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3D printed lost-wax casted soft silicone monoblocks enable heart-inspired pumping by internal combustion

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Experimental Section

Pump-fabrication:

Injection molds were manufactured by 3D printing (Designjet Color 3D, Hewlett-Packard, USA) of computer-aided design models (CAD) (NX 7.5, Siemens, Germany) using a model/support material system on the base of poly(acrylonitrile-co-butadiene-co-styrene) (ABS). In detail, molds were printed on a low-density level using layer resolutions of 0.254 mm (Model material: ABS P430L; Support material: SR30L, both from Stratasys, USA). The support material was removed by washing the molds in a detergent containing bath of sodium hydroxide solution (WaterWorks Soluble Concentration P400SC, Stratasys, USA). Polydimethylsiloxane (PDMS) rubber material was obtained by degassing a mixture of monomer (RTV23, 70 wt%, Altropol, Germany) and crosslinking agent (A7, 30 wt%, Altropol, Germany). The mixture was then injected into the ABS-mold using an in-house built syringe press (Figure S1) and vulcanized at 65 °C for 2 hours. Thereafter, the ABS-molds were dissolved in acetone until only the PDMS monoblock shape was left behind.

Pump-setup:

The PDMS pump was fed with a combustible air - methane mixture as shown as in **Figure S2**. The gas was mixed at a flow rate ratio of 10:1 using two flow controllers connected to a Y-mixer, one for air and one for methane (Red-y compact series, Vögtlin, Switzerland). Overall flow rates varying within 2-10 L/min were applied. The gas mixture was then split and fed to the two combustion chambers of the pump. In order to prevent any backdraft, two safety valves (RF53 N for combustion gases, PanGas, Switzerland) were installed directly at the combustion chamber inlets. Gas ignition was performed using spark gap igniters (4.8 V, SparkFun Electronics, USA) addressed by a programmable logic controller (PLC) (LOGO!, Siemens, Germany). Electrical power was supplied by a DC power source (PS-2403D, Conrad Electronics, Germany). In order to control the flow direction of the liquid inside the pumping chamber, check valves (inner diameter 20 mm, Aqua2004, Germany) were connected to the soft pump. During actuation by the combustion chamber, one valve per chamber closes, while the other one opens. All other sanitary hose couplings were purchased at a local do-it-yourself-store (Bauhaus, Schlieren, Switzerland).

Pump-expulsion volume against different hydrodynamic heads:

Pump expulsion volumes were measured using the above mentioned pump-setup without any valves, also shown in **Figure S4**. In detail, the rigid tubing was replaced by soft silicone tubes (12 mm in diameter) on one side of each pumping chamber, while the other side was blocked by a clip. The baseline for the expulsion measurement is given by the height of the closed pumping chamber connector. The pump was then filled with colored water (diluted procion blue MXR, ABCR, Germany) to get clear contrasts during movie recording. The actual hydrodynamic head was then given by the difference from the base line and the filling level inside the silicone tubes. Video recording (25 frames per second, camera: Legria HFG25 HD, Canon, Japan) was then performed for hydrodynamic heads of 0, 50 and 80 cm, while operating the soft pump at a pace of 60 beats per minute (bpm), no ignition lag time between the two combustion chambers at an overall gas flow rate varying within 3.0 – 4.0 L/min. The obtained recordings were then evaluated frame-by-frame. For every evaluated frame, the average height of the two water levels inside the silicone tubes was taken, resulting in an overall number of 150 time-resolved displacement points per hydrodynamic head. These points were then used to calculate the displaced volume, using the displacement height and the silicon tube diameter.

Stress test without liquid pumping:

Here, the soft pump was not connected to the liquid pumping cycle, which disables the cooling by pumped water. The overall gas flow rate was varied within 2.7 - 3.4 L/min at an ignition rate of 60 – 150 bpm. The ignition pulse and the delay time width were set to 0.1 s each. Heat flow was observed using an IR camera (i7, FLIR, USA). The running performance was again recorded by video camera. After the stress test, the soft pump was cut open along top side. Scanning electron microscopy (SEM) (Nova NanoSEM 450, FEI, Netherlands) images were recorded of damaged regions. Particle size distribution was established by measuring a number of 217 particles. Light microscopy (Axio Imager M2m, Zeiss, Switerland) images were taken from the same regions. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) (PikeDiffuseIR with Tensor27, Bruker, USA) was performed as well from debris on the silicon and then compared to silicon dioxide (Aerosil 200, Evonik, Germany) and bulk PDMS (RTV 23 / A7, Altropol, Germany). To investigate the point of thermal decomposition of bulk PDMS, thermogravimetric analysis was performed (STA Platinum Series, Linseis, Germany).

Estimation of the energy released by a pulse, the total power output and the energy efficiency:

The volume flow V_{CH4} of methane is transformed into mole flow n_{CH4}, using its density ρ_{CH4} at 298 K and the molar weight MW. n_{CH4} is then divided by the ignition frequency f in order to obtain the actual amount of methane available per cycle, assuming no residual methane available form former combustion cycles. By multiplying this value with the standard enthalpy of methane combustion, we get an estimation of the heat Q released by one combustion cycle. The total heating power output P is then derived by multiplying again with the ignition frequency.

$$\dot{n}_{CH4} = \frac{\dot{V}_{CH4} \cdot \rho_{CH4}}{MW_{CH4}} \rightarrow Q = \frac{\dot{n}_{CH4}}{f} \cdot \Delta H_c^{\circ} \rightarrow P = Q \cdot f$$

$$\Delta H_c^{\circ} = -890.7\,\frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\rho_{CH4} = 0.66\,\frac{\mathrm{g}}{\mathrm{L}}\,(@\,298\,K)$$

At an ignition frequency of f = 1 Hz, a combustion chamber volume of 75 cm^3 (2 x) with complete gas recharging of the combustion chambers after each pulse and considering the methane volume share as 1/11 in the fuel gas stream, the methane volume flow and respectively the molar flow calculate as follows:

$$\dot{V}_{CH4} = 2 \cdot 0.075\,\mathrm{L} \cdot f \cdot \frac{1}{11} = 0.0136\,\frac{\mathrm{L}}{\mathrm{s}}$$

$$\rightarrow \dot{n}_{CH4} = \frac{0.0136\,\frac{\mathrm{L}}{\mathrm{s}} \cdot 0.66\,\frac{\mathrm{g}}{\mathrm{L}}}{16.04\,\frac{g}{mol}} = 5.61 \cdot 10^{-4}\,\frac{\mathrm{mol}}{\mathrm{s}}$$

Considering the combustion standard enthalpy of methane we can estimate the total heating power:

$$Q = \frac{5.61 \cdot 10^{-4}\,\frac{\mathrm{mol}}{\mathrm{s}}}{f} \cdot \Delta H_c^{\circ} = 499.8\,\mathrm{J}$$

$$P = Q \cdot f = 499.8\,\mathrm{W}$$

We calculated the energy efficiency of the designed soft motor by the ratio of gained potential energy of a pumping pulse (water displacement in height and thus lifted mass) and the energy delivered by the combustion process for one chamber pair. Using the data shown as in **Table S1**, we obtained the following efficiency for an initial water column of 0 cm:

$$E_{pot} = m \cdot g \cdot \Delta h = V_{displaced} \cdot \rho \cdot g \cdot \Delta h = 0.08\,J$$

$$E_{comb} = Q \cdot f = 249.9\,J$$

$$\eta_{Motor} = \frac{E_{pot}}{E_{comb}} = 0.03\,\%$$

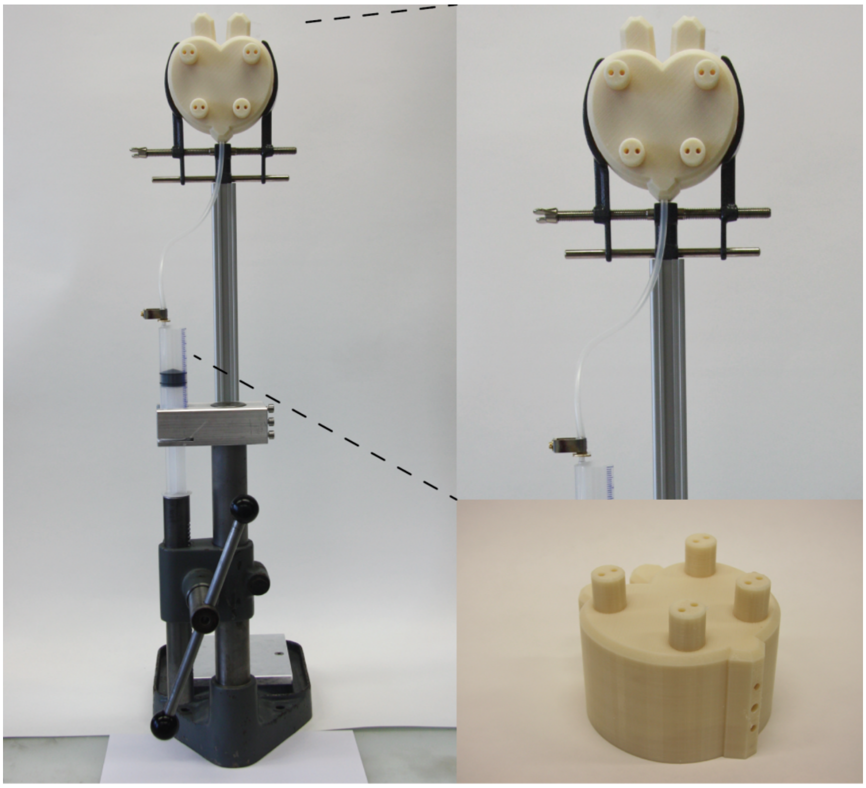


Figure S1. In-house built PDMS syringe press connected to an ABS injection mold: Viscous monomer – crosslinker mixtures can be injected conveniently into the molds. A sufficient amount of holes in the structure helps to avoid bubble retention. While injection, these holes can be subsequently clogged upwards as soon as the silicone mixture drops out.

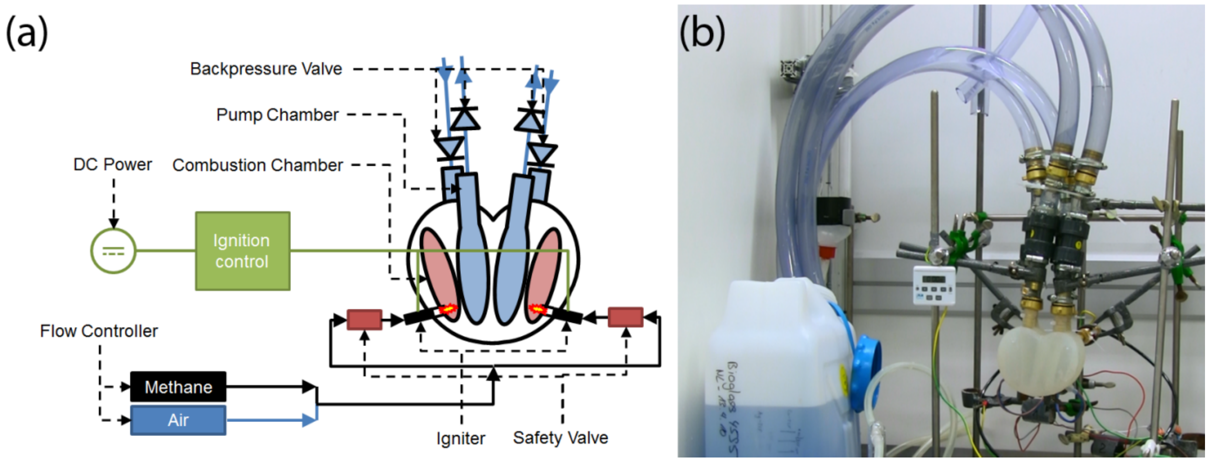


Figure S2. (a) Schematic view of the heart-inspired soft pump with all connected devices. Check valves for the liquid enable single directional pumping. The two liquid pump chambers are actuated by two thin barriers using gas combustion in two outer chambers. Both of these chambers have a separate gas inlet (protected from possible backdrafts by safety valves) and high-voltage spark gap igniters which are operated by a programmable logic controller. Two mass flow controllers are used for premixing the combustion gas at a desired ratio. (b) A view of the real setup including the soft pump which is connected to check valves by brass fittings.

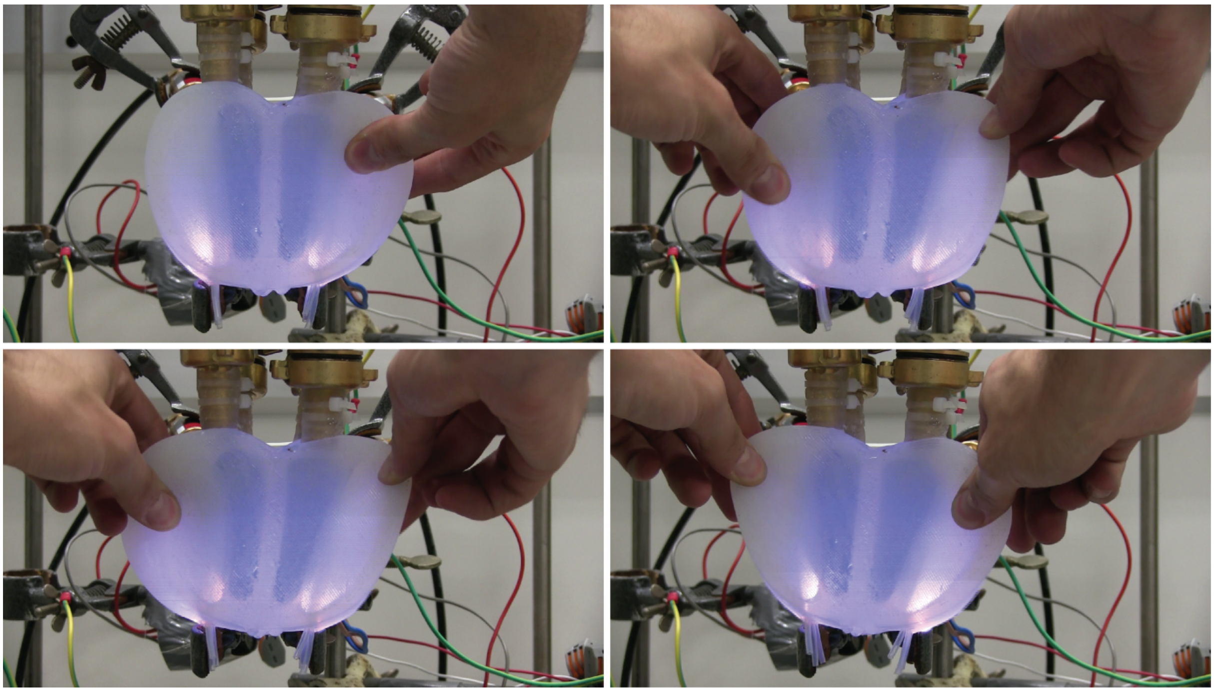


Figure S3. Different *in situ* deformations of an operating soft silicon pump. The pace was set to 60 beats per minute (bpm) under simultaneous ignition mode. Ignition and expulsion of volume was kept throughout the deformation process.

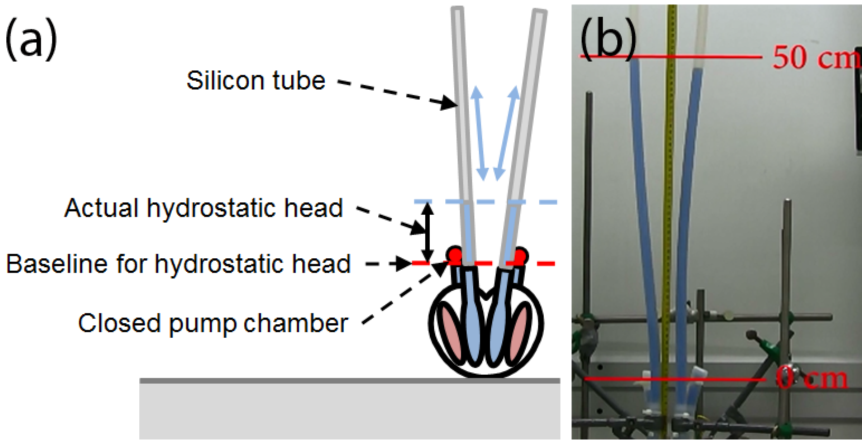


Figure S4. (a) Scheme of the hydrostatic head setup to measure the expulsion volume of the pumping chambers. The actual hydrostatic head was controlled by the amount of water inserted at the beginning into the silicon tubes. (b) A snap shot of the recorded movie of the setup.

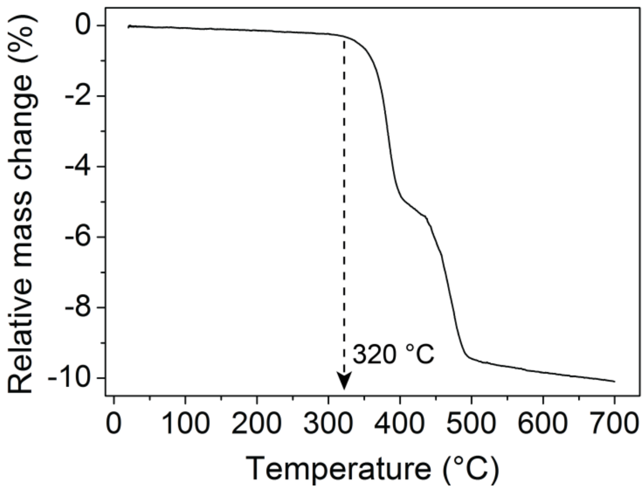
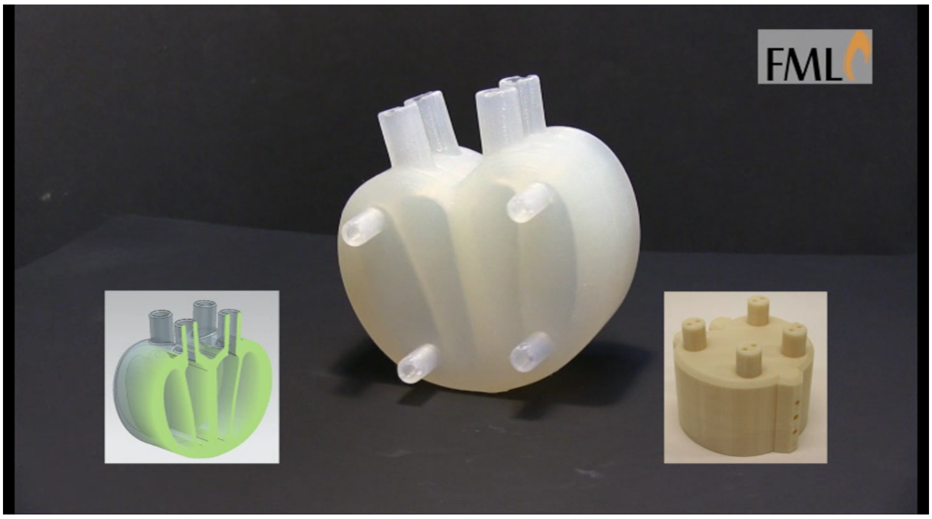


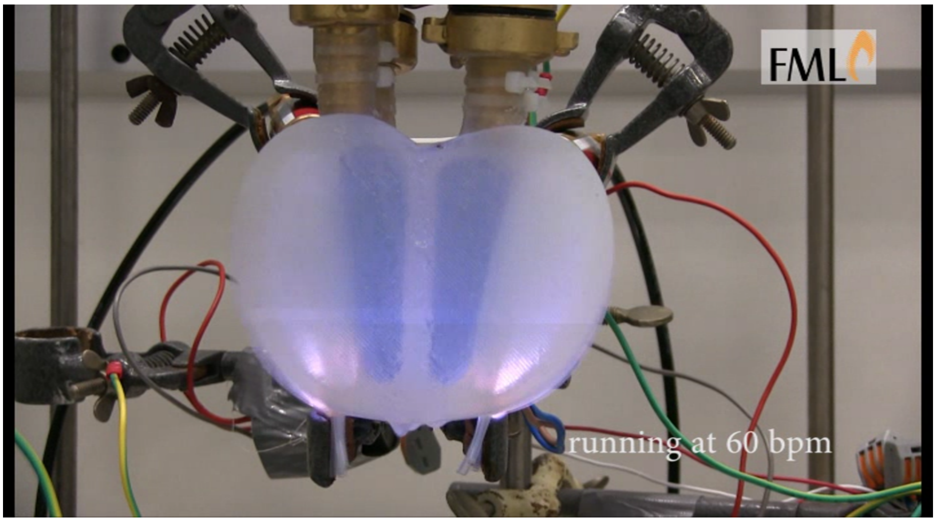
Figure S5. Thermogravimetric analysis of the PDMS material: At 320 °C, thermal degradation starts. This is around 100 °C above the maximally achieved steady-state operation temperature of the soft pump.

Table S1. Data for the calculation of the energy efficiency is shown in per cent. Combustion energy released for a frequency of 0.5 Hz is calculated to be 250 J per pulse. The potential energy is calculated using a tubing diameter of 13 mm and a water density of 977 kg/m^3 (at RT).

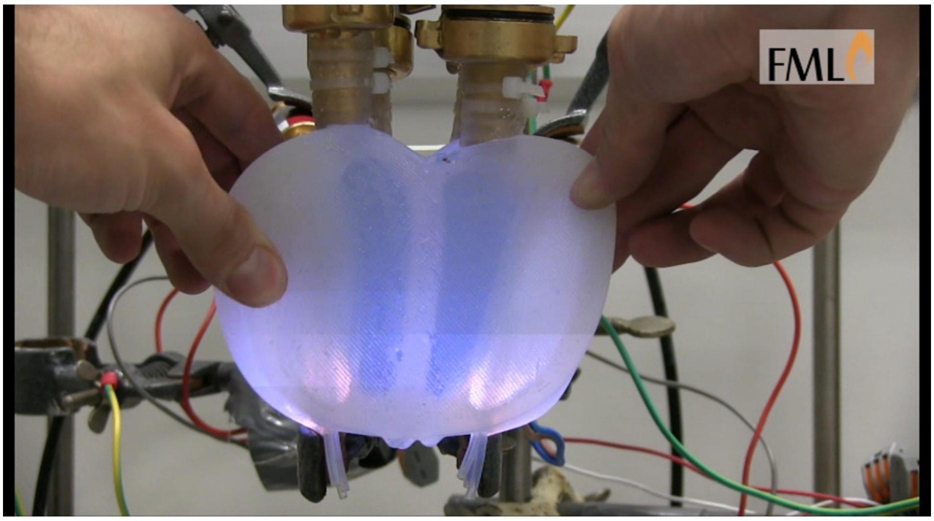
column height [cm]	**height difference** [cm]	**potential energy** [J]	**energy efficiency** [%]
0	25	0.080	0.0318
50	10	0.013	0.0051
80	4	0.002	0.0008



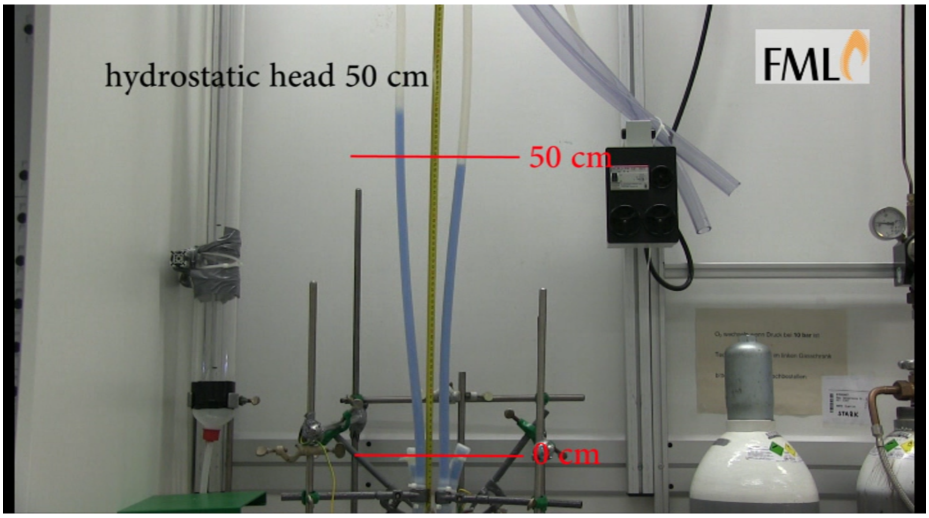
Movie S1. Presentation of the internal combustion powered soft silicone pump after injection molding and washing procedure. Precise ABS injection mold design was enabled by 3D printing. http://www.n.ethz.ch/~schumacc/download/MovieS1.wmv



Movie S2. Operating soft silicone pump at paces of 60, 120 and 150 beats per minute (bpm). http://www.n.ethz.ch/~schumacc/download/MovieS2.wmv



Movie S3. Tripartite movie first showing the possibility of simultaneous and subsequent ignition. Secondly, contraction analysis using slow motion caption supported by color boundary. Last, *in situ* silicon pump deformation during operation process. http://www.n.ethz.ch/~schumacc/download/MovieS3.wmv



Movie S4. Measuring the displaced volumes by the pumping process against hydrostatic heads of 0, 50 and 80 cm. http://www.n.ethz.ch/~schumacc/download/MovieS4.wmv