Title	A perspective on 3D printed membrane: direct/indirect fabrication methods via direct laser writing
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Citation	Lee, J.-Y., An, J., Chua, C. K., Fane, A. G., & Chong, T. H. (2016). A perspective on 3D printed membrane: direct/indirect fabrication methods via direct laser writing. Proceedings of the 2nd International Conference on Progress in Additive Manufacturing (Pro-AM 2016), 182-187.
Date	2016
URL	http://hdl.handle.net/10220/41756
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A PERSPECTIVE ON 3D PRINTED MEMBRANE: DIRECT/INDIRECT FABRICATION METHODS VIA DIRECT LASER WRITING

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Abstract

This conference paper mainly comprises three parts: (1) a brief introduction to the current state of research; (2) a clear description of the additive manufacturing technique and fabrication methods; (3) a brief description of the structure-performance relationship. The idea is based on the notion that membranes with 'controlled architecture' could achieve enhanced performance, and that additive manufacturing techniques, also known as 3D printing, have a great potential in fabricating membranes with controlled architecture.

Keywords: Membrane; Spiral wound module; 3D printing; Additive manufacturing; Rapid prototyping

1. Introduction

The research of 3D printed (3DP) membranes is pioneered by Professor Dr.-Ing. Matthias Wessling and his co-workers at the Chemical Process Engineering (CVT)/Aachener Verfahrenstechnik (AVT), and the DWI - Leibniz Institute for Interactive Materials at the RWTH Aachen University, Germany. To date, the major developments focus on module and device fabrication with typical 3D printers with high resolution (~30 µm). Their work is mainly based on a common liquid-based 3D printing technique, called Digital Light Processing (DLP), which could be used for a variety of applications. In 2014 Wessling *et. al.* proposed a novel approach to directly print via the DLP technique a ladder-shaped polydimethylsiloxane (PDMS) membrane, which is not feasible to produce with traditional machining techniques [1]. PDMS is one of the common polymers used in gas-

Proc. of the 2nd Intl. Conf. on Progress in Additive Manufacturing
Edited by Chee Kai Chua, Wai Yee Yeong, Ming Jen Tan, Erjia Liu and Shu Beng Tor

Published by Research Publishing, Singapore
ISSN: 2424-8967

liquid-contactors due to its high permeability for various gases. In gas-liquid contactors, it is important to note that membrane surface geometry plays an important role in their performance and hence PDMS membranes fabricated by 3DP technique with sheet-like 'triple-periodic minimal surfaces' (TPMS) architectures gave a better performance relative to conventional membrane geometries.

Wessling and his co-workers have also developed a new sacrificial lithography technique to produce a tri-continuous TPMS-PDMS membrane with a complex geometry via a sacrificial resist [2]. Compared to flat-sheet and hollow-fiber membranes, these TPMS-PDMS membranes give a better boundary-layer mass transport due to the improved hydrodynamics. In addition, TPMS-PDMS membranes with different shapes were created to systematically study their structure-performance relationship in terms of heat transfer and pressure drop. In this study non-geometrical influences were prevented and other effects decreasing membrane performance, such as concentration polarization, were identified [3]. Furthermore, based on the 3DP method, a PDMS membrane device with mixers based on a staggered herringbone structure was fabricated via soft lithography to increase mass transport and reduce pressure drop [4]. This herringbone structure was designed as a static mixer to induce secondary flows such as Dean vortices and Taylor flows, which significantly reduce the concentration polarization on the membrane surface in a microfluidic gas-liquid contactor. These studies demonstrate the potential benefits of 3D printed membrane macrostructures (>30 µm). However, to apply the 3D printing approach to print a microporous membrane requires 3D printers with submicron resolution [5, 6]. The interesting research question is, '*Can 3D printing produce prototypes of such idealized membranes*?'

2. Direct Laser Writing

Direct laser writing (DLW) is one of 3D printing techniques that can directly print a three-dimensional membrane with well-defined sub-micron pores. This DLW technique was recently developed by Prof. Dr. Martin Wegener from Karlsruhe Institute of Technology (KIT), Germany for the fabrication of nanostructures such as photonic crystals. A new spin-off company, called Nanoscribe, is currently selling this advanced 3D laser lithography system and photoresists materials. This DLW technique is based on a laser light source for two-photon polymerization (TPP) of photoresist. The system is called *Photonic Professional GT* with the unique possibilities to fabricate microporous membranes with feature sizes down to 500 nm. Typically, there are two types of scanning modes: Piezo mode and Galvo mode. The Piezo scanning mode is a fixed-beam moving-sample (FBMS) method with x-y-z-movement and a writing field up to 300 x 300 x 300 μm^3. On the other hand, the Galvo scanning mode is a moving-beam fixed-sample (MBFS) method with only x-y-movement and for which the writing field depends on the objective. The key difference between the Piezo and Galvo modes is that Piezo mode can achieve arbitrary 3D trajectories with an optimized speed to accuracy ratio while the Galvo mode can print only the object layer-by-layer with a higher speed but lower accuracy. For the fabrication process the overview of the whole process mainly consists of three steps: (a) design structure; (b) choice of materials; and (c) membrane fabrication. Based on this DLW technique, two fabrication methods, (a) direct method and (b) indirect method, can be used to fabricate a membrane with different pore size and pore shape (Figure 1).

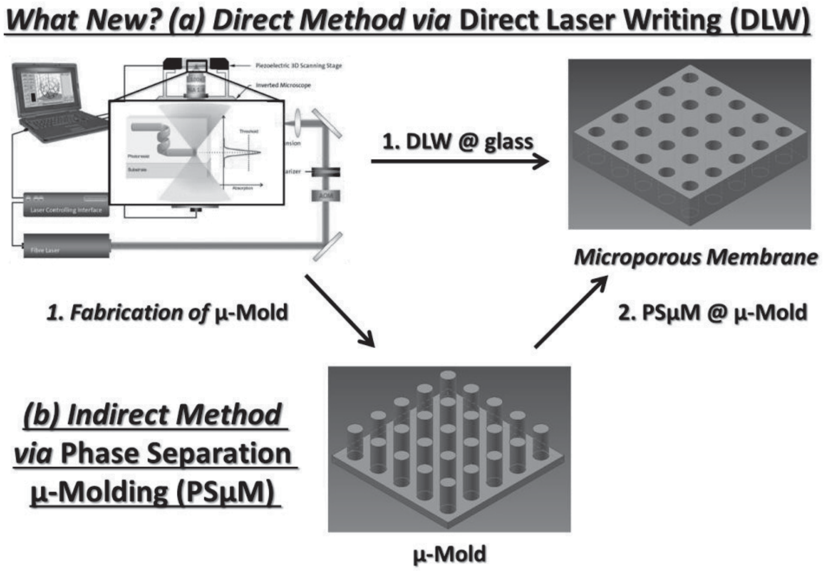

Figure 1. The schematic diagram of (a) direct method via direct laser writing (DLW) and (b) indirect method via phase separation µ-molding (PSµM).

3. Direct and Indirect Fabrication

For the direct method, a microporous membrane with a well-defined sub-micron pore structure is designed using computer-aided design (CAD) software followed by the direct fabrication of these membranes using the DLW technique. For the indirect method, a µ-mold, which consists of a microarray with different size and shape, is fabricated by the DLW technique followed by the phase separation µ-molding (PSµM) to produce these membranes [7, 8]. PSµM is one of the novel microfabrication methods based on phase separation of a polymer solution and a broad range of materials has been structured, including both polymers and inorganic materials. An ideal microporous membranes would have surface isoporosity, be highly porous, possibly with interconnected pores and with tunable surface chemistry [9]. However, the feasibility of fabricating an ideal microporous membrane with different pore size and shape via direct/indirect methods based on the DLW technique still remains untested.

4. Investigation of Structure-Performance Relationship

It is important to understand the structure-performance relationship of microporous membranes because these membranes are not only the basis for microfiltration (MF) and ultrafiltration (UF) separations, but also are integral to other membrane processes where they provide a substrate layer for thin film composites for nanofiltration (NF), reverse osmosis (RO), forward osmosis (FO), and pressure-retarded osmosis (PRO) membranes. It is well-recognized that the overall performance of these membranes is critically dependent on the substrate morphology and property, such as membrane porosity [10]. From a theoretical point of view, the membrane porosity is defined as the volume of pores divided by the volume of the whole membrane. In this study the membrane porosity is determined by the pore size, pore shape and interconnectivity of the membrane; however, controlling these pore characteristics in a well-defined manner is still almost impossible based on the traditional fabrication methods, such as non-solvent-induced phase separation (NIPS) or thermally-induced phase separation (TIPS). In our new approached microporous membranes with well-defined pore structure and morphologies could be fabricated and characterized to understand the structure-performance relationship in terms of permeability and fouling tendency.

For the first step, microporous membranes will be designed by computer-aided design (CAD) software such as Autodesk Inventor and Solidwork. It is important to note that there is an additional option for microporous membranes with either interconnected pores or two different shape/size pores on the same membrane for the direct method via DLW technique (Figure 2).

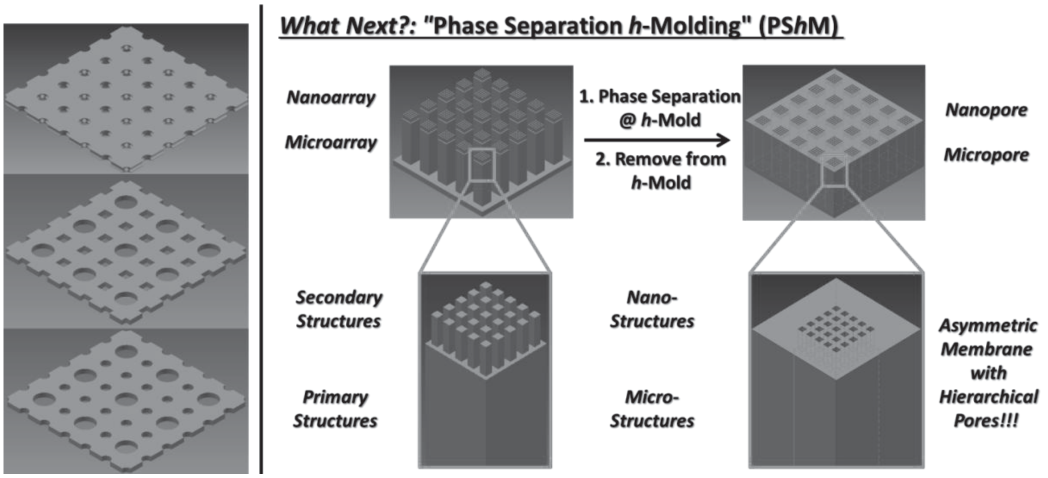

Figure 2. The CAD design of 3DP membranes with either interconnected pores or two different shape/size pores (left) [11] and (right) the schematic diagram of phase separation hierarchical-molding (PS*h*M).

On the other hand, a new concept, called "phase separation hierarchical molding" (PS*h*M), is proposed based on the indirect method of phase separation μ-molding. It is critical to note that a hierarchical-structured mold, which consists of a nanoarray as the secondary structures (nanostructures) and a microarray as the primary structures (microstructures), could be fabricated via DLW technique followed by the phase separation hierarchical-molding (PS*h*M) to obtain an asymmetric membrane with hierarchical pores.

To establish the structure-permeability relationship, the number of pores is fixed while the pore diameter is varied for the same total membrane area. Next, a suitable photoresist is chosen based on the desired optical, chemical, physical, and pre-and-post processing properties. For the last step a reasonable writing mode will be selected based on the objective after which the 3DP microporous membrane will be fabricated. In summary, the three key considerations of the whole process development in DLW techniques are design parameters, materials parameters and process parameters. It is also critical to bear in mind that there are several disadvantages of the DLW technique based on the direct/indirect methods compared to the conventional NIPS and TIPS fabrication techniques, such as (1) a small membrane area (<300 x 300 μm^2); and (2) a relatively time-consuming process to achieve a complex structure that depends on scanning mode.

5. Conclusion

In summary, this conference paper briefly describes the recent research and development of 3DP membranes in the first part followed by the description of the DLW technique and the direct and indirect methods for the fabrication of the 3D printed membrane in the second and third part. In the last part, the importance of structure-performance relationship of 3D printed membranes is also briefly described. If the 3DP microporous membrane with controlled architecture via the direct/indirect fabrication methods using DLW technique can be fabricated successfully, then this will be a significant breakthrough in 3DP membranes in term of resolution from micrometer scale to submicron or even nanometre scale. For the scientific benefits and applicability of the results, the knowledge generated from this fundamental study will help us to better understand the structure-performance relationship of microporous membranes. For the economic benefits and applicability of the results, the impact of this research will be significant for advancement of the membrane industries in Germany, not only for MF and UF membranes but also for other types of membranes, such as NF, RO, FO, and PRO.

Acknowledgements

The Singapore Membrane Technology Centre under the Nanyang Environment and Water Research Institute at the Nanyang Technological University is supported by the Economic Development Board of Singapore. The Singapore Centre for 3D Printing is funded by the Singapore National Research Foundation. J.-Y.Lee would like to thank Professor Matthias Wessling, Dr. Tim Femmer, and Mr. Jonas Loelsberg for their valuable discussion as well as the Green Talents Programme for financial support.

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