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# Integration of subtractive 3D printing into micromolding of biodegradable implants for spinal cord treatment

**J. M. von Poblotzki[1], and H.K. Trieu[1*]**

[1] *Institute of Microsystems Technology, Hamburg University of Technology, Hamburg, Germany*
[*] *Hoc Khiem Trieu, email: trieu@tuhh.de*

*Abstract: Spinal cord injury (SCI) is a life-changing event potentially leading to permanent paralysis. We developed a mechanical microconnector system (mMS) to promote regeneration after SCI. The new micromolding of the mMS starts with a premaster build from a subtractive 3D printing method called selective laser induced etching (SLE). We additionally could facilitate molding of the silicone master through a monolayer coating of Trichloro(1H, 1H, 2H, 2H-perfluorooctyl)silane (FOTS) and Dimethyldichlorosilane (DDMS). This technology enables us to build complex biodegradable implant structures in a range from 25 micrometers up to several millimeters.*

## I. Introduction

A biocompatible mechanical microconnector system (mMS) was developed to promote regeneration after spinal cord injury (SCI). The mMS efficacy has been reported by Estrada et al. after a rodent animal study [1]. However, an mMS, which is easily individualized and degrades after restoration of spinal cord function is desired for therapeutic use in humans. This study tested a 3D printed premaster for this purpose.

## II. Material and methods

Micromolding starts with a complex 3D quartz glass premaster and yields the desired mMS structure as biodegradable implant after three steps.

### II.I. Quartz glass Premaster

Lesion model for the first implant designs was the complete spinal cord transection, implemented in a half-shell premaster using an optimized selective laser induced etching method (SLE) (Fig. 1) [2].

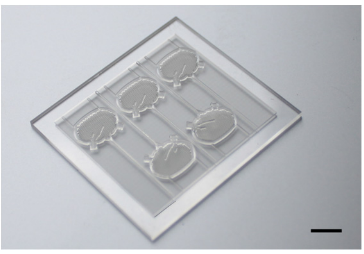

*Figure 1: Quartz glass premaster for micromolding of implant for complete spinal cord transection. Scale bar represents 5 mm.*

A transfer of the mMS working principle, further described by Estrada et al., to other lesion models will be reviewed in a subsequent report [1]. Transition from CAD file to printed structure takes 2 h 50 minutes for the premaster, with subsequent 24 h etching. Complete separation of quartz glass premaster from intact silicone (Aquasil® Soft Putty; Dentsply DeTrey GmbH, Konstanz, Germany) master though was quite challenging. Parts of the silicone would stick inside the quartz glass structure as shown in fig.2B. Strong adhesive forces between master and premaster could lead to fractures inside the premaster.

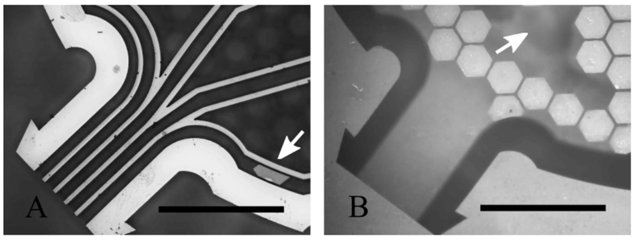


*Figure 2: Microscopic pictures of top view, channel structure of the premaster. White arrow marks defect of not removed quartz glass part (A). Comb structure of silicone master. Marked with a white arrow are missing comb structures, which stayed inside the premaster due to stiction (B).Scale bar represents 1000 µm*

The coating of a self-assembled monolayer of Trichloro(1H, 1H, 2H, 2H-perfluorooctyl)silane (FOTS) and Dimethyldichlorosilane (DDMS) was applied to the premaster to prevent stiction. In one out of five premaster structures minor defects of incomplete removed quartz glass parts appeared (Fig. 2A). Detachment through longer etching time or vibrations in an ultrasonic bath needs to be tested.

### II.II. Micromolding of biodegradable mMS

The quartz glass premaster is the first mold deployed for fabrication of biodegradable mMS, its accuracy and transferability are therefore crucial to the mMS quality.

A schematic representation of the three-step process for fabrication of biodegradable mMS is given in fig. 3. In the first step the master material is molded into the premaster. Master and premaster are manually separated. In a second step the master and a plate of biodegradable material are stacked inside a heatable vacuum chamber. After melting the biodegradable material (PLGA compounds, poly(lactic-co-glycolic acid)), it is molded into the master. Master and formed biodegradable material are manually separated after cooling down. An excess of biodegradable material, which was formed with the

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molding process, is polished down to get the desired structure in the last step. A detailed description of all micromolding process parameters is presented in recent literature [3].

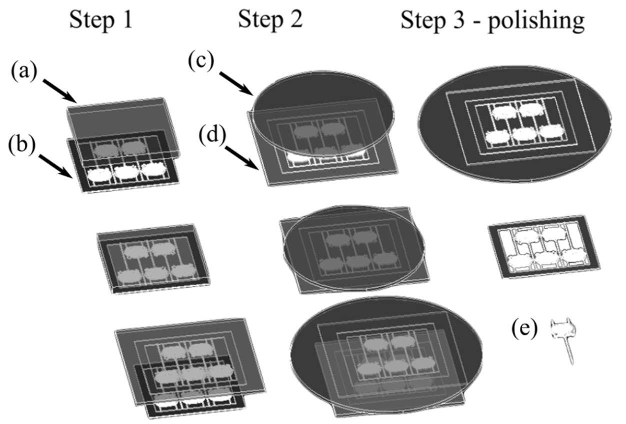


*Figure 3: Schematic fabrication process. Step 1: Molding of Aquasil® master (a) from SLE built quartz glass premaster (b). Step 2: Molding of prepared biodegradable material (c) from Aquasil® master(d). Step 3: Polishing down of excess material to stabilizing frame and liberated mMS half-shell(e).*

## III. Results and discussion

Evaluation of the premaster showed a reproduction of challenging aspect ratios with tolerances smaller than five micrometers. Fig. 4A displays a microscopic cross section of a quartz glass premaster. The combs in the premaster are 250 µm high just as the separating trenches. The comb walls have a width of 25 µm.

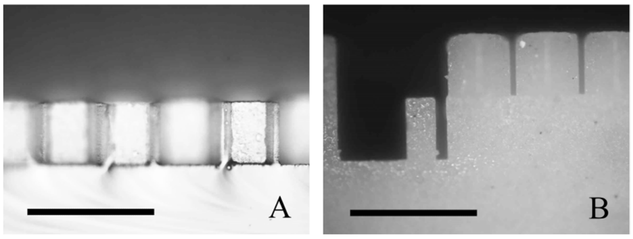


*Figure 4: Microscopic cross section of the premaster (A) and silicone master (B). Scale bar represents 500 µm.*

The aspect ratio in the comb structure is therefore 1:10. After micromolding of silicone into the premaster a cross section structure like in Fig. 4B is obtained. The final structure is evaluated using molding accuracy. Again the structure depths are 500 µm, more specifically 250 µm in the comb structure and 25 µm in the trenches. The black scale bar represents 500 µm.

A hydrophobic change of the surface is shown through sessile drop method with contact angle measurement [4]. The untreated premaster is very hydrophilic with a contact angle of 21.1 ° (Fig. 5A). Some of the silicone remains on its surface after one mold with silicone and leads to a contact angle of 46.7 ° (Fig. 5B). The silicone has a contact angle of 102.8 ° (Fig. 5C). Coating of the premaster with a mixed monolayer of FOTS and DDMS leads to a contact angle of 110 °, as shown in fig. 5D.

Modification of the premaster surface resulted in smooth separation of premaster and master. No remaining silicone parts were observed in the premaster. Additionally, asymmetric pressure exertion was reduced, which led to a longer durability.

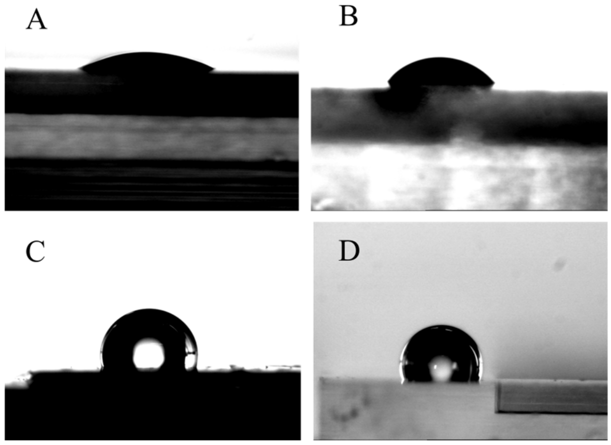


*Figure 5: contact angle of untreated quartz glass premaster 21.1 ° (A). Contact angle of silicone contaminated premaster 46.7 ° (B). Contact angle of silicone master 102.8 ° (C). Contact angle of FOTS and DDMS coated premaster 110 ° (D).*

## IV. Conclusions

In this work, we demonstrated the integration of a 3D printing method into manufacturing of biodegradable mechanical microconnector systems (mMS) for spinal cord regeneration. The micromolding process was further facilitated and made more reliable through a FOTS and DDMS coating of the quartz glass premaster. This opens up the possibility to faster manufacture individualized implants for spinal cord injury.

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#### AUTHOR'S STATEMENT

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