 · Burhanuddin Yeop Majlis1

Received: 10 December 2015 / Accepted: 1 March 2016 / Published online: 8 March 2016 © Springer-Verlag Berlin Heidelberg 2016

Abstract In this work, effect of oxygen diffusion on curing of materials which are sensitive to ultra violet light (UV) in fabrication of microchannels using micromolds with oxygen permeability is investigated. The effects of physical boundary conditions of mold on microfabrication of polymeric arrays of high aspect-ratio microchannels in presence of oxygen inhibition and under variable UV intensity and dose are studied analytically and experimentally. Polydimethylsiloxane (PDMS) as the oxygen-permeable material and polyurethane methacrylate (PUMA) as the UV-curable substrate are selected for experiments. It is shown that for a wide range of exposure intensity and dose, a thin layer of PUMA resin with thickness of a few micrometers in contact with the mold remains uncured and inhibited by high concentration of oxygen molecules while the overall curing rate is reduced by about tenfold for PDMS compared to impermeable silicon mold. The direct impact of presence of high concentration of oxygen in both of mold and resin during UV curing and due to insuffcient exposure dose and intensity is a considerable alteration in geometries of manufactured microstructures. The obtained results are crucial for method of use of micromolding and evaluation of fdelity of the replicated microstructures with the proposed design in terms of verticality of the walls and details of the transferring patterns that are important to microfuidic applications.

1 Introduction

Molding is the most common method of fabrication of layers of microstructures in experimental microfuidic devices (Folch et al. [1999\)](#page-7-0). The elastomeric substrates such as thermally-cured PDMS and UV-curable PUMA or polyurethane acrylate (PUA) have been used in soft lithography of microstructures (Fujii [2002\)](#page-7-1). The materials such as solid silicon or SU-8 which are impermeable to air, and highlyfexible PDMS as the permeable substrate are widely being used in manufacturing of the molds for microfuidic application (Kim et al. [2008\)](#page-7-2).

During UV-molding, polymerization of a UV-curable material is completed when the casted resin receive enough dose of light for conversion of the pre-polymers to a fullycured structure. The UV-curable PUMA has been used in casting of the arrays of pillars using solid silicon and elastomeric PDMS molds by employing a source of UV radiation with pre-defned intensity for polymerization process (Alvankarian and Majlis [2012;](#page-7-3) Jafar and Burhanuddin Yeop [2015](#page-7-4)). Inhibition of polymerization of the UV-curable materials such as PUA by oxygen trapped or permeated through mold into the resin during casting and curing has been demonstrated and used for microfabrication of hierarchical structures by UV-assisted capillary force lithography (Jeong et al. [2009](#page-7-5)), also for irreversible bonding of microchannels (Jeong [2008\)](#page-7-6).

The polymerization rate in a layer of UV-curable resin is changed by air because the molecules of oxygen scavenge the radical species needed for crosslinking initialization (Dendukuri et al. [2008;](#page-7-7) Alvankarian and Majlis [2015](#page-7-8)). Diffusion of oxygen from a high concentration zone into a pre-polymer resin during UV curing requires an additional amount of UV energy to consume the dissolved and diffused oxygen (Jeong [2008\)](#page-7-6). It is proven that inhibition of

 \boxtimes Jafar Alvankarian alvankarian@gmail.com

¹ Institute of Microengineering and Nanoelectronics (IMEN), National University of Malaysia (UKM), 43600 Bangi, Selangor, Malaysia

polymerization can be totally stopped by isolation of resin from ambient air using techniques such as covering it with a sheet of impermeable or with very low permeability to oxygen. Other techniques of reducing the inhibition effect are by covering the sample using nitrogen gas or using a high vacuum condition (Jeong et al. [2009;](#page-7-5) Alvankarian and Majlis [2015](#page-7-8)).

In this article, effect of oxygen diffusion in a permeable mold of PDMS on UV curing of PUMA resin (Polydiam, UK) casted for manufacturing of arrays of high-aspectratio microchannels is investigated. It is demonstrated that the effect of oxygen diffusion is limited to a thin flm of a few micrometers at the contact surfaces of mold and resin and a fully-cured microstructure is achievable by increasing the exposure dose and intensity. For designs in which the order of magnitude of thickness of the undercurred flm is close to microchannel dimensions, fdelity of pattern transfer from oxygen permeable mold to the layer of microstructures is infuenced.

Motivation of the present research is to have a better understanding of oxygen diffusion effect on micromolding process using UV-curable materials. Moreover, results of the investigation can be exploited in microscale alteration of microchannels through controlling of exposure dose and intensity.

2 Materials and methods

2.1 Physics of the problem

During molding process, oxygen of the air is dissolved into the external surfaces of an air-permeable mold before flling it with a polymer resin. The gas molecules diffuse in directions of lower concentration of O_2 until they reach to an equilibrium level. At ambient conditions of pressure and temperature, dissolving coefficient, diffusion coefficient (D) and permeability of oxygen in PDMS solid polymer are measured and reported as 1.25 mM atm⁻¹, 7.88×10^{-9} m² s⁻¹, and 4.65×10^{-15} m³ s⁻¹ Pa⁻¹ respectively (Kim et al. [2013\)](#page-7-9). The volume of dissolved gas depends on size of oxygen molecules (0.346 nm), voids or free volumes in between the molecules of solid PDMS and geometries of mold (Thomas et al. [2011](#page-7-10)). The rough order of magnitude of time needed for a molecule of oxygen to transport in PDMS can be calculated using dimensional analysis of diffusion coefficient defined by $D\left(\frac{l^2}{l}\right)$ $\frac{r^2}{t}$ where l is the characteristics dimension of mold. For a typical thickness of 5.0 mm in PDMS block, it takes about ~53 min for oxygen to pass through with the rate of \sim 1.6 µm s⁻¹.

Due to the high viscosity of PUMA resin which is ~22500 cp (of PDMS is ~4600 cp) (Alvankarian and Majlis [2012](#page-7-3)) and during pouring it on PDMS mold, air bubbles are trapped in arrays of microcavities and channels designed for present experiments. We observed that the nano scale bubbles formed are slowly dissolved in PDMS and resin and fnally disappear within about 30 min depends on dimensions of microstructures. By flling the mold with a resin that has a different level of dissolved oxygen compared to PDMS (Jeong et al. [2009\)](#page-7-5), diffusion and dissolving of $O₂$ resume again in direction of gradient until a saturation point reaches depends on chemical composition of the substrate.

Exposure of utilized UV-curable resin by UV light initiates chemical reactions that consume the diffused and dissolved oxygen into the molded liquid while generating a fresh level of oxygen gradient. The chemical compositions of UV-curable materials have ability to overcome the dissolved oxygen during cross-linking to a limited level and further diffusion of O_2 from the external and internal boundaries which have higher oxygen concentration than the resin itself delays the crosslinking or stops it from complete curing (Jeong [2008](#page-7-6); Alvankarian and Majlis [2015](#page-7-8)). Therefore, in using PDMS mold and PUMA as the main substrate in micromolding, the high concentration of molecules of oxygen in resin has inhibitory effect on polymerization process. Completion of the polymer crosslinking by UV light in such condition demands a longer curing time or a higher intensity of light to compensate for the negative effects of high concentration of oxygen due to diffusion compared to curing time required for casting using impermeable mold.

As Fig. [1](#page-2-0)a schematically shows, diffusion of oxygen due to its gradient direction into resin is possible by two ways of diffusion from its top surface that is in direction contact with air and from its interface with internal surfaces of permeable micromold that contains a higher oxygen concentration than the resin itself. Both ways of inhibitions can be prevented by using an impermeable mold and covering the upper surface of resin with an UV-transparent and impermeable sheet (Alvankarian and Majlis [2015\)](#page-7-8). The exposure process is conducted on PUMA resin molded with physical boundaries as it is demonstrated in Fig. [1](#page-2-0)b. If upper surface of resin is covered by an impermeable or very low permeability material, a continuous inhibition takes place only by diffusion of oxygen from PDMS mold. The cross-linked PUMA in contact with the resin has no inhibitory effect related to oxygen diffusion (Alvankarian and Majlis [2015](#page-7-8)).

A reference curing time, t_{ref} is defined as a measure of full crosslinking of PUMA in absence of excessive $O₂$ molecules with conditions that all surfaces of the resin are isolated from external oxygen as shown in Fig. [1c](#page-2-0). If the molded PUMA is exposed by UV for duration of t_{ref} , while the oxygen diffusion is occurring from the permeable boundaries, a layer of resin is remained uncured on all **Fig. 1** Schematics for illustration of microfabrication using UV-curable resin and permeable mold with consideration of oxygen diffusion. **a** Micromold with permeated oxygen and resin before UV exposure, **b** exposure of casted resin with permeable boundaries, **c** a fullycured layer of microstructure after exposure with impermeable boundaries, **d** peeled off layer of microstructure with partially cured surface after micromolding at reference curing time, **e** a one-dimensional form of micromolding in presence of oxygen diffusion, **f** non-uniformity in thickness of uncured resin in molding of high-aspect-ratio microchannel

internal surfaces of the fabricated microstructures following peeling of the cured PUMA from the mold as shown schematically in Fig. [1d](#page-2-0). The thickness of uncured resin, H_{Pr} as depicted in Fig. [1](#page-2-0)e is washed out during fabrication steps. The size of H_{Pr} must be kept uniform and very low to maintain the pattern transfer at high precisions. During polymerization of the uncured resin which is confned by solid PUMA with very low level of O_2 and PDMS mold with high level of O_2 , high gradients of oxygen concentration in the mold is expected. The non-uniformity in diffusion and consumption of oxygen in microstructures such as high-aspect-ratio walls of the mold changes the H_{p_r} and therefore the molded product appears as shown schematically in Fig. [1f](#page-2-0).

The crosslinking of PUMA starts by absorbing part of the radiated UV light and producing the radicals needed in polymerization while reaction is inhibited by the oxygen diffused in pre-polymer. The molecules of oxygen are consumed via scavenging the radicals and terminating the reactions. Diffusion of oxygen from mold to the curing resin is the main factor in continuous inhibition of polymerization as shown schematically in Fig. [1e](#page-2-0). The amount of oxygen permeated into a layer of the resin by diffusion from its boundaries is governed by the rate of change of oxygen concentration in the body of mold, C_{Q_2} which is defned by a time-dependent Fick's second diffusion model given by:

$$
\frac{\partial C_{O_2} - Mold}{\partial t} = D_{O_2 - Mold} \frac{\partial^2 C_{O_2} - Mold}{\partial z^2}
$$
 (1)

where, *D*_{*O*2−*Mold* is diffusion coefficient of PDMS mold} with thickness of *H*. The one-dimensional model is for simplicity of numerical solution and has good validity in present analysis. In fact, in casting for microfuidic applications, the width and length of the PDMS mold are considerably larger than its thickness and therefore the diffusion gradient dominates between top and bottom surfaces.

The driving factor for oxygen permeation from boundaries of mold into the uncured resin is consumption of O_2 by polymerization. While, transporting of oxygen molecules from mold into the film of resin with thickness of H_{pr} is resisted by mold diffusion coefficient, however, the rate of oxygen diffusion from crosslinked PUMA to the resin is zero. In the uncured resin with very low thickness, the change of oxygen consumption rate across the PUMA flm is negligible and consequently the oxygen diffusion gradient. Therefore, a 1-d model of time-dependent kinetic equation for O_2 with approximation of uniform concentration of oxygen can be derived as given by:

$$
\frac{\partial C_{O_2-\text{Resin}}}{\partial t} = -k_c (1 - k_d) C_{O_2-\text{Resin}}
$$
 (2)

where the coefficient of consumption of oxygen, k_c , is a function of UV absorbance of material at H_{sp} which is mathematically modeled by:

$$
k_c \infty \left(\frac{\partial I(z)}{\partial z}\right)_{z=H} = k_1 \mu I_0 e^{-\mu H_{sp}} \tag{3}
$$

where, k_1 is the constant of proportionality that depends on chemical composition of the material, μ (mm⁻¹), the measured radiation attenuation coeffcient that is about 0.54 for PUMA with thickness of $H_{sp} = 1.0$ mm for exposure time of 0–120 s and I_0 is the light intensity at first incidence point to photopolymer which is defned according to employed UV source. The effect of resistance of permeable mold against diffusion is defined by k_d , which can take a value between 0.0 as the impermeable substrate and 1.0 as a substrate with maximum permeability. The exact solution of the Eq. [2](#page-3-0) is given by:

$$
\frac{C_{O_2-\text{Resin}}}{(C_{O_2-\text{Resin}})} = e - k_c (1 - k_d)^t
$$
\n(4)

2.2 Fabrication

Design of arrays of micropillars for the present experiments was directly printed on a chrome-coated glass as a photomask using a laser write system (DWL 66, Heidelberg). In a lithography process, the patterns of same design but with negative and positive polarities on the photomask were transferred onto a silicon wafer (type P <100>) coated with a flm of 0.7 µm photoresist followed by aluminum deposition with thickness of 0.2 µm and a fnal lift-off step. The patterned silicon with aluminum mask was anisotropically etched uniformly for depth of 37.0 µm by deep reactive ion etching (ICP OXFORD PlasmaLab System 100). The plasma etching method of the silicon in present work create vertical wall profle and rough surface that considerably reduces the optical refectance compared to polished silicon which is $~50~\%$ for UV range.

The etched silicon with positive polarity patterns as shown in Fig. [2](#page-3-1)a was used in casting process as a positive master for fabricating the negative mold from soft

Fig. 2 SEM images of the fabricated hard and soft molds. **a** Arrays of micropillars in silicon master mold made by DRIE, **b** PDMS mold consisted of arrays of microwells fabricated using silicon master, **c**

magnified image of two silicon micropillars with spacing of 5.5 μ m, **d** a magnifed zone of PDMS mold, **e** Schematic of selected zone of negative mold in symmetry plane of *b*–*b*

PDMS for producing fnal PUMA product. The etched silicon with negative polarity was used as the gas-impermeable substrate for direct molding of PUMA microstructures. By pouring the degassed pre-polymer on the mold and full curing at 75 °C for at least 2 h, a PDMS negative mold as shown in Fig. [2](#page-3-1)b was made and peeled off from the master. The negative mold is consisted of parallel cavities isolated by thin walls with thickness of $w_g = 5.5 \mu \text{m}$. The height, width, and length of each one of the cavities are 37, 48, and 48 µm respectively building a volume of -0.09 nL.

The overall thickness of PDMS mold, $h_b + h_g$ is 5.0 mm including the height of microstructures. The PDMS soft mold and silicon hard mold were employed for making the layers of PUMA microstructure. Lastly, PUMA resin was dispensed on PDMS and silicon mold and then exposed to UV for crosslinking. As the UV source for experimental work, a mask aligner unit (MDA-400LJ, Midas System, Korea) capable of producing a light of only 365 nm wavelengths with uniform intensity of \sim 15.2 mW/cm² and a low-power unit (Model UVL-56, Black-Ray, 6 Watts Lamp, 365 nm wavelengths, UVP, Uplard, CA USA) was used for the range of intensities $0.5-3.0$ mW/cm². After peeling the fabricated microstructure from mold, the crosslinked PUMA is washed from the uncured resin in 20 min using ultrasonic agitator flled partially with water.

Images of the arrays of cavities and micropillars on Silicon (Fig. [2](#page-3-1)a, c), PDMS (Fig. [2b](#page-3-1), d) and PUMA substrates were obtained using scanning electron microscope (SEM) (JSM-6510) operating at an accelerating voltage of 5 kV without sample coating. The charging effects were noticeable especially for samples with incomplete curing.

3 Results and discussion

3.1 One‑dimensional model

The modeling results of oxygen concentration in PDMS mold and curing PUMA is summarized in Fig. [3](#page-4-0). The nondimensional oxygen concentration versus exposure dose in curing resin is graphed for the permeable (dotted lines) and impermeable (solid lines) molds at UV intensities of 0.5, 2.5 and 15.2 mW/cm² as shown in graphs of Fig. $3a$ $3a$. In crosslinked PUMA, concentration of oxygen falls below its critical level in uncured resin that is defned by $\frac{\partial C_{O_2}-PUMA}{\partial C_{O_2}-RESIN}$ ≤ 0.01 and the inhibiting effect of oxygen diffu-sion through it is almost zero (Jeong [2008](#page-7-6)). As the graphs show, impact of the radiation intensity on curing time follows an exponential trend. At low amounts of UV power, the photopolymer needs either a long exposure time for full crosslinking or practically it cannot completely be cured. The time required for the oxygen concentration ratio in layer with the thickness of h_{Pr} to reach the critical level in crosslinking (curing time) is \sim 2, 12 and 60 min for permeable and 0.2, 1.2 and 6 min for impermeable mold for the range of radiation intensities of 15.2, 2.5 and 0.5 mW/ cm² respectively. Experimentally, a complete curing of a flm of PUMA with thickness of 1.0–4.0 mm in absence of oxygen inhibition is achieved when it receives a radiation dose of 50.0–810 mJ cm⁻² corresponding to exposure time of $24-340$ s and intensity of 2.5 mW/cm² (Alvankar-ian and Majlis [2015\)](#page-7-8). Under UV intensity of 15.2 mW/cm², exposure time required for full curing process is reduced to $~15-30$ s.

The Effect of mold permeability on curing time needed for crosslinking of a flm of PUMA with the thickness of 1.0 mm is presented in Fig. [3b](#page-4-0). As can be seen, at each

Fig. 3 Modeling results of consumption and diffusion of oxygen in resin and mold. **a** Oxygen concentration and exposure duration of the thin layer of resin in impermeable (*solid lines*) and permeable (*dotted* lines) molds for exposure intensities of 0.5, 2.5 and 15.2 mW/cm²,

b effect of exposure intensity on curing time, **c** variation of oxygen concentration in PDMS mold while curing is in progress for different exposure intensities

setting of the exposure intensity, ratio of the overall curing time of PUMA by using permeable mold to the impermeable one is \sim 10. The curing time at low exposure intensities is increasing exponentially so that it is nearly impossible to have a fully cured PUMA at very low UV power setting as reported previously for UV-curable PUA (Jeong [2008](#page-7-6)).

The Eq. [1](#page-2-1) with the appropriate boundary conditions are solved numerically to determine the oxygen concentration in mold during UV curing as a function of time and coordi-nate and the results are given in Fig. [3c](#page-4-0). The initial oxygen concentration in mold is defined by $\frac{C_{O_2-Mold}(t_0)}{C_{O_2-Air}} = 1.0$. The boundary condition on bottom side of the PDMS mold or $z = 0$ is given by $C_{O_2-Mold} = C_{O_2-Air}$ and $\frac{\partial C_{O_2-Mold}}{\partial z} = 0$ for permeable and impermeable cases respectively. At $z = H$, the relation $C_{O_2-Mold} = C_{O_2-Resin}$ is used for permeable boundary. The assumption of impermeable boundary on external surface of the mold is valid for the cases in which the ratio of thickness of the mold to the uncured resin is substantial. The presented graphs indicate that the effect of oxygen gradient only reach to the distances of 0.95, 1.5 and 2.15 mm when the exposure is continued for 120 s with the intensities of 0.5, 2.5 and 15.2 mW/cm² respectively. Therefore, the mold of 5.0 mm thickness is deep enough so that the impermeable boundary condition is applicable in modeling and experiment for the exposure duration used here.

3.2 Arrays of microchannels

Initially, the reference curing time, t_{ref} , is measured by condition of complete crosslinking of PUMA in absence of oxygen diffusion using silicon mold. Under UV intensity of 15.2 mW/cm² and for resin thickness of 1.0 mm, t_{ref} is obtained as \sim 15 s with average curing rate of \sim 67 µm/s.

Then, using the gas-permeable PDMS mold of Fig. [2b](#page-3-1), d and by applying UV radiation of 15.2 mW/cm^2 , the curing time is extended to 120 s with overall curing rate of ~8.3 µm/s for overcoming the diffused oxygen. The exposure time is increased to more than *tref* till the thickness of inhibited film of resin, H_{Pr} is reduced from maximum to almost zero. The array of micropillars in PUMA as shown in Fig. [4](#page-6-0)a and inset is a replica of microstructure in silicon in Fig. [2a](#page-3-1), c. At frst glance, smoothness of the surfaces of pillars in master mold and fnal product is obvious to the level of magnifed images of SEM. This can be considered as an evidence of good transfer of patterns after two molding steps. Each pillar in master mold and product has a width of 48.0 µm, height of 37.0 µm with inter-pillar spacings of 5.5μ reflecting the good fidelity in molding process. Figure [4](#page-6-0)b and inset show the arrays of pillars in PUMA fabricated using PDMS mold with inadequate UV dose for complete curing. The most notable and measureable effect is a wider spacing of pillars in the array which is critical for microfuidic applications. Reducing the extended exposure time down to 30 s has increased the gap size at tip of pillars to ~9.0 µm and reduced the height of micropillars for \sim 2.0 µm. The calculated angle of gap at this condition is $\sim 3.3^{\circ}$. Further reduction of exposure time to 20 s has caused a thicker layer of the resin remaining inhibited in present of oxygen as shown in Fig. [4c](#page-6-0) and inset. The incomplete curing had signifcant effects on the surfaces and dimensions of micropillars and gaps. The rough surfaces of microstructures are clearly visible at this level of image magnifcation. The pillars have round edges due to incomplete curing in corners of the mold. The pillars with cubical shapes have a tapering deformation due to the oxygen inhibition effect. At root and tip of gaps in the array, there is a gain of 3.0 and 10.0 µm in size respectively that is increasing linearly from bottom to top in a V-shape form while the height is reduced for 5.0 µm. On the other hand, the pillar width has reduced for 3.0–10.0 µm at its root to tip. Accordingly, thickness of the uncured resin has increased linearly from 1.5 to 5.0 µm at root to tip of the pillars for those surfaces facing the gaps. The calculated angle of gap, θ is ~12.5°. The minimum thickness of the uncured resin is located at tip of the thin wall in the mold shown in Fig. [2](#page-3-1)e where the oxygen concentration level is at its lowest value. Additionally, further reduction of the exposure time to \sim 15 s which is the reference curing time for UV intensity of 15.2 $mW/cm²$ has caused incomplete formation of arrays of micropillars during fabrication due to insuffcient dose of radiation to consume the dissolved oxygen in the array of wells.

For further investigation into the effects of oxygen diffusion, measurement data of geometries of the fabricated microstructures are used to produce the graphs given in Fig. [4.](#page-6-0) The impact of diffusion on profle and size of the gaps in array of pillars is presented in Fig. [4d](#page-6-0). By reducing the exposure time closer to reference curing time, the negative effect of diffusion that appears in the form of infdelity of gap profle in the product and the master mold is worsened specially at tip of micropillars. In direction of z-coordinate, the depth of diffusion is evaluated by measurement of the change in height of the micropillars by exposure time as shown in Fig. [4e](#page-6-0). The maximum loss of the height of pillars is $h_{pr} \simeq 5.0 \,\mu\text{m}$ which is in good agreement with the experimental results for oxygen diffusion depth reported previously (Jeong et al. [2009\)](#page-7-5). The crosslinking of inhibited film of 5.0 μ m takes \sim 100.0 s with average curing rate of ~0.05 µm/s. The difference of gap size in presence of oxygen diffusion and in absence of it is being used here as an indicator of depth of oxygen diffusion in x-direction in graphs of Fig. [3f](#page-4-0). The range of change of diffusion effect in z-direction in Fig. [4e](#page-6-0) and x-direction at pillar tip in Fig. [4f](#page-6-0) are equal. The reduction in thickness of the inhibited layer on walls of the gaps from tip to root of the pillars is due to

Fig. 4 Micromolding of arrays of pillars with high aspect-ratio and vertical gaps using PUMA substrate and PDMS mold. **a** SEM image of fully cured micropillars by UV intensity of 15.2 mW/cm² and curing time of 120 s, **b** insufficient exposure has caused the change of dimensions of structure for exposure time of 30 s, **c** highly tapered pillars and V-shape gaps due to the oxygen diffusion and incomplete

curing with exposure time of 20 s, **d** experimental graph of changing of gap profle at different exposure times, **e** graph of changing of pillar height versus exposure time indicating the thickness of inhibited layer of resin, **f** graph of changing of thickness of the inhibited layer due to oxygen diffusion through the thin walls of the mold at different exposure conditions

the fact that the diffusing oxygen in tips of the thin walls in Fig. [2](#page-3-1)e is consumed more rapidly than the bases.

Finally, in this article, two approximations to 1-d have been applied on governing equations for simplifcation of analysis during UV-molding, diffusion equation in PDMS mold and kinetic relation of $O₂$ in the thin film of uncured resin. Validity of the assumptions employed in equation of polymer crosslinking conditions is that the inhibited flm of PUMA is a very thin layer so that across it the uniformity of oxygen concentration and consumption is maintained. According to experimental results, thickness of the inhibited flm covering the PUMA microstructures and is less than 5.0 µm which is suffciently low in microfabrication technology so that the 1-d assumption is valid as it is used in the typical lithography processes. The three dimensional effects appear in the form of varying inhibited flm of resin between 1.5 and 5.0 µm is considerably too low to contradict the 1-d approximation. The 1-d modeling can effectively predict the time and UV power needed crosslinking for real molding with 3-d microstructures and the results match together. The 1-d approximation of diffusion equation in PDMS mold is close to reality when the depth of the microstructures and thickness of the mold is considerably smaller than the overall width and length of the mold. In this case, the oxygen diffusion gradient dominates between top and bottom surfaces and the effect of side walls is negligible. In present work, the ratio of length of the mold to its thickness (5.0 mm) is about 10 and considering the

calculated typical oxygen diffusion rate of 1.6 µm/s in PDMS, the effect of diffusion from side walls toward the microstructure surfaces is absolutely zero for the range of PUMA curing time of 0–120 s. The curing time obtained experimentally for full crosslinking of the PUMA microstructures by using PDMS mold is ~120 s for UV exposure of 15.2 mW/cm² which is in a good agreement with the result of 1-d modeling.

4 Conclusion

The inhibitory effect of oxygen diffused from PDMS mold into the curing PUMA during microfabrication was investigated. Impact of the effect was analyzed by 1-d modeling and experiments through parametric study of curing by UV exposure and geometries of the fabricated arrays of micropillars. Our important fndings are summarized here.

First, in overcoming the inhibitory effects of oxygen diffusion, exposure dose and intensity are the key parameters. For high intensities of UV exposure, external surfaces of the thick molds demonstrate impermeable while crosslinking is completing and inhibition is happening only by the oxygen previously dissolved in PDMS.

Second, the presence of diffused oxygen during UVmolding impacts the fabricated microstructures in two ways. At high exposure doses, the inhibited layer is limited to a very thin film of less than ~ 1.0 µm on surface of the microstructures. At low exposure doses, the effect of oxygen can dominate a resin layer of about 5.0 µm which can be crucial for designs such as high aspect-ratio gaps addressed here.

Findings of the present work are important for design optimization of the permeable molds and curing process for manufacturing of microfuidics structures using photopolymers. Finally, the investigated effect has the potential to be exploited in a curing-based technique for rapid minor modifcation of design of the microstructures as presented in this work.

Acknowledgments The present research was funded by the ministry of education of Malaysia under project name "MEMS for biomedical" and Grant Number AKU-95.

References

- Alvankarian J, Majlis BY (2012) A new UV-curing elastomeric substrate for rapid prototyping of microfuidic devices. J Micromech Microeng 22(3):035006
- Alvankarian J, Majlis BY (2015) Exploiting the oxygen inhibitory effect on UV curing in microfabrication: a modifed lithography technique. PLoS ONE 10(3):e0119658
- Dendukuri D, Panda P et al (2008) Modeling of oxygen-inhibited free radical photopolymerization in a PDMS microfuidic device. Macromolecules 41(22):8547–8556
- Folch A, Ayon A et al (1999) Molding of deep polydimethylsiloxane microstructures for microfuidics and biological applications. J Biomech Eng 121(1):28–34
- Fujii T (2002) PDMS-based microfuidic devices for biomedical applications. Microelectron Eng 61:907–914
- Jafar A, Burhanuddin Yeop M (2015) A technique of optimization of microfltration using a tunable platform. J Micromech Microeng 25(8):084011
- Jeong HE (2008) On the role of oxygen in fabricating microfuidic channels with ultraviolet curable materials. Lab Chip 8(11):1787–1792
- Jeong HE, Kwak R et al (2009) UV-assisted capillary force lithography for engineering biomimetic multiscale hierarchical structures: from lotus leaf to gecko foot hairs. Nanoscale 1(3):331–338
- Kim P, Kwon KW et al (2008) Soft lithography for microfuidics: a review. Biochip J 2(1):1–11
- Kim M-C, Lam RH et al (2013) Mathematical analysis of oxygen transfer through polydimethylsiloxane membrane between double layers of cell culture channel and gas chamber in microfuidic oxygenator. Microfuid Nanofuid 15(3):285–296
- Thomas PC, Raghavan SR et al (2011) Regulating oxygen levels in a microfuidic device. Anal Chem 83(22):8821–8824