Hierarchically structured membranes manufactured by inkjet technology

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Abstract

Membranes with micro pores smaller than 30 µm are required in many micro systems dedicated to biological and chemical applications. However, the challenges of manufacturing these membranes rise with decreasing pore sizes. Similar requirements have to be met regarding the dependence of flow resistance and membrane thickness. Currently, the mechanical stability of these membranes has to be improved to establish appropriate industrial micro systems fabrication.

The paper outlines a new route to manufacture those micro membranes based on inkjet as a digital fabrication technology.

Single droplets of a qualified liquid are inkjet printed onto a temporary supporting substrate. These droplets are used as molds for the pores of a thin polymer membrane. The macroscopic membrane structure is made by casting a curable polymer solution onto the droplet pattern. The digital fabrication character of the patterning process enables the manufacturing of hierarchically structured membranes as a variable pattern of pores and support structures in one single patterning step. This technology allows free three-dimensional membrane design.

Introduction

Porous membranes are used as filters in many technical applications. For example, membranes are used for cleaning of gases [1] or as an alternative method for the separation of liquid/ liquid systems, e. g. extraction or distillation [2]. The major potential of application is seen in biology, pharmacy and medical science, where membranes are used as filters as well as culture medium for living cells [3].

For an efficient filtration two membrane parameters are important: a high permeability and a high selectivity. The high selectivity can be realized with a uniform pore size. The high permeability can be achieved with a high number of pores in comparable thin membrane.

With a decreasing thickness of the filtration membrane its mechanical stability also decreases. Thus, the implementation of support structures into the membrane design is essential. This is usually done by fixing the fragile membrane to a coarse porous sieve-like structure. This technique is called hierarchical structuring [4]. These additional structures could also be used for further functions of the membrane system (e. g. electrical, magnetic properties).

The purpose of the research efforts discussed here was to develop a flexible and additive manufacturing method for hierarchically structured membranes. Therefore, inkjet technology turned out to be an ideal method for creating non-permanent molds for membrane pores.

Materials and Methods

The base for inkjet aided membrane technology is a temporary support substrate. A hydrophobic surface (silane) was applied onto commercially available aluminum foil by CVD processes. Water has a contact angle of nearly 90° on this surface.

The next step was the deposition of single droplets of an aqueous liquid on that surface which will be employed in the following steps as molds for pores of a membrane. The droplet deposition was carried out by using a Dimatix Materials Printer with 10 pl printheads. The typical droplet diameter was about 35 microns. It is obvious that the inkjet technology is enabling the fabrication of well-defined patterns of liquid droplets and therefore of pore molds. To avoid a too fast evaporation of the droplets, we used a solution of water and ethylene glycol as the printing liquid. In the next step, a solution of polymethyl methacrylate (PMMA) in chloroform (5 wt%) was poured onto the convex water molds and the support substrate. The result, after evaporation of the solvent and glazing of the polymer, was a thin polymer layer with well-defined concave cavities which are the pores. After evaporation of the volatile aqueous molds a membrane structure remains on the aluminum substrate. To get the final membrane the support substrate has to be removed by etching with hydrochloric acid (36.5 %). Figure 1 shows the main steps of membrane manufacturing.

Due to the digital fabrication nature of the inkjet process it is possible to manufacture different areas with variable pore densities in only one process step. The mechanical stability of the membrane is adjustable by varying the size of the areas without pores. The more extended these areas are the more stable the membrane will be.

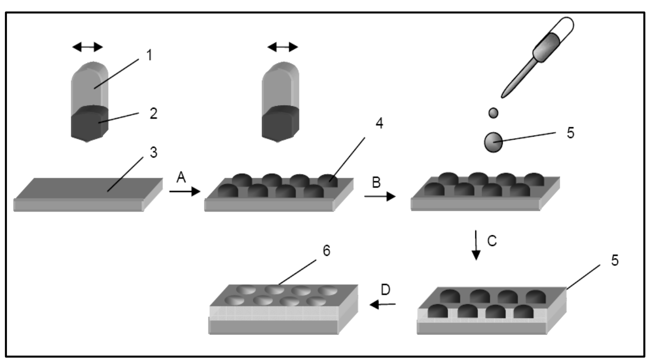

***Figure 1**. Principle of membrane manufacturing (1 inkjet printhead, 2 mold liquid, 3 temporary support substrate, 4 printed droplets, 5 solved polymer, 6 glazed polymer).*

The diameter of the pores can be adjusted by varying the thickness of the polymer film from a value slightly higher then the height of the droplets down to almost zero. A thick layer which covers the droplets completely gives a pore size of zero, a thin layer (compared to the droplet height) gives a pore diameter which is close to the diameter of the water droplet. This effect is illustrated in figure 2. The final film thickness we varied between 5 and 100 microns.

To get different pore diameters within one membrane, the molds can be enlarged by printing different numbers of single droplets onto one point or very close together to provoke a merging of the droplets to a single big drop.

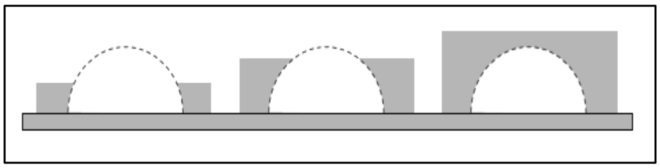

***Figure 2**. Adjusting the diameter of the pores by varying polymer layer thickness.*

Results and Discussion

Generally, short drying times of printed liquids are beneficial in printing processes. But due to the fact that printed water droplets have to serve as molds, the drying time of the droplets has to be increased considerably. The main reason for fast evaporation of the droplets is a relatively high vapor pressure of water in ambient air. In principle, there are two different ways to decrease vapor pressure. The first one is to increase water concentration in the ambient air. A high humidity, however, causes the risk of malfunctioning of electronic components of the printer. The other possibility is to decrease the vapor pressure of the liquid droplets. From thermodynamics it is well known that solutions have a lower vapor pressure than their pure phases because of colligative properties. To reduce the vapor pressure of water, one can use a solution of water and ethylene glycol. To keep up the phase interface between the printed droplets and the polymer it is not possible to use only ethylene glycol. If one would print pure ethylene glycol, the mold droplets would be solved in the PMMA solution and no pores would emerge. Best results with the 10 pl head of the Dimatix Materials Printer regarding the stability of the droplets and getting a defined phase interface between mold and polymer (cf. figure 3) have been achieved by employing a 70 % concentration of ethylene glycol in deionized water. The lifetime of these droplets in ambient air is about 10 minutes. This is sufficient time to print large droplet patterns (some square centimeters) and apply the polymer film without excessive evaporation of the droplets that have been printed first.

To generate small pores the 10 pl droplets have to be deposited discretely onto the substrate. With the utilized setup the minimum grid width between single droplets was 60 microns. Using lower distances would result in a coalescence of the droplets which would cause bigger molds and subsequently bigger pores in the membrane. Figure 4 shows the variation of pore sizes by using different numbers of droplets for creating bigger molds.

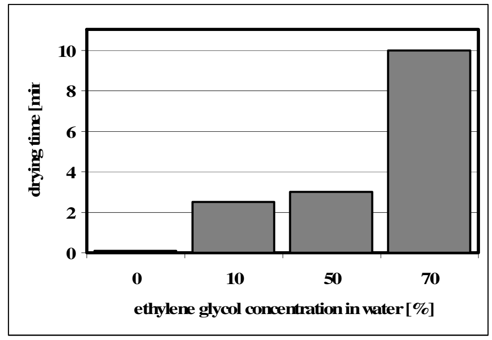

***Figure 3.** Stabilization of droplets.*

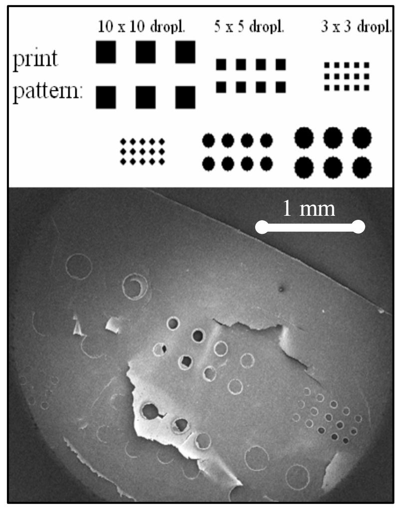

***Figure 4**. Pore size variation through mold size variation.*

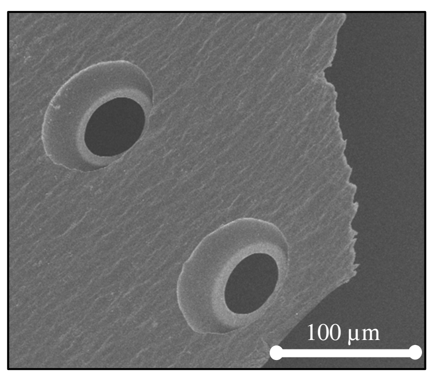

***Figure 5**. Pore size variation through polymer layer thickness variation.*

The possibility to vary pore sizes through polymer thickness variation is illustrated in figure 5. Figure 5 shows a SEM view of the bottom side of a membrane fabricated following the route described in this paper. The hemispherical shape of the molds is clearly visible. The effective pore diameter of the membrane is about 40 µm, the pore diameter at the bottom of the membrane is about 80 µm and the thickness of the membrane is 10 µm. Contemplating the hemispherical shape of the pores, figure 5 illustrates the opportunity to modify the pore size by polymer thickness variation.

The flexibility of inkjet technology allows a free design of the membrane structure. Besides pore size, various additional elements with miscellaneous functions could also be easily integrated. To improve the mechanical stability of the membrane, areas without pores should be integrated into the design. Thus, the manufacturing of the membrane and its mechanical support structure is possible with only one technology in a single process step.

To achieve a high pore density and mechanical stability a hexagonal pattern of pores with support structures in between was fabricated. The thickness of the membrane in figure 6 is about 15 microns. The pore diameter is about 30 microns. Another advantage of inkjet technology is shown in figure 6: the distribution of pore sizes is pretty tight. If the film thickness is homogenous the pore sizes will be almost equal for all pores. The reason for this is the precise dosing properties of the inkjet technology per droplet. The evaporation of the printed molds is the main influence factor on the pore diameter. Using more inkjet nozzles to increase the printing speed would allow printing larger areas of molds. The parallel inkjet application of the mold droplets and the polymer onto the support substrate is a possible way to shorten the time between mold printing and coating of the molds.

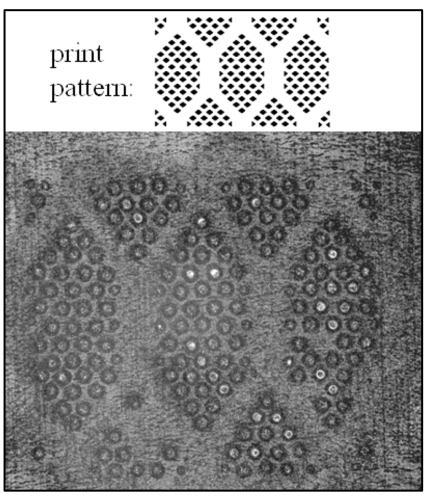

***Figure 6**. Membrane with support structures.*

The application of the polymer film was carried out manually with a pipette. For speeding up the fabrication and an increasing deposition precision it is also possible to apply the polymer film by means of inkjet. Additional layers, e. g. for a higher mechanical stability or electrical connections, could also be applied by inkjet. It seems possible that the manufacturing of a micro membrane could be done exclusively through inkjet printing technology.

Conclusion

An alternative technology for manufacturing micro membranes was demonstrated. These membranes were fabricated by employing inkjet printed droplets of appropriate liquids as molds for polymer membrane pores.

To avoid a rapid evaporation of the 10 pl droplets an aqueous solution of ethylene glycol was found as an appropriate ink. Time for complete evaporation of the printed droplets reaches from a few seconds in case of pure water up to about 10 minutes if the ink is an 70 % aqueous solution of ethylene glycol. This long evaporation time was sufficient for printing the whole pore pattern and applying the polymer.

It was demonstrated that pore diameter can be varied by enlarging the molds with additional droplets or by applying different polymer thicknesses. Hierarchically structured membranes can be manufactured by inserting areas without pores. This technique allows a higher mechanical stability without additional components.

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Author Biography

Stephan Jahn received his diploma in Micromechanics/ Mechatronics in 2005 from Chemnitz University of Technology. Since then he has been working as junior researcher and Ph.D. student at the Institute for Print and Media Technology at Chemnitz University of Technology. At the institute he belongs to the digital printing team. His work is focused on digital fabrication by inkjet printing.

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