Digital Fabrication of Support Structures for Improved Mechanical Stability of Fragile Microsieves

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Abstract

We introduce a method to improve the mechanical stability of thin sieves by applying a support matrix through inkjet printing. Different suitable materials are printed in defined structures, such as honeycombs, either directly on the sieve or on a subcarrier. The digital technology allows the variation of the three-dimensional geometry of the printed pattern, whereby an optimum has to be found between the coverage of the pores, the permeability of the microsieve and its mechanical stability. The benefit of this method is the opportunity to produce and apply the microsieves in large-area-applications.

Introduction

With the main fundamentals about the production of functional elements through inkjet printing understood [1–4], the usage of digital fabrication techniques for the build-up of micro-three-dimensional (µ3D) structures is a natural consequence of the technological development. By additive deposition of polymer layers on top of each other, architectures having small dimensions in length, width and height can be realized [5]. Recently, the positioning of droplets with high accuracy was reported to be used for manufacturing of micro-porous membranes [6] and micro lenses [7]. A combination of materials, showing electrical conductivity or insulating properties, enables the production of complex structures like crossovers or interconnections for electronic circuits [8].

The mechanical stabilization of microsieves, which are produced via the principle of particle-assisted wetting [9,10], represents a further field of application for inkjet-printed µ3D-structures. Microsieves are membranes with pores in the size of micro- and nanometers showing a thickness smaller than the pore size [11–14]. They exhibit high size selectivity and a minimum flow resistance and are suitable for the application in microfluidic systems to filter very small volumes of liquids. However, membranes of this type bearing holes of sub-micrometric diameters are highly fragile due to their small thickness. Stabilization can be ensured by mounting the microsieves on a prefabricated coarse porous sieve-like structure [15]. Compared with these mounting of two prefabricated structures, the selective deposition of polymer through inkjet printing directly onto the microsieve offers the advantage to obtain optimized area coverage for different pore sizes and membrane thicknesses. Thereby the stability of the microsieve is maximized at minimal coverage of pores. Increased stability and decreased permeability can be adjusted to fulfill individual requirements of different filtration-applications.

The purpose of this work is the additive production of µ3D-structures, the characterization of the layer geometry and the evaluation of the layers regarding the usage as mechanical support structure for microsieves.

Materials and Methods

The geometry of a honeycomb was chosen as basic unit for the support structure due to its complex layout having lines in and across printing direction. Therewith both wet-in-wet and wet-in-dry printing can be investigated using only one unit. The description of the print patterns results on the basis of three parameters (figure 1): the drop space *DS* (in µm) determines the resolution and thus the deposited material per area, the radius *r* (in px) is the radius of the perimeter of the non-covered free area of the honeycomb, and the distance *a* (in px) depicts the width of the printed lines, the real printed supporting elements.

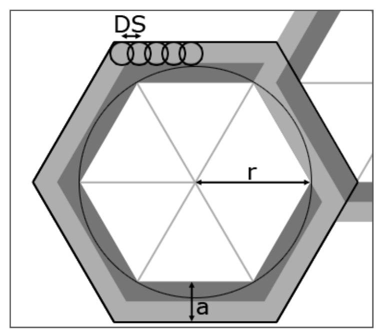

***Figure 1**. Geometry of a honeycomb with parameters to compile patterns.*

The production of support structures through inkjet printing was realized with the Dimatix Materials Printer 2831 and its 10 pL printheads. A customized voltage waveform to control the piezo element was used. It was printed with one nozzle at a frequency of 3 or 5 kHz.

The final goal is to print supportive structures onto microsieves that consist of polymerized trimethylolpropane trimethacrylate (TMPTMA). This polymer has chemical properties comparable to poly(methyl methacrylate) (PMMA). Hence, PMMA foil with a thickness of 175 µm was used as reference substrate. After preliminary tests with different polymer inks 1 wt% PMMA dissolved in anisole was chosen for further examinations. To characterize the ink regarding the formation of µ3D-structures both, single lines and honeycombs were printed. The microscopic evaluation of the printed patterns was done with the mobile USB microscope Cellcheck CIL-ZX-USB (M-Service) and the layer profiles were recorded with Dektak M8 (Veeco). Contact angle and surface tension of the ink were determined with the Contact Angle System OCA 20-3 (Dataphysics) and the viscosity was measured with Physica MCR (Anton Paar).

For the accomplishment of stability tests a PMMA membrane was produced with a calculated thickness of 4.5 µm. For this purpose a thin uniform layer of a solution of 0.15 g ml^{-1} PMMA dissolved in chloroform was applied manually with a squeegee (gap: 30 µm) onto commercially available aluminum foil. After printing the support structure on the membrane, the aluminum foil was removed with hydrochloric acid.

***Table 1**. Properties of solvent [16] and ink (measured) at ambient conditions. Viscosity was determined at a shear rate of 1000/s.*

Substance	ρ [g/cm³]	η [mPas]	γ [mN/m]	bp [°C]	Pv [hPa]
pure anisole	0.9940	1.056	35.1	153.7	0.472
1 wt% PMMA in anisole	1,005 ± 0.005	2,40 ± 0,04	35.7 ± 0.04	-	-

Results and Discussion

PMMA in anisole as µ3D-ink

If one assumes, that a liquid printed along a line resembles a segment cut off a cylinder parallel to its axis, its cross sectional area is given by the ratio of volume per length (respectively the drop space *DS* and the volume *V* of the drops) and its borderline assuming the advancing contact angle *θ* (expressed in rad). One obtains a width of this line at its base given by equation (1) [3]:

$$w = \sqrt{\frac{\frac{V}{DS}}{\frac{\theta}{4sin^2\theta} - \frac{\cos\theta}{4\sin\theta}}} \tag{1}$$

For the fabrication of three-dimensional structures a contact angle greater than 0° is needed to ensure the possibility for the polymer to be arranged in the height dimension. The used PMMA solution exhibits a contact angle of 10° on the PMMA foil.

The evaporation of the solvent after printing gives rise to a significant reduction in volume. During this process the three-phase-contact line usually is pinned and connection processes redistribute material within the line, both processes giving rise to deposit with non cylindrical geometry. In a first approximation one might assume that the line has a cross section in the form of a rectangle, with width given by the value calculated from equation (1) and its height given by equation (2) [3]:

$$h = \frac{V \cdot C}{DS \cdot w} \tag{2}$$

To get information about achievable maximal multi layer thicknesses, single lines with varying number of layers were printed at a constant drop space of 5 µm. Figure 2 shows a typical cross-section of a line composed of 10 layers. The line shape is characterized by a strong bulging which results in a varying line width. The average widths of the printed lines shown in figure 3 fit well to the value of 260 µm calculated from equation 1 and is within our accuracy independent of the number of layers. Furthermore, the material does not arrange in a homogenous layer thickness or in a typical coffee ring shape. A thin layer with an approximate height of 50 to 100 nm is formed and on top of it a typical coffee ring structure with a distinctly smaller width of 160 µm arranges. The achieved average thickness by printing 20 layers is 2 µm with peaks between 4 and 6 µm. Due to the fact that there was always material in the valley of the coffee ring with reasonable layer thicknesses between 25 and 60 % of the peak-heights no strategies were taken into account to minimize the effect. The values of the average thickness correlate with the calculated values, if the inner line width of 160 µm is used in equation (2) (figure 4).

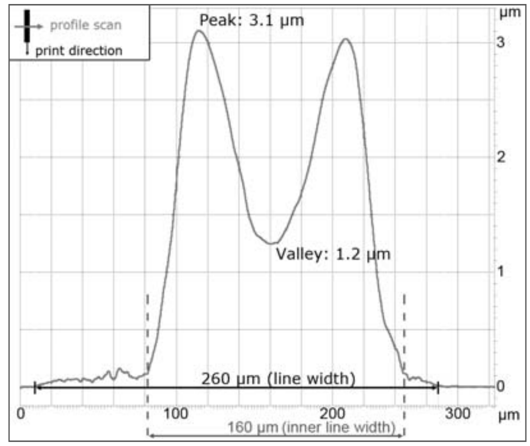

***Figure 2**. Profile scan of a 1 px wide line at 5 µm drop space with 10 layers.*

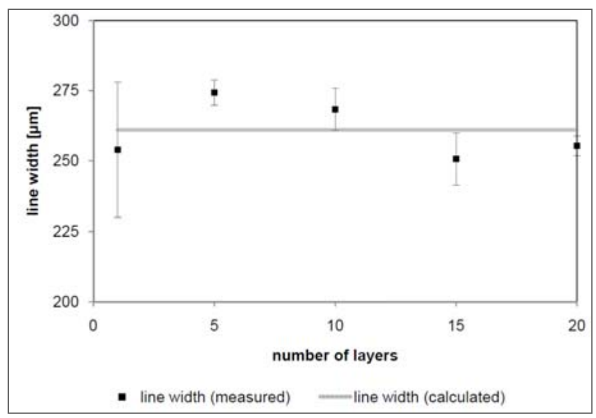

***Figure 3**. Line widths at different number of layers at drop space of 5 µm.*

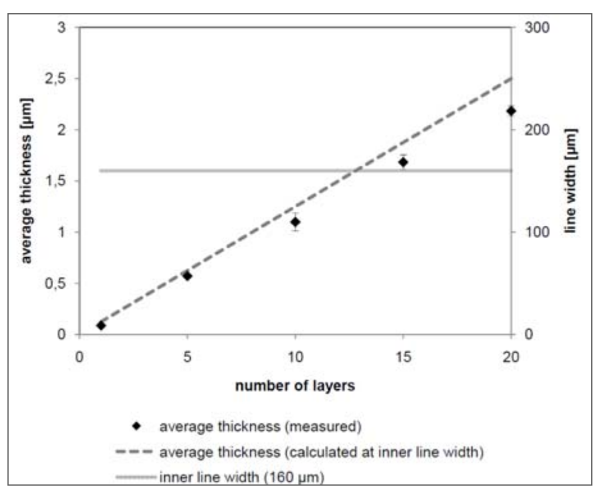

***Figure 4**. Average line thickness at different number of layers, DS = 5 µm.*

Regarding the application, the resulting line width at a drop space of 5 µm is too big and also the inhomogeneous line shape is not satisfying. Thus, experiments with bigger drop spaces were conducted. Figure 5 shows the resulting line widths.

As done by *Soltman and Subramanian*, the quality of the lines can be evaluated and related to different inkjet-typical shapes [4]. Shown in figure 6, lines at small drop spaces (< 10 µm) are bulging, above 50 µm they are scalloped and at drop spaces between 20 and 40 µm uniform lines are formed which indicates the optimum range.

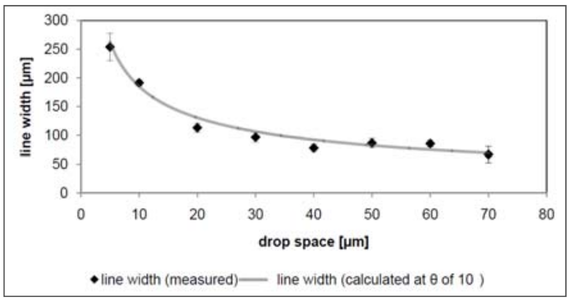

Figure 5*. Line widths at different drop spaces, 20 layers.*

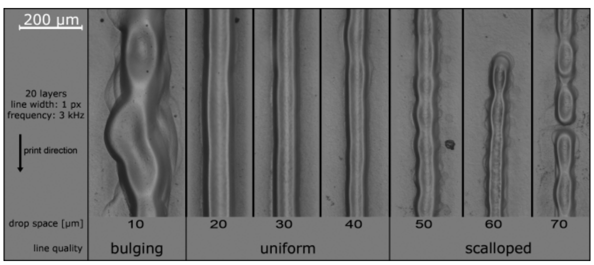

Figure 6*. Line quality at different drop spaces.*

In summary, for the use of PMMA in anisole as ink for producing µ3D-structures, the following can be pointed out:
For uniform lines, the optimum drop space is at 20 to 40 µm with resulting widths of 110 to 80 µm. By printing 20 layers at 5 µm drop space suitable layer thicknesses can be achieved. The line width is independent from the number of layers.

Printing complex structures

When printing more complex structures like honeycombs some lines are positioned in printing direction and some perpendicular to it. If only a few nozzles are used to print and a print system, which generates the print pattern line by line, the delay between the deposition of neighboring droplets varies between 0.3 milliseconds and 7 seconds. Thus, depending on the line direction, a partially wet-in-wet and wet-in-dry-printing occurs, and therefore, one obtains various line shapes depending on the line direction (illustrated in figure 7a). In printing direction (wet-in-wet), a strong bulging occurs; in cross direction stacked coins are generated. This can be avoided by choosing a suitable orientation of the pattern like shown in figure 7b. The deposition delay is about 7 seconds (depending on the pattern length) and only a wet-in-dry printing takes place. Another possibility is the increase of the drop space to values where uniform lines are printed.

The tremendous advantage of printing wet-in-dry, however, is that the line width is always minimal and conforms to the drop diameter. The drop space has no influence on the quality of the line, even at the lowest drop space of 5 µm no bulging occurs.

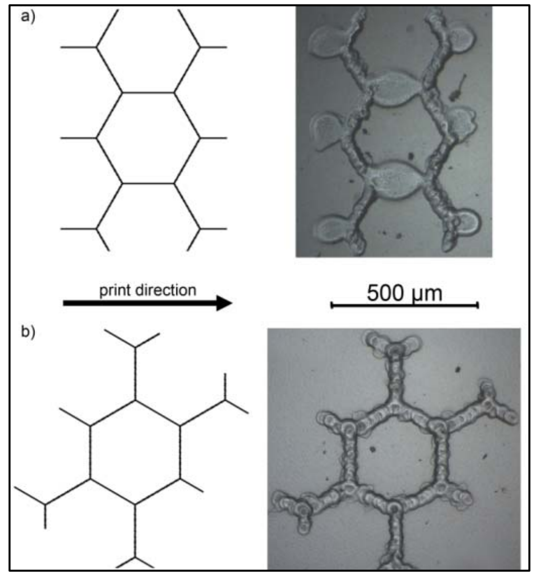

Figure 7*. Structures of honeycombs (DS = 5 µm, r = 70 px, a = 2 px), printed line by line with one nozzle and a frequency of 3 kHz, 20 layers; a) with areas of printing wet-in-wet; b) angled pattern leads to only wet-in-dry printing*

When printing the honeycomb of figure 7 with a drop space of 5 µm it should be noticed, that the line is printed with a distance of a = 2 px, which means two drops are set side by side and wet-in-wet to build the line instead of one. Due to this, a larger line width could be expected, but the measured values of the wet-in-dry lines in the honeycomb exhibit widths of 127 ± 16 µm and are therewith 50 % thinner than the wet-in-wet line (figure 8). The reason for this is that the material of two printed dots in printing direction is dried before the next two drops are set in the next printing line – the dots do not merge together. Additionally the lines do not show the coffee ring effect. Furthermore the lines of the wet-in-dry structure exhibit along the middle of the lines a rough layer, but are consistent at an average height of 2 ± 0.3 µm and thus suitable for the application.

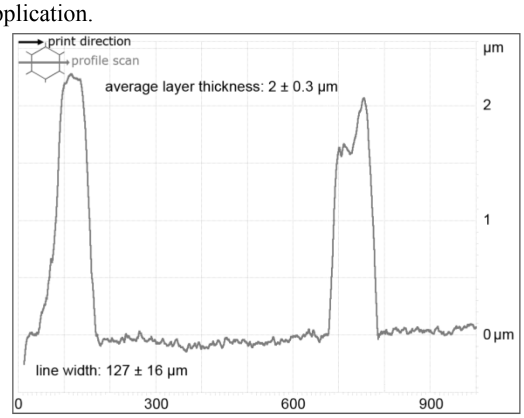

Figure 8*. Profile scan of a 2 px wide line at 5 µm drop space with theoretically 20 layers. Two dots in printing direction are deposited wet-in-wet, the complete line-structure is printed wet-in-dry.*

µ3D-structures as support matrix for microsieves.

After investigation of the µ3D-structure of the PMMA ink on PMMA foil in detail, larger scaled prints could be produced. An area of 3 x 1 cm² was printed on a thin layer, which was prefabricated with a squeegee on top of an aluminum foil. The parameters of the print pattern for the given example in figure 9 were *DS* = 5 µm, *r* = 23 px and *a* = 2 px, the theoretical area coverage was 9.33 %. The number of layers was 30.

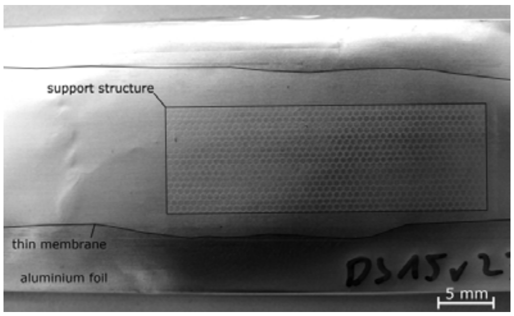

Figure 9*. Support structure on a PMMA-membrane on aluminium foil.*

The aluminum substrate was removed by exposure to hydrochloric acid (18.5 wt% HCl in water) and a polymer membrane was formed, that floated on top of the aqueous phase. After that the floating membrane was manually lifted off on one side with a pipette. When lifting up membranes without an inkjet printed support structure a strong creasing was observed (figure 10a). However, the membrane with the support structure remained dimensionally stable (figure 10b). This indicates that the mechanical stability of thin membranes can be increased by printing a support structure on them.

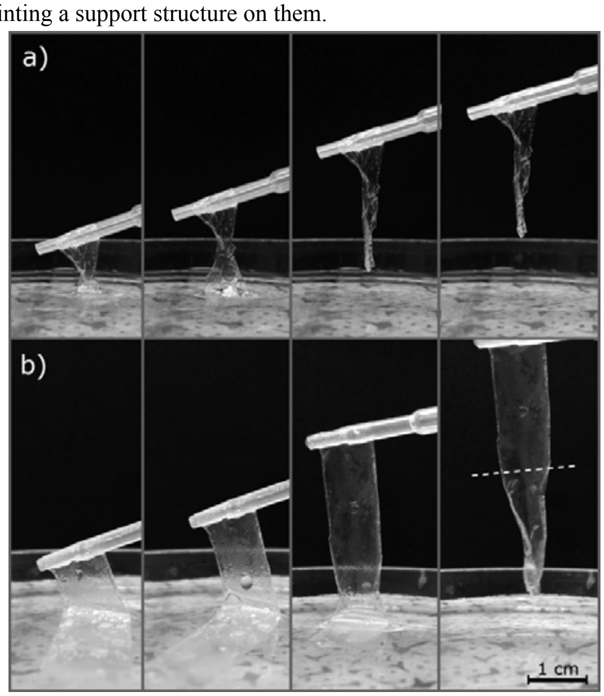

Figure 10*. Lifting membranes out of liquid: a) membrane without support structure; b) membrane with partial support structure (the area above the dashed line stays dimensionally stable due to the support structure, the area below without a support structure creases)*

Conclusion

We introduced a method to produce support structures for fragile microsieves. Honeycomb architectures were built directly onto thin membranes by applying a polymer through inkjet printing. It was demonstrated that suitable structure dimensions and layer thicknesses can be achieved by using inkjet technology. The structures enhance the mechanical stability of the membranes.

The polymer PMMA dissolved in anisole was evaluated regarding its possibility to create µ3D-structures through layer-by-layer lamination. Furthermore it was noticed that printing wet-in-dry leads to thinner lines at low drop spaces than printing wet-in-wet. The production process can now be adapted to microsieves.

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Jens Hammerschmidt has received his Master of Arts in German and Print and Media Technology media production in 2008 at Chemnitz University of Technology. Since then he is Ph.D. Student at the Institute of Print and Media Technology in Chemnitz in the department of digital printing and his scientific interests are focused on digital fabrication technologies based on inkjet printing technology.