PDMS curing inhibition on 3D printed molds: Why? And, how to avoid it?

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Table S1. Post-treatments reported in the literature to prevent PDMS curing inhibition by 3D-printed molds.

| Reference          | Resin                  | Printer                | Post-treatment                                                                 |
|--------------------|------------------------|------------------------|---------------------------------------------------------------------------------|
| Comina et al.¹     | Micraft proprietary resin | Miicraft Suite        | UV post-curing for 10 min (dose not specified), sonication in ethanol for 2 min and airbrushing of ink (Pentel NN60) |
| Chan et al.²       | Not specified          | Miicraft               | UV post-curing for 10 min (dose not specified), 4 h at 130°C, oxygen plasma treatment and silanization with trichloro(1H,1H,2H,2H)-perfluoro-octyl)silane. |
| Costa et al.³      | PIC 100                | Perfactory 3 mini-multi lens | UV post-curing using 3500 cycles in the Otolash G171 apparatus (dose not specified) then immersed in ethanol at 37°C for 7 h, changing the ethanol every 2 h. |
| Dinh et al.⁴      | Not specified          | Da Vinci Nobel 1.0A    | UV post-curing (dose not specified) and heated at 80°C for 24 h                |
| Bazaz et al.⁵      | Custom resin           | Miicraft               | UV post-curing (dose not specified)                                             |
| King et al.⁶       | VeroWhitePlus, VeroGrey or VeroClear | Connex350              | Heated overnight at 80°C followed by silanization with trichloro(1H,1H,2H,2H-perfluoro-octyl)silane for 1 h. |
| Waheed et al.⁷     | BV003                  | Miicraft +             | UV post-curing for 5 min (dose not specified), immersed in isopropanol for 6 h, then treated with air plasma corona (BD-20AC) for 1 min and then silanised using triethoxy (1 H1 H2 H2H-perfluoro-1-octyl) silane for 3 h. |
| Olanrewaju et al.⁸ | HTM140 resin           | Perfactory MicroEDU    | Treatment with a silicone spray (Ease Release 200)                             |
| Ferraz et al.⁹.¹⁰  | Fun-To-Do Industrial Blend resin | FlashForge Hunter      | UV post-curing for 2 h at 14mW/cm², 405 nm followed by 24 h at 60°C.          |
Table S2. Post-treatment screening for 16 resins using a combination of UV post-curing and heating at 120°C. Values correspond to the apparent step width as defined in the main article (no value reported when PDMS curing was too inhibited) and the color to the critical aspect ratio, as defined in the main article.

| UV (min) | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 |
|----------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|          | 10  | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 | 105 | 110 | 115 |
|          | 120 | 135 | 150 | 165 | 180 | 195 | 210 | 225 | 240 | 255 | 270 | 285 | 300 | 315 | 330 | 345 | 360 | 375 | 390 | 405 | 420 | 435 |
| Heating 120°C (h) | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 |
| Formlabs Clear | 38 | 42 | 45 | 48 | 51 | 54 | 57 | 60 | 63 | 66 | 69 | 72 | 75 | 78 | 81 | 84 | 87 | 90 | 93 | 96 | 99 | 102 |
| Formlabs HT | 182 | 187 | 192 | 197 | 202 | 207 | 212 | 217 | 222 | 227 | 232 | 237 | 242 | 247 | 252 | 257 | 262 | 267 | 272 | 277 | 282 | 287 |
| Formlabs Black | 30 | 34 | 38 | 42 | 46 | 50 | 54 | 58 | 62 | 66 | 70 | 74 | 78 | 82 | 86 | 90 | 94 | 98 | 102 | 106 | 110 | 114 |
| Formlabs Flex | 147 | 152 | 157 | 162 | 167 | 172 | 177 | 182 | 187 | 192 | 197 | 202 | 207 | 212 | 217 | 222 | 227 | 232 | 237 | 242 | 247 | 252 |
| Critical aspect ratio | <0.8 | 0.8 | 0.91 | 1.1 | 1.3 | 1.6 | >2.1 |

| UV (min) | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 |
|----------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|          | 10  | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 | 105 | 110 | 115 |
|          | 120 | 135 | 150 | 165 | 180 | 195 | 210 | 225 | 240 | 255 | 270 | 285 | 300 | 315 | 330 | 345 | 360 | 375 | 390 | 405 | 420 | 435 |
| Heating 120°C (h) | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 |
| R11 | 39 | 43 | 47 | 51 | 55 | 59 | 63 | 67 | 71 | 75 | 79 | 83 | 87 | 91 | 95 | 99 | 103 | 107 | 111 | 115 | 119 | 123 |
| E-shell 300 | 118 | 122 | 126 | 130 | 134 | 138 | 142 | 146 | 150 | 154 | 158 | 162 | 166 | 170 | 174 | 178 | 182 | 186 | 190 | 194 | 198 | 202 |
| PIC100 | 143 | 147 | 151 | 155 | 159 | 163 | 167 | 171 | 175 | 179 | 183 | 187 | 191 | 195 | 199 | 203 | 207 | 211 | 215 | 219 | 223 | 227 |
| Critical aspect ratio | <0.8 | 0.8 | 0.91 | 1.1 | 1.3 | 1.6 | >2.1 |

| UV (min) | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 |
|----------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|          | 10  | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 65 | 70 | 75 | 80 | 85 | 90 | 95 | 100 | 105 | 110 | 115 |
|          | 120 | 135 | 150 | 165 | 180 | 195 | 210 | 225 | 240 | 255 | 270 | 285 | 300 | 315 | 330 | 345 | 360 | 375 | 390 | 405 | 420 | 435 |
| Heating 120°C (h) | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 | 0 | 1 | 2 | 4 |
| DWS DL260 | 30 | 34 | 38 | 42 | 46 | 50 | 54 | 58 | 62 | 66 | 70 | 74 | 78 | 82 | 86 | 90 | 94 | 98 | 102 | 106 | 110 | 114 |
| DWS DS3000 | 111 | 115 | 119 | 123 | 127 | 131 | 135 | 139 | 143 | 147 | 151 | 155 | 159 | 163 | 167 | 171 | 175 | 179 | 183 | 187 | 191 | 195 |
| DWS GL4000 | 141 | 145 | 149 | 153 | 157 | 161 | 165 | 169 | 173 | 177 | 181 | 185 | 189 | 193 | 197 | 201 | 205 | 209 | 213 | 217 | 221 | 225 |
| DWS GM08 | 53 | 57 | 61 | 65 | 69 | 73 | 77 | 81 | 85 | 89 | 93 | 97 | 101 | 105 | 109 | 113 | 117 | 121 | 125 | 129 | 133 | 137 |

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Table S3. Post-treatment screening for 16 resins using a combination of UV post-curing and heating at 120°C. Values correspond to the apparent step width as defined in the main article (no value reported when PDMS curing was too inhibited) and the color to the critical aspect ratio, as defined in the main article.
Table S4. Comparison between the recommended post-curing treatment by Formlabs and the required treatment to avoid PDMS curing inhibition, as defined in this study.

| Resin         | UV exposure time (Formlabs)* | Duration of a 60°C treatment (Formlabs) | UV exposure time (this study) | Duration of a 60°C treatment (this study) |
|---------------|------------------------------|-----------------------------------------|------------------------------|------------------------------------------|
| Formlabs Clear| 7.5 min                      | 7.5 min                                 | 0                            | 8 h                                      |
| Formlabs Flex | 7.5 min                      | 7.5 min                                 | 2h                           | 0                                        |
| Formlabs Black| 15 min                       | 15 min                                  | 0                            | 24 h                                     |
| Formlabs HT   | 30 min                       | 30 min                                  | 0                            | 60 min                                   |

*As the Formlabs post-curing device has a dose twice lower than our custom-made UV oven, these time durations are expressed as equivalent exposure time for our custom-made UV oven. Formlabs data were obtained from https://support.formlabs.com/s/article/Form-Cure-Time-and-Temperature-Settings?language=en_US
**Figure S1:** Influence of the post-treatment on the dimensions of the 3D printed molds.

**Left.** Drawing of the square tiles used for characterizing shrinkage of the 3D-printed structures after post-treatment.

**Right.** Variation of the lateral dimensions of squares patterns on the tiles, expressed as % of the initial value (mean of the variation over 6 patterns on a single tile).

To evaluate the possible variation in dimensions of the 3D printed molds after treatment, square tiles (7 mm x 7 mm x 1 mm) with three extruded squares (1 mm x 1 mm x 0.5 mm) and three squared holes (1 mm x 1 mm x 0.5 mm) were casted on a PDMS counter-mould, produced from treated 3D printed molds. These molds were prepared from four resins (FTD Industrial Red, Envisiontec PIC100, Formlabs Clear and DWS GL4000) and the protocol described in the main article (Materials and Methods section). Three tiles of each resin were exposed to 405-nm UV light in a Formlabs Cure (6 mW/cm²) for 4 h, and next treated for 4 h in a 120°C oven. Similarly, the dimensions of the structures (squares and holes) on one tile per resin were measured using a Dino Lite USB camera and Image J before the treatment, after UV exposure and after the thermal treatment.
Table S5. Comparison of the bands found in the Raman spectra (expressed in rel.cm⁻¹) between the resins before polymerization, their condensed liquids, BAPO and TPO-L condensed liquids and the two monomers - methyl methacrylate (MM) and hexanediol di-methacrylate (HDM).

| Bands present on the Raman spectra of both the resins before curing and acrylate monomers, but not detected after curing and post-treatment. | Clear | Clear condensed liquid | PIC100 | PIC100 condensed liquid | Ind. Red. | Ind. Red. condensed liquid | GI4000 | BAPO condensed liquid | TPO-L condensed liquid | MM | HDM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3106 | 3095 | 3103 | 3101 | | | | | | 3105 | 3105 |
| 1634 | 1634 | 1634 | 1629 | | | | | | 1640 | 1640 |
| 1390 | 1401 | 1405 | | | | | | | 1402 | 1402 |

| Bands present in the Raman spectra of the resin condensed liquids, and those of the condensed liquids of the BAPO and TPO-L photo-initiators. | Clear condensed liquid | PIC100 condensed liquid | Ind. Red. condensed liquid | BAPO condensed liquid | TPO-L condensed liquid | MM | HDM |
|---|---|---|---|---|---|---|---|
| 3068 | | | | | | 3062 |
| 3025 | | | | | | 3024 |
| 2966 | | | | | | 2965 |
| 2965 | | | | | | 2965 |
| 2932 | 2937 | | | | | 2930 |
| 2930 | | | | | | 2928 |
| 2855 | 2857 | | | | | 2856 |
| 2732 | 2742 | | | | | 2738 |
| 2738 | | | | | | 2728 |
| 1726 | | | | | | 1711 |
| 1634 | 1634 | | | | | 1633 |
| 1597 | 1611 | 1602 | 1602 | | | 1596 |
| 1443 | 1441 | | | | | 1443 |
| 1385 | 1381 | | | | | 1380 |
| 1295 | 1297 | 1296 | 1296 | | | 1297 |
| 1104 | | 1103 | | | | |
| 972 | 988 | 988 | | | | 988 |
| 963 | | 960 | 952 | | | 952 |
| 883 | | 882 | | | | 882 |
| 767 | 764 | 764 | | | | 764 |
| 701 | | 705 | | | | 705 |
| 620 | | 617 | | | | 617 |

| Bands present in the Raman spectra of the resin condensed liquids, the resins before polymerization and the acrylate monomers, but not detected in the spectra of the BAPO and TPO-L photo-initiators. | Clear condensed liquid | PIC100 condensed liquid | Ind. Red. condensed liquid | BAPO condensed liquid | TPO-L condensed liquid | MM | HDM |
|---|---|---|---|---|---|---|---|
| 3103 | 3103 | | | | | 3105 |
| 3039 | 3039 | | | | | 3039 |
| 1452 | 1452 | | | | | 1452 |
| 1401 | 1401 | 1405 | 1405 | | | 1402 |
| 1401 | 1405 | 1405 | | | | 1402 |
| 1110 | 1110 | | | | | 1110 |
| 1003 | 1003 | 1003 | | | | 1007 |

| Additional bands present in the Raman spectra of the resin condensed liquids. | Clear condensed liquid | PIC100 condensed liquid | Ind. Red. condensed liquid | BAPO condensed liquid | TPO-L condensed liquid | MM | HDM |
|---|---|---|---|---|---|---|---|
| 2942 | | 2942 | | | | |
| 1663 | 1663 | | | | | 1663 |
| | | | | | 1229 | |
| | | | | | 1173 | |
| | | | | | 1157 | |
Figure S2. Raman spectroscopy analysis of (top) methacrylate monomers, methyl methacrylate (blue) and hexanediol dimethacrylate (red), and (bottom) of the photo-initiators BAPO (Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, top) and TPO-L (Ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate, bottom) (see inset for the structures) before (light blue), after treatments using UV for 1 h at 14 mW/cm² and 405 nm, (purple) and combined treatment (UV for 1 h at 14 mW/cm² and 405 nm followed by 2 h at 120 °C) (red) and spectra of the condensed liquid obtained after thermal treatment (green).
Figure S3. Representative microscopy pictures of PDMS after curing and release from fully treated test-molds; PDMS was supplemented with different components at 1% (w/v) as specified under the pictures, without pre-treatment or after 1 h UV exposure as defined in the article and/or 2 h at 120° C. If the replicas were too viscous or liquid, pictures were taken while moving away a scalpel blade from the PDMS drop or paste. Scale bar: 1 mm.
Figure S4. $^{31}$P NMR spectra of the BAPO (*top*) and TPO-L (*bottom*) photo-initiators before treatment (green), after treatment (UV for 1 h at 14 mW/cm² and 405 nm followed by 2 h at 120 °C) (blue) and spectra of the condensed liquid obtained after thermal treatment (red).
Figure S5. Identification of compounds from the mass spectrum of the treated BAPO (A) and TPO-L (B), and possible formation mechanisms. The formula obtained by very high resolution with a precision better than 0.1 ppm are exact, the structures and mechanisms are hypothetical.

A. BAPO

C$_8$H$_3$O$_3$P + H$^+$
m/z 159.0206

C$_{28}$H$_{19}$O$_3$P + H$^+$
m/z 419.1770

C$_{23}$H$_{17}$O$_3$P + H$^+$
m/z 407.1769

C$_{38}$H$_{19}$O$_3$P + H$^+$
m/z 583.2608

C$_{32}$H$_{16}$O$_3$P$_2$ + H$^+$
m/z 579.2060

C$_{32}$H$_{16}$O$_3$P$_2$ + H$^+$
m/z 561.1954

C$_{28}$H$_{19}$O$_3$P + H$^+$
m/z 435.1720

C$_{28}$H$_{27}$O$_3$P + H$^+$
m/z 437.1877

C$_{23}$H$_{20}$OP + H$^+$
m/z 377.2029

C$_{16}$H$_{12}$O$_3$P + H$^+$
m/z 289.0988

C$_{16}$H$_{12}$O$_3$P + H$^+$
m/z 273.1039

C$_{15}$H$_{10}$OP + H$^+$
m/z 259.1246

C$_{18}$H$_{12}$OP + H$^+$
m/z 245.1090

C$_{16}$H$_{12}$O$_3$P + H$^+$
m/z 303.1144

C$_{18}$H$_{12}$O$_3$P + H$^+$
m/z 273.1039

C$_{15}$H$_{10}$OP + H$^+$
m/z 249.1090
B. TPO-L

\[
\text{C}_{10}\text{H}_{15}\text{O}_3\text{P} + \text{H}^+ \\
\text{m/z} 215.0831
\]

\[
\text{C}_{18}\text{H}_{21}\text{O}_3\text{P} + \text{H}^+ \\
\text{m/z} 317.1300
\]

\[
\text{C}_{36}\text{H}_{32}\text{O}_5\text{P}_2 + \text{H}^+ \\
\text{m/z} 487.1796
\]

\[
\text{C}_{28}\text{H}_{31}\text{O}_3\text{P} + \text{H}^+ \\
\text{m/z} 447.2082
\]

\[
\text{C}_{38}\text{H}_{43}\text{O}_3\text{P} + \text{H}^+ \\
\text{m/z} 611.2921
\]
References

(1) Comina, G.; Suska, A.; Filippini, D.; German Comina, A. S.; Filippini, D. PDMS Lab-on-a-Chip Fabrication Using 3D Printed Templates. Lab Chip 2013, 14 (207890), 424–30.

(2) Chan, H. N.; Chen, Y.; Shu, Y.; Chen, Y.; Tian, Q.; Wu, H. Direct, One-Step Molding of 3D-Printed Structures for Convenient Fabrication of Truly 3D PDMS Microfluidic Chips. Microflu Nanoflu 2015, 19 (1), 9–18.

(3) Costa, P. F.; Albers, H. J.; Linssen, J. E. A.; Middellkamp, H. H. T.; van der Hout, L.; Passier, R.; van den Berg, A.; Malda, J.; van der Meer, A. D. Mimicking Arterial Thrombosis in a 3D-Printed Microfluidic in Vitro Vascular Model Based on Computed Tomography Angiography Data. Lab Chip 2017, 17, 2785-2792.

(4) Dinh, T.; Phan, H.-P.; Kashaninejad, N.; Nguyen, T.-K.; Dao, D. V.; Nguyen, N.-T. An On-Chip SiC MEMS Device with Integrated Heating, Sensing, and Microfluidic Cooling Systems. Adv Mater Interfaces 2018, 5 (20), 1800764.

(5) Razavi Bazaz, S.; Kashaninejad, N.; Azadi, S.; Patel, K.; Asadnia, M.; Jin, D.; Ebrahimi Warkiani, M. Rapid Soft lithography Using 3D-Printed Molds. Adv Mater Technol 2019, 4 (10), 1900425.

(6) King, P. H.; Jones, G.; Morgan, H.; de Planque, M. R. R.; Zauner, K.-P. Interdroplet Bilayer Arrays in Millifluidic Droplet Traps from 3D-Printed Moulds. Lab Chip 2014, 14 (4), 722–729.

(7) Waheed, S.; Cabot, J. M.; Macdonald, N. P.; Kalsoom, U.; Farajikhah, S.; Innis, P. C.; Nesterenko, P. N.; Lewis, T. W.; Breadmore, M. C.; Paul, B. Enhanced Physicochemical Properties of Polydimethylsiloxane Based Microfluidic Devices and Thin Films by Incorporating Synthetic Micro-Diamond. Sci Rep 2017, 7 (1), 15109.

(8) Olanrewaju, A. O.; Robillard, A.; Dagher, M.; Juncker, D. Autonomous Microfluidic Capillary Circuits Replicated from 3D-Printed Molds. Lab Chip 2016, 16 (19), 3804–3814.

(9) de Almeida Monteiro Melo Ferraz, M.; Nagashima, J. B.; Venzac, B.; Le Gac, S.; Songsasen, N. 3D Printed Mold Leachates in PDMS Microfluidic Devices. Sci Rep 2020, 10 (1), 994.

(10) de Almeida Monteiro Melo Ferraz, M.; Nagashima, J. B.; Venzac, B.; Le Gac, S.; Songsasen, N. A Dog Oviduct-on-a-Chip Model of Serous Tubal Intraepithelial Carcinoma. Sci Rep 2020, 10 (1), 1575.