Inkjet System for Printing Mechanical Reinforcing Patterns Directly on Fragile Membranes Floating on Liquid Surfaces

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Abstract

Ultrathin porous membranes can be employed for applications in the field of micro- and ultrafiltration and offer a low flow resistance. However, due to their thickness below 1 µm they are very fragile. Therefore, we recently reported on a process to increase the mechanical stability by inkjet printing of UV curable inks to create reinforcing patterns on top of these membranes [1]. Based on this laboratory approach we realized now a specific inkjet printing system to apply the process efficiently on larger areas.

The membranes are first manufactured on a water surface in a Langmuir trough [2]. Therefore, the inkjet system realized here is composed of a 3D motion system for a multi-nozzle printhead and a UVLED-lamp. In order to prevent waves leading to undefined displacements of the floating membranes the filled trough is stationary while the printhead and the UVLED-lamp are moved. The positioning stages have a high accuracy and enable a precise movement of the printing and UV curing device relative to the membranes. Deviating from previous procedures that needed intermittent support of the porous membrane by a solid support, the reinforcing patterns now are created directly on top of the floating membranes. Deposition is done by multiple motion procedures combined with triggered printing and UV curing events. The patterns can be deposited in several minutes with resolutions of up to 800 dpi covering an area of about 130 cm². While the porous membranes before application of reinforcement pattern are very fragile, the reinforced porous membranes are stable enough to be lifted off the water surface and handled manually without special precautions.

Introduction

Today, printing technologies are not only used for graphical applications, but also as manufacturing methods for thin and flexible devices like batteries, sensors, organic light-emitting diodes, antennas or micro-3D patterns [3-7]. The applied inks have certain non-graphical properties to build layers with specific functionalities. The development and manufacture of such printed devices starts small scales in scientific laboratories. When the developed processes have to be transferred to industry-related manufacturing systems, the applied machines mostly customized to the process parameters.

Following, this approach is demonstrated by the manufacturing process of reinforced thin porous membranes. The basis for this report is a process which was developed on laboratory scale [1] in which inkjet printing was applied to print pattern reinforcing fragile microsieves mechanically. The microsieves were fabricated by float casting [8] in a Petri dish. Thus, the microsieves have a thickness less than 1 µm, a uniform pore size and distribution as well as a higher pore diameter compared to the thickness. Hence, for filter applications like blood filtration and human cell filtration, microsieves have excellent characteristics in high selectivity and a minimum of flow resistance. However, due to the low thicknesses they are very fragile. To increase the mechanical stability reinforcing honeycomb patterns were printed on top. This was done with the small format printer Fujifilm Dimatix DMP2831 using 1 nozzle of the printhead. The summarized manufacture of a reinforced microsieve with an area of 1 cm² lasted approximately 2.5 hours. The following developed inkjet system was designed to increase the manufactured area while simultaneous decreasing the manufacturing period.

Concept of the Machine and Printing Process

Process Development

The process steps to manufacture reinforced porous membranes on laboratory scale are as follows [1] (figure 1 a-f):

(a) A suspension consisting of monomer, particles and organic liquids spreads on a water surface in a Petri dish.
(b) A UV-radiation curing of the liquid film on top of the water surface resulting in a thin polymeric monolayer with embedded particles with hexagonal dense packing.
(c) A carrier substrate (aluminum foil) is used to lift off the pre-finished microsieve from the water surface and subsequently print honeycomb patterns on top using a small format inkjet printer and a UV-curable ink.
(d) Curing the ink manually with a separate UVLED-lamp.
(e) Etching of the carrier substrate using a hydrochloric acid solution
(f) Etching of the embedded particles using hydrofluoric acid in an encapsulated system

For a industry-related manufacture the following process- and equipment amendments were done:

- For the microsieve manufacturing a Langmuir Trough System KSV 2000 from KSV Instruments Ltd. instead of a Petri dish was applied to increase the manufactured area.
- Usage of a multi-nozzle inkjet printhead to speed up the printing process.
- Automated usage of an UVLED-Lamp for curing the suspension as well as the printed patterns.

- Printing of the reinforcing pattern directly on top of the floating membrane to avoid the transfer to an carrier substrate and whose etching (figure 1 c*-d*). In laboratory scale, this was the most critical process step where the pre-finished microsieve could be damaged.

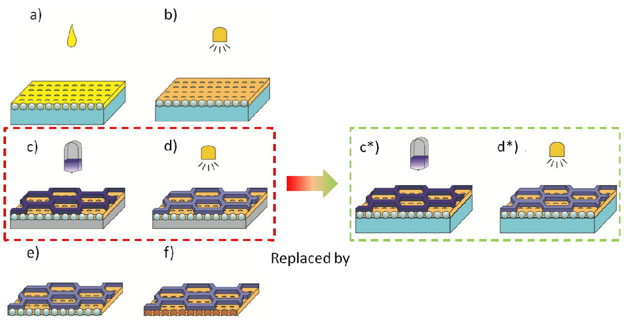

Figure 1 Fabrication process of a microsieve by float casting. a) Spreading a suspension onto a water surface. b) Polymerization by UV-curing. c) Usage of a carrier substrate and printing of a pattern on top. d) UV-curing of the pattern. e) Remove of the carrier substrate. f) Etching of the particles. c) Printing of a pattern directly onto a floating microsieve d*) UV-curing of the printed pattern.*

Experimental Setup - Printing System

To realize the optimized manufacturing process the developed printing system (figure 2 d) has to fulfill certain important conditions. A Fujifilm Dimatix Galaxy AAA 256/50 inkjet printhead was inserted and was suitable for the chosen UV-ink. The printhead has 256 nozzles arranged in a line with 254 µm nozzle spacing. Each nozzle has a diameter of 42 µm which allows generating drops with volumes of 50 pL, respectively. For curing the UVLED-lamp RX FireFlex from Phoseon TECHNOLOGY with a wavelength peak at 395 nm was deployed. For both, UV-lamp and printhead, a dedicated holding fixture with a shutter unit to protect the printhead nozzles against UV-radiation was developed (figure 2 a-c).

The substrate for the process is a membrane floating on a water surface. To enable a precise manufacture of the reinforcing patterns on top, no waves should be formed. Hence, the Langmuir Trough cannot be moved. Instead a 3-dimensional motion system, consisting of 3 linear stages with high accuracies, was applied to move both the UV-lamp and the printhead (table 1).

Table 1 Properties of the 3-dimensional motion system

Direction	Description	Travel length	Velocity [mm/s]	Accuracy [µm]
PD	M414-K012 (Physik Instrumente)	500	100	±5
CD	UTS 50CC (Newport Corporation)	50	20	±1
Vertical	M414-2PD (Physik Instrumente)	200	100	±5

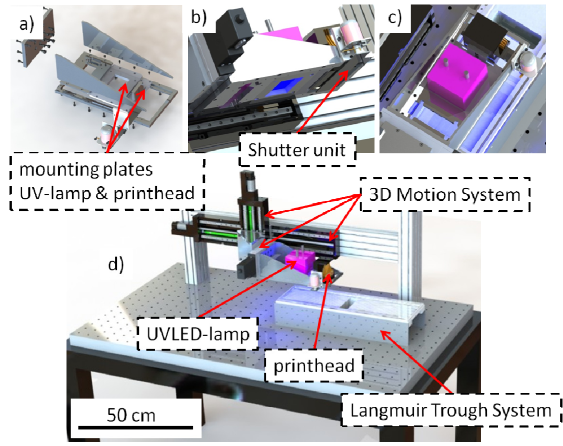

Figure 2 CAD-model of the developed inkjet printing system. a) Exploded view of the holding fixture. b) Side view of the holding fixture with UV-lamp and printhead inserted. c) Top view. d) CAD assembly of the Printing System.

The drop spacing in printing direction is defined by the velocity (v) of the linear stage M414-K012 and the drop ejection frequency (f) of the printhead:

$$v \div f = DS \qquad (1)$$

The drop spacing perpendicular to printing direction is achieved by the offset of the linear stage UTS 50CC. The distance between the floating membrane and the nozzle plate is adjusted by the vertical linear stage M414-2PD.

Preparation of the Pattern

The printed pattern consists of printed lines in form of honeycombs. The primary properties of the line dimensions are a small width and high thickness to achieve an adequate mechanical stability at a low area-covering. Preliminary investigations have shown that the line morphology of "Stacked Coins" [10] features this dimensions. Therefore, it was necessary to print Wet-In-Dry, which means a printing and subsequently curing of single droplets without coalescing of uncured droplets. To achieve that behavior and to decrease the drop space in CD, the digital printing pattern has to be divided and printed over several printing.

Figure 4 schematically shows the preparation of the digital printing images and the Wet-in-Dry printing based on a honeycomb pattern with 127 µm drop spacing. First, a pixel based digital image is separated into 2 images shown as black and red pixels (figure 3 a). Next, the first printing step prints the black image, by moving the printhead in PD (figure 3 b) with a defined velocity and drop ejection frequency calculated by Eq. 1. Through the positioning of the digital printing image referred to CD and PD the drop space of the printout is high enough to prevent coalescing of the uncured droplets. Subsequently, the printout is cured by back driving the disabled printhead and the enabled UV-lamp (figure 3 c). During this period the shutter unit is closed to protect the nozzles against UV-radiation. After the first printing step, the printout has a drop space 254 µm in CD, equal to the nozzle spacing. To decrease the drop space to 127 µm in CD a next printing step of the red pixel printing image will be done. Therefore a 127 µm deposition of the printhead in CD is necessary (figure 3 d). Following, a further curing step is done, similar to the previous one (figure 3 e). This approach is scalable to lower drop spaces and can be calculated by:

$$254\ \mu m \div DS\ [\mu m] = n \qquad (2)$$

where n is the number of printing steps and DS is the desired drop space as well as the deposition of the printhead in CD after each printing step (Eq. 2 is only valid when DS is a divider of 254 µm).

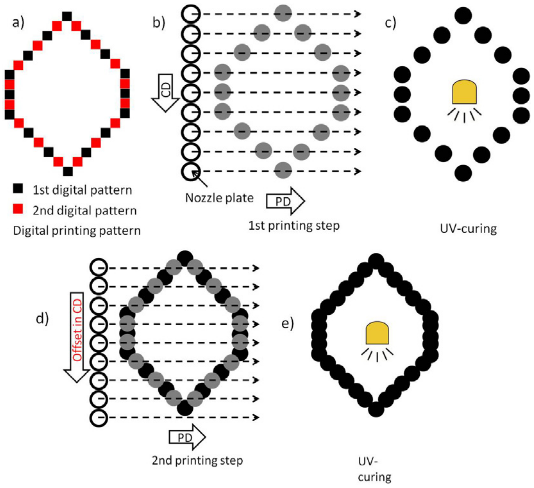

Figure 3 Schema of the used printing process for a 127 µm drop space. a) Digital printing image. b) First printing step. c) UV-curing of the first droplets. d) Second printing step. e) UV-curing of the second droplets.

Experimental Setup

The suspension for the float casting process consists of the following components:

- Silicon dioxide particles with 3-(Methacryloyloxy)propyltrimethoxysilane coating; 1 % by weight of the suspension
- Trimethylolpropane trimethacrylate and Hyperion Pro Wet Black ink; ratio: 1:1; 1: 3 ratio related to the particle weight
- Ethanol, Trichloromethane and Ethylbutyrylacetate; ratio: 50:49.5:0.5 [%]

The Langmuir trough was filled with water. By using a syringe the suspension spreads onto a water surface of 270 cm² between 2 barriers. Subsequently, the barriers were automatically moved against each other to compress the suspension to an area of 202 cm² and to form a hexagonal dense packing of the particles. Following, the suspension is cured over 8 minutes. Finally, the barriers were removed and the free edges of the pre-finished microsieve were fixed using 2 strings.

A honeycomb pattern were printed at a theoretical drop space of 42,3 µm, a drop ejection frequency of 600 Hz and a printing velocity of 25.4 mm/s. Additionally, to enlarge the thickness of the lines, 4 printing layers were applied on top of each other. The curing process took approximately 6 seconds at a vertical distance of 100 mm. The printing distance between the floating membrane and the nozzle plate was 3 mm. The size of the printout was 6.5 cm x 20 cm.

Results and Discussion

The designed manufacturing system was successfully assembled and installed shown in figure 4. Using this machine the developed manufacturing process can be carried out.

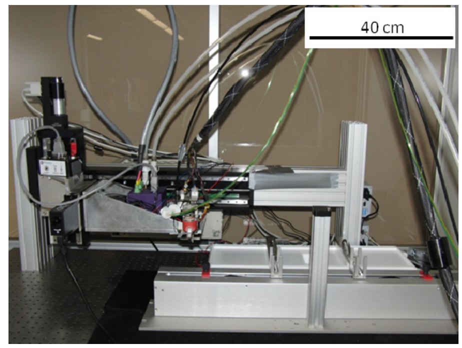

Figure 4 The assembled inkjet printing system

The machine enables a manufacturing of a porous pre finished microsieves and a printing of reinforcing pattern directly on top of this floating membrane at a water surface in one device. The fabrication period was decreased to 40 minutes for an increased area of 130 cm². Furthermore, the lift up of a unprinted compared to imprinted microsieve proves the reinforcing effect of the printed pattern on top of the microsieve. While the blank microsieve is completely destroyed during the lift up (figure 5 a-b), the reinforced microsieve was successfully removed from the water surface (figure 5 c-d).

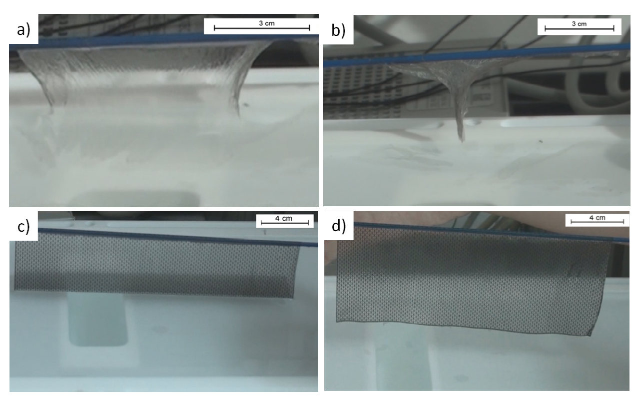

Figure 5 a) Unprinted microsieve during the lifted up from the water surface using a thin metal bar. b) Unprinted microsieve after lifted up. c) A reinforced microsieve during lifted up from the water surface d) A reinforced microsieve after lifted up.

Before and after removing the particles from the microsieve, the printed pattern remained without broken or cracked lines (figure 6 a-b). However, in both pictures inhomogeneous line morphologies are visible. Possible reasons for this issue are:

- a high printing distance between nozzle plate and microsieve which results in imponderable deflections of flying drops
- a movement of the floating microsieve evoked by small waves in the range of micrometers
- repeating accuracy of the linear stages
- airstreams, generated during the movement of the printhead and the UV-lamp

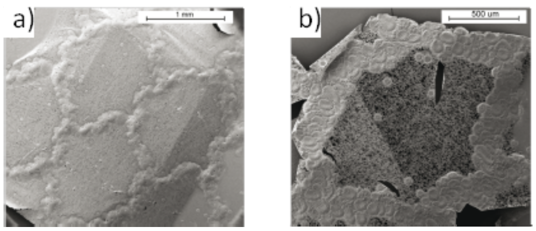

Figure 6 Scanning electron microscope images of stabilized microsieves. a) Honeycomb pattern on a pre-finished microsieve. b) Backside of an etched microsieve with a Honeycomb pattern

Additionally, the removing of the particles from the microsieve causes defects and rifts in the range of micrometers. Possible reasons are the curing duration of the prefinished microsieve, the manually spreading process using a syringe as well as the components and the composition ratio of the suspension.

Conclusion

An manufacturing system was successfully developed, designed and assembled, to optimize the manufacture of stabilized microsieves. A particular feature of the system was to print pattern directly on floating microsieves. Therefore, the critically process steps (usage of a carrier substrate to transfer the pre-finished microsieve to a separate small format inkjet printer; additional etching process of the carrier substrate) of previous laboratory scaled fabrication was avoidable. Furthermore, by the usage of an industrial multi-nozzle printhead, a UVLED-lamp, a Langmuir Trough System and a high precise 3-dimesional motion system consisting of 3 linear stages the fabrication time was distinctly decreased to approximately 40 minutes for an area of 130 cm^2. An unscathed lift off of the imprinted pre-finished microsieve from the water surface is now possible and demonstrates the reinforcing effect of the printed pattern. Beyond, the removing of the particles has no negative effect onto the printed pattern. However, by microscopic examinations of the printed structures inhomogeneous line morphology was ascertained. Therefore, possible reasons are the high printing distance between nozzle plate and microsieve, a deposition of the microsieve during the printing process, airstreams generated by the movement above the microsieve and the repeating accuracy of the linear stages. Furthermore, after the etching of the particles non uniform pore sizes and rifts in micrometer scale are visible. Further investigations and optimizations have to be done to solve these problems.

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Peter Ueberfuhr has received his Diploma degree in Mechanical Engineering in 2011 at Chemnitz University of Technology. Currently, he is a Ph. D. student at the Institute for Print and Media Technology in Chemnitz in the Department of Digital Printing and Imaging Technology. His scientific research is focused on machine design and fabrication processes based on gravure and inkjet printing technology.

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