Characterization of fully inkjet-printed microsieves and of patterns for the mechanical reinforcement of fragile membranes

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Abstract

Microsieves are "permeable membranes densely interspersed with uniform pores with a thickness smaller than the pore diameter" [1]. They exhibit excellent properties for filtration applications such as high size selectivity and a high flow rate [2]. We report on the further development of already published, inkjet-based approaches to (1) manufacture microsieves [3, 4] and (2) to reinforce microsieves mechanically [1]: (1) With the inkjet technology microsieves with pores in the micrometer range can be manufactured [4]. However, the distribution of the pore diameters is high which is disadvantageous for a precise size selection in filtration applications. In this report the printing processes are improved to obtain microsieves with uniform pores. In addition, the samples are characterized in terms of porosity and achievable flow rates. (2) Microsieves with pore diameters in the nanometer range can be obtained by float-casting [5]. These are extremely thin and fragile. We developed a process to apply patterns for the mechanical reinforcement by inkjet printing [1, 6]. The patterns which were reported are composed of inhomogeneous lines with high deviations in width and thickness [1, 6]. This probably leads to weak spots which diminish the reinforcing effect locally. Therefore the printing process is improved to obtain patterns with homogeneous lines by a liquid-on-pinned printing strategy [7]. Furthermore a tensile test is applied on a non-porous membrane with a pattern for the reinforcement on top.

Introduction

Fully inkjet-printed microsieves

Inkjet printing of microsieves is based on the following main steps [4]: An aqueous ink is printed on a hydrophobic substrate to form a mold pattern of separated, sessile drops. Subsequently a UV curable ink is printed to cover the area of the sessile drops. Both inks do not merge and the sessile drops imprint their shape into the UV ink layer. The pores are formed because the height of the sessile drops is higher than the thickness of the UV ink layer. The diameters of the pores can be adjusted by changing the volume of the sessile drops [3]. After UV curing the microsieves are detached from the substrate.

The application of this process enables to manufacture polymeric microsieves and to adjust the pore diameters in the micrometer range [4]. However, the so far obtained throughput is low due to the slow speed of the applied printing system. Thus the initial volume of the sessile drops is reduced by evaporation during the long manufacturing process. Furthermore the volume loss is different for all sessile drops within a mold pattern. As the pore diameter depends on the volume of the sessile drop, the inhomogeneous volume loss results in a broad distribution of the pore diameters (up to 20 % within a microsieve). Two main aspects influence the volume loss: (1) Time effect: The time period between the deposition of the sessile drops and the formation of the pores by curing of the UV ink is different for each sessile drop of the mold pattern. Sessile drops, which are printed first, rest on the substrate for a longer time than the last printed sessile drops. Hence the evaporation-driven volume loss is higher for the first printed sessile drops. (2) Saturation effect: The evaporation of the sessile drops increases the saturation of the atmosphere close to the mold pattern with molecules of the aqueous ink. This saturation is higher in the center of the mold pattern compared to the edges. Hence the volume loss of the sessile drops at the edges is higher than for the sessile drops in the center (the evaporation process is comparable to the evaporation of a film of water where the area shrinks from the edges towards the center).

The improved approach, which is reported here, is based on a higher throughput to overcome the time effect. Furthermore the saturation effect shall be avoided by printing a mold pattern which is larger than required for the area of the final microsieve. It is assumed that the additional sessile drops around the microsieve area compensate the mentioned difference of the saturation.

Patterns for the mechanical reinforcement

Float-casted microsieves with pores in the nanometer range have a thickness in the same range [5] and are thus mechanically fragile [1]. Therefore a pattern for the reinforcement is inkjet-printed on top [1] with industrial relevant printheads [6]. The patterns are composed of grids of the edges of hexagons and printed with UV curable ink. Two printing strategies were applied:

- Liquid-on-liquid: A first deposited drop stays liquid before the next, adjacent drop is printed. Here the ink spreads and forms bulging lines [7].
- Liquid-on-solid: A first deposited drop is cured before the next adjacent one is printed. Here the lines are not continuous. Instead single drops without contact to other drops are formed [7].

In the approach, which is reported here, the liquid-on-pinned strategy is applied [7]: A first deposited drop of the UV ink is only shortly exposed to UV light to initiate a short-time cross-linking without a complete curing. This increases the viscosity of the drop and prevents its spreading (the drop is pinned, but not solid). The next, adjacent drop is then deposited on the pinned drop. This results in continuous and uniform lines. The process was so far only applied on areas of 1 mm² [7] and is now adapted for the manufacture of hexagon patterns on areas of about 1600 mm² by using industrial relevant printheads.

Experimental setup

Two printers were used: The Autodrop System AD-E (Autodrop) with the dispenser head MD-K-130-684 (both supplied by Microdrop Technologies), and the PROTOprinter which is a self-built machine [6] to deposit functional inks with the Galaxy Printhead 256/50 AAA driven by the Apollo 2 Printhead Support Kit (both supplied by Fujifilm Dimatix Inc). In the printing processes the UV curable ink Hyperion Pro Wet (Tritron GmbH) is applied. Glass substrates (Menzel GmbH & CoKG) with an area of 30 mm by 100 mm are used. The solvents which are mentioned in the following were purchased from the chemistry stock of Technische Universität Chemnitz. Light microscopic images were taken using Leica DM4000 (Leica Microsystems).

Manufacture and characterization of microsieves

The preparation of microsieves follows the steps which are introduced above. The materials are mainly adapted from previous publications [3, 4]: A glass substrate is immersed in a bath of a mixture of toluene and 0.19 wt% 1,1,1,3,3,3-hexamethyldisilazane (Merck) for 24 hours to obtain a hydrophobic surface. An aqueous ink composed of 30 wt% water and 70 wt% ethylene glycol is printed with the Autodrop to form the mold pattern on the hydrophobic surface. The pattern is an array of 38 by 38 sessile drops which have a distance of 400 µm. The substrate is then transferred to the PROTOprinter. Here the UV ink is printed with a resolution of 600 dpi in the center of the mold pattern to cover a circular area with a diameter of 13 mm. The UV ink layer is cured with the RX FireFlex (Phoseon Technology). The substrate is immersed in a bath of water to detach the microsieve. The diameter d of a pore is calculated by the measured pore area A_{pore} with $d = 2\sqrt{A_{pore}/\pi}$. With this method it is assumed that the pores are ideally circular. The porosity is here defined as the ratio of the area of all pores to the overall area of the microsieve. For the determination of achievable flow rates the microsieve is clamped in a syringe filter holder (Celcon Kunststoff-Filterhalter 13 mm, Pieper Filter GmbH) between two sealing rings. This is attached to a water-filled syringe. A linear stage (M-IMS400PP, Newport Corp.) moves the plunger of the syringe with a preset velocity. The corresponding flow rate can be adjusted between 0.0375 mL/min and 1875 mL/min.

Printing of patterns for the reinforcement

For the development of the printing process the patterns are not printed on float-casted microsieves, but on thin, non-porous membranes. These are prepared on glass substrates by printing the UV ink with the PROTOprinter at a resolution of 600 dpi. The UV ink layer is cured with the above mentioned UV lamp. The patterns for the reinforcement are printed with the UV ink on top of the membranes with a resolution of 1200 dpi or 1800 dpi in twelve or eighteen swaths. After each swath the just deposited drops are exposed to UV light for ≤ 0.5 s. The irradiance of the light was varied between 0.4 W/cm² and 8 W/cm² in order find a setting to pin the drops. The patterns are composed of hexagons with an edge length of 420 µm. The membranes are detached from the substrate by immersing the substrate into a bath of water.

Results and discussions

Fully inkjet-printed microsieves

An example of a fully inkjet-printed microsieve resulting from the improved process is shown in Figure 1a. The distribution of the pore diameters which are not covered by the sealing ring of the syringe filter holder is given in Figure 1b. The corresponding average diameters of the pores within each row of printed sessile drops (in a row in print direction) are plotted in the diagram of Figure 1c.

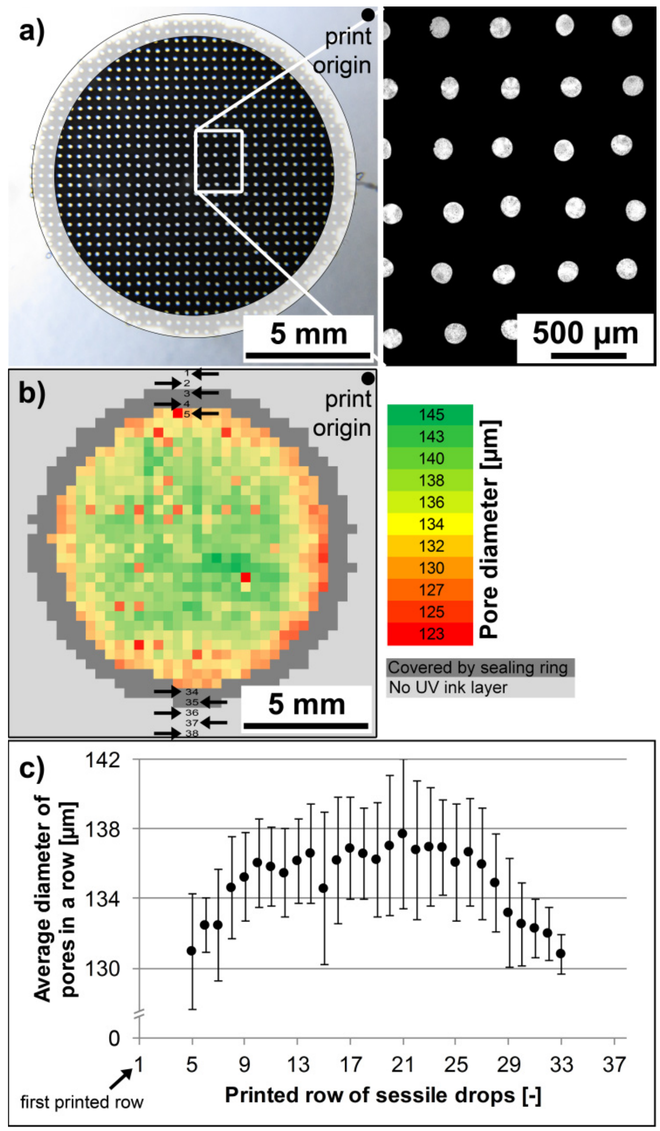

Figure 1: a) Photo of a fully inkjet-printed microsieve which rests on the glass substrate; the white ring represents the area of the sealing ring which covers pores; the white frame shows the region which is shown in the light microscopic image on the right; b) Distribution of the pore diameters for pores which are not covered by the sealing ring; the black arrows give exemplary print directions for the rows of sessile drops (printing is done from top right and then bidirectional row-by-row); the numbers give the row number; c) Average values for the diameters of pores within a row; the 1st, 2nd, 37th and 38th row of sessile drops was not covered with UV ink; the 3rd, 4th, 34th and 35th row of pores is covered with the sealing ring

Characterization of the pore size distribution

The average diameter of the pores is 136 µm ± 3 µm, the minimum value is 123 µm and the maximum value is 145 µm. The porosity is 13 %. The range of the pore diameters and the deviations represent an improvement in comparison to microsieves of the previous reported process [4] (here an exemplary microsieve had an average diameter of 111 µm ± 10 µm with a minimum of 81 µm and a maximum of 127 µm).

The influence of the above introduced saturation effect was not completely avoided: the pores with a larger diameter are still located in the center area of the microsieve and the pores at the edges are smaller (Figure 1b and Figure 1c). It is assumed that the area of the mold pattern has to be further increased to compensate the saturation difference which means more sessile drops have to be printed around the actual area of the microsieve.

The influence of the above introduced time effect is avoided by the enhanced throughput of the process (Figure 1c): There is only a small difference in the values of the average pore diameters between the pores of the earlier printed sessile drop row 5 (131 µm ± 3 µm) and the later printed row 33 (131 µm ± 1 µm). This means that the volume of the sessile drops was the same when the UV ink was cured. The sessile drops lost approximately the same volume due to evaporation although the sessile drops of row 5 rested longer on the substrate than the sessile drops of row 33.

Evaluation of achievable flow rates

A microsieve which is attached to the syringe filter holder is shown in Figure 2a. The test station to adjust the flow rate of the flow through the microsieve is given in Figure 2b.

A microscopic image of a microsieve which was exposed to flow rates ranging from 0.0375 mL/min to 1875 mL/min is shown in Figure 2c. It was found that the microsieve area is completely intact after the flow test. This means the microsieves withstand the pressure resulting from the maximum applied flow rate. It is assumed that the flow rate can further be increased.

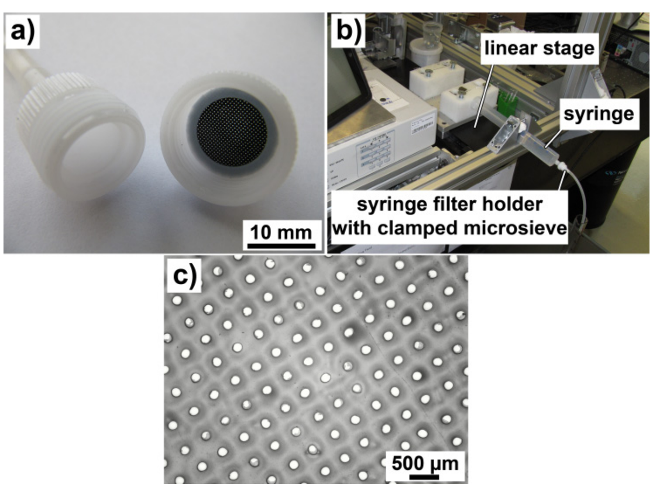

Figure 2: a) Microsieve in the syringe filter holder; b) Test station for flow experiments; c) Intact microsieve which was first exposed to low flow rates and then to high flow rates

Patterns for the mechanical reinforcement

Printing liquid-on-pinned on large areas

The irradiance of the swath-by-swath applied UV light was varied in order to find a setting for printing the drops liquid-on-pinned (Figure 3).

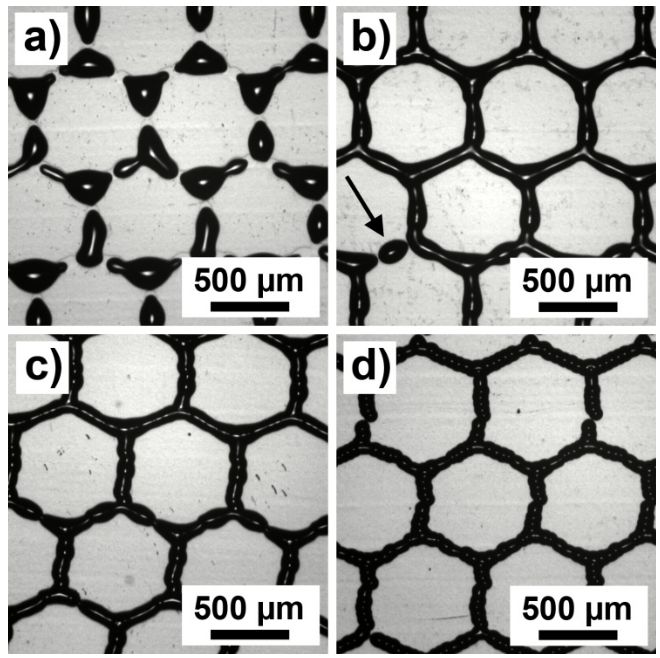

Figure 3: Hexagon patterns printed with a resolution of 1200 dpi; the irradiance of the UV light was varied: a) no UV light is applied; b) 0.4 W/cm² (the arrow points to a location where the drops were not pinned and the contact lines retracted); c) 0.8 W/cm²; d) 4 W/cm²

Without an intermediate exposure to UV light the drops are printed liquid-on-liquid, coalesce and the contact lines retract which results in interrupted and inhomogeneous lines as shown in Figure 3a. As reported before [7] this printing strategy is disadvantageous because the liquid drops interact with each other and with the substrate until being cured – this can lead to undesired effects like spreading [7] or retracting of the contact lines (depending on the respective applied substrates).

With an irradiance of up to 0.8 W/cm² the drops get pinned (Figure 3b-c). However, the pinning was only reproducible for all drops in a printed swath with an irradiance of 0.8 W/cm². Below this value the retraction of the contact line still occurred at many locations of the patterns (see the arrow in Figure 3b).

Above 2 W/cm² the drops are cured (Figure 3d). Here the lines have a morphology which is comparable to stacked coins [8]. These patterns are probably adequate for the mechanical reinforcement of fragile membranes because the lines are continuous and show only few interruptions. However, the continuity of the lines, which are printed liquid-on-solid, depends on the interfacial tensions between the liquid impinging drop, the solid drop resting on the substrate, and the surface of the substrate. For example it has already been reported that the UV ink wets more likely a glass substrate than a solid drop of the UV ink [7]. If this is the case, the adjacent drops do not have such an intimate contact to each other like the drops in Figure 3d. Instead the impinging drops flow from the surface of the solid drops to the substrate and form separate drops next to the solid drops. In addition, it was already observed that the ink spreads on the float-casted microsieves (which are the final target substrate for the application) – hence it is expected that here no continuous lines will be formed when the drops are print liquid-on-solid. Furthermore it is assumed that the cohesion between liquid-on-pinned printed drops is higher compared to liquid-on-solid printed drops.

Based on these considerations further printing experiments were done with an irradiation of 0.8 W/cm² where all drops of a printed swath are pinned.

Tensile test on non-porous membranes

Hexagon patterns were printed with a resolution of 1800 dpi on the membranes. The compound of both was clamped to a tensile test station as shown in Figure 4a. A first measurement revealed that such a compound breaks at a tensile force of 4 N (Figure 4b).

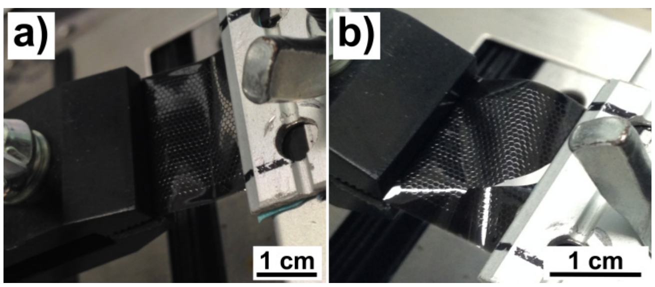

Figure 4: Membrane with a reinforcing pattern on top, clamped in a tensile test station: a) before applying the tensile force; b) after applying the tensile force

Conclusion

Microsieves with an improved uniformity of the pore size distribution were manufactured by inkjet printing. The evaporation-driven volume loss of the sessile drops of the mold pattern was minimized by the application of a process with an enhanced throughput. The microsieves with porosities of 13 % withstand the pressure resulting from the maximum applicable flow rate of the used flow test station (1875 mL/min). It is assumed that this value can even be increased.

The morphology of the patterns for the mechanical reinforcement of thin membranes and float-casted microsieves was improved. Therefore the drops were printed liquid-on-pinned. This printing strategy can now be applied on large areas.

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Author Biography

Jens Hammerschmidt received his Master of Arts in German and Media Production in 2008 at Technische Universität Chemnitz. Since then he has worked at Technische Universität Chemnitz in the department of Digital Printing and Imaging Technology. His scientific interests focus on the manufacture of functional patterns with the inkjet technology.