3D printing of feed channel spacers for spiral wound membrane modules

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2018

Tan, W. S. (2018). 3D printing of feed channel spacers for spiral wound membrane modules.
Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/75017>

<https://doi.org/10.32657/10356/75017>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**3D PRINTING OF FEED CHANNEL SPACERS FOR
SPIRAL WOUND MEMBRANE MODULES**

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INTERDISCIPLINARY GRADUATE SCHOOL
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A thesis submitted to the Nanyang Technological University in
partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2018

ACKNOWLEDGEMENTS

First and foremost, I would like to express my greatest gratitude and appreciation to my supervisor, Professor Chua Chee Kai, co-supervisor Assistant Professor Chong Tzyy Haur, mentor Professor Anthony Gordon Fane for their generous support, feedback and patient guidance throughout my candidature. I am also grateful to Professor Wang Rong whom joined my Thesis Advisory Committee as my new mentor. Their dedication to research has inspired and motivated me to work harder. I would also like to thank them for providing me the opportunity to pursue this interdisciplinary research in the field of 3D printing and water industry.

Special thanks to Dr. An Jia whom has helped me often by providing comments and suggestions to improve my research work. I would like to thank the staff and students of Singapore Centre for 3D Printing and the School of Mechanical and Aerospace Engineering: Cheung See Lin, Edgar Tan, Kenneth Tan, Clarrisa Choong and Quek Shao Xuan for their help in 3D printing, simulations, mechanical and material testing. All the laboratory technicians, especially Mr Chia Yak Khoong, Mr Soh Beng Choon, Mr Tony Wee, Mr Mack Wong and Mr Wong Hang Kit for their help in the lab. Not forgetting other fellow researchers and friends in SC3DP, including Lee Jia Min, Yap Yee Ling, Ratima Suntornnond, Chua Zhong Yang and Gregory Chua for their companionship and support which makes this PhD journey more fun and interesting.

I would also like to thank all the staff and researchers in Singapore Membrane Technology Centre: in particular, Ms Pee Wenxi for her generosity in sharing her knowledge in DOTM with me, Dr. Lee Jian Yuan for his advice and suggestions in the project, Dr. Stanislaus Raditya Suwarno for his great help in biofouling tests, confocal microscopy and atomic force microscopy measurements, Dr. Sim Lee Nuang and Dr. Lee Jia Shin for their help in optical sensors testing and flow cytometer measurements, Chen Yunfeng, Phua Zhenghui, Yang Qin, Lim Siow Kee, Gu Jun and Zhu Wenyu for

their companionship in CleanTech One.

I would also like to acknowledge Interdisciplinary Graduate School (IGS) and Nanyang Environment and Water Research Institute (NEWRI) for the scholarship opportunity. Also, the Environment and Water Research Programme, administered by Public Utilities Board (PUB) under Singapore National Research Foundation for the research funding.

Last but not least, I thank my family, friends and loved ones for their constant encouragement, support and understanding throughout my PhD journey.

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LIST OF PUBLICATIONS AND PATENTS

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- 1) **Wen See Tan**, Chee Kai Chua, Tzyy Haur Chong, Anthony G. Fane, and An Jia (2017) *Optimisation of sinusoidal spacers for enhancement of mass transfer and pressure drop. (manuscript in preparation)*
- 2) Bing Wu, Yanjun Zhang, Ziming Mao, Wen See Tan, Yong Zen Tan, Jia Wei Chew, Tzyy Haur Chong, Anthony G. Fane. (2017) *Fouling Control of Submerged Flat Sheet Membranes by Vibrating Spacers, Water Research (submitted)*
- 3) Xin Liu, Weiyi Li, Tzyy Haur Chong, Jing Wee Koo, Wen See Tan. (2017) *Mitigating Membrane Fouling Using 3D-Printed Sinusoidal Spacers: Quantitative Analysis Based on 3D Optical Coherence Tomography Imaging, Environmental Science & Technology (submitted)*
- 4) **Wen See Tan**, Stanislaus Raditya Suwarno, Jia An, Chee Kai Chua, Anthony G. Fane, Tzyy Haur Chong. (2017) *Comparison of solid, liquid and powder forms of 3D printing techniques in membrane spacer fabrication, Journal of Membrane Science , 537 (2017) 283-296*
- 5) **Wen See Tan**, Chee Kai Chua, Tzyy Haur Chong, Anthony G. Fane, and An Jia. (2016) *3D printing by selective laser sintering of polypropylene feed channel spacers for spiral wound membrane modules for the water industry. Virtual And Physical Prototyping. Vol. 11, Iss. 3, p151-158*
- 6) Jian Yuan Lee, **Wen See Tan**, Jia An, Chee Kai Chua, Chu Yang Tang, Anthony G. Fane, Tzyy Haur Chong. (2016) *The potential to enhance membrane module design with 3D printing technology, Journal of Membrane Science, 499 (2016) 480-490.*

Conference presentations

- 1) *Jia An, Wen See Tan, Chee Kai Chua, Tzyy Haur Chong, Anthony G. Fane. Design considerations for additive manufacturing of feed channel spacers for spiral wound membrane modules. International Conference on Sustainable Smart Manufacturing (S2M), 20-22 Oct 2016, Lisbon, Portugal*
- 2) **Wen See Tan**, *Jia An, Chee Kai Chua, Anthony G. Fane, Tzyy Haur Chong. 3D Printed Feed Spacers For Spiral Wound Membrane Modules –Enhancement Of Mass Transfer. Paper presented at Rome 2016 Desalination for the Environment: Clean Water and Energy, Rome, Italy, 22 –26 May 2016.*
- 3) **Wen See Tan**, *Chee Kai Chua, Tzyy Haur Chong, Anthony G. Fane and Jia An. (2016, May). Selective Laser Sintering of Polypropylene Feed Spacers for Spiral Wound Membrane Modules. Paper presented at The 2nd International Conference on Progress in Additive Manufacturing (ProAM 2016), Singapore, 16-19 May, 2016.*
- 4) **Wen See Tan.**, *Chee Kai Chua, Anthony G. Fane, Jia An , Tzyy Haur Chong ., “Morphological comparison of 3d printed feed spacers for spiral wound membrane modules”, 1st International Conference on Progress in Additive Manufacturing, Singapore, 26 - 28 May 2014.*

Patents

1) Title: Spacer For A Membrane Module

Inventors: LI Weiyi; TANG Chuyang; WANG Yi-Ning; Anthony Gordon FANE; TAN Wen See; LEE Jian Yuan; AN Jia; CHUA Chee Kai; CHONG Tzyy Haur

PCT Application No: PCT/SG2016/050592

International Filing Date: 6 December 2016

2) Title: Vibration Of Scraper-Like Spacer For Membrane Fouling Control

Inventors: WU Bing; Anthony Gordon FANE; CHONG Tzyy Haur; TAN Wen See

Singapore provisional patent application number 10201705042U

Filing Date: 19 June 2017

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LIST OF SYMBOLS

Letters

Total volume of empty channel (m ³)	V_{tot}
Total volume of the spacer (m ³)	V_{sp}
Hydraulic diameter (m)	d_h
Mesh length (m)	l_m
Filament diameter (m)	d_f
Specific surface of the spacer (m ⁻¹)	S_{vsp}
Surface area of the spacer (m ²)	S_{sp}
Linear velocity (m/s)	u
Width of the channel (m)	b
Height of the channel (m)	h_{ch}
Feed flow rate (m ³ /s)	Q
Diffusivity (m ² /s)	D
Membrane permeability coefficient (L/m ² h.Pa)	L_p
Permeate flux (L/m ² h)	J
Concentration at the membrane wall (kg/m ³)	c_w
Concentration of the bulk feed solution (kg/m ³)	c_b
Mass transfer coefficients (m/s)	k
Channel length (m)	L
Strand eccentricity	e
Shortest semi-axis of the filament cross-section	b
Longest semi-axis of the filament cross-section	a
Effective cross flow velocity (m/s)	u_{eff}

Sherwood number (Sh)

$$Sh = \frac{k_{av} d_h}{D} = \alpha Re_h^\beta Sc^\gamma \left(\frac{d_h}{L}\right)^\delta$$

Reynolds number (Re)

$$Re_h = \frac{u_{eff} d_h \rho}{\mu}$$

Schmidt number (Sc)

$$Sc = \frac{\mu}{\rho D}$$

Fanning friction factor

$$f = \frac{d_h \Delta P_{ch}}{2 \rho u_{eff}^2 L}$$

Power number P_n

$$P_n = \frac{\Delta P}{L} u_{eff} \left(\frac{\rho^2 h_{ch}^4}{\mu^3} \right)$$

Surface coverage rate

$$\frac{dC}{dt} = \frac{\% Area_{10min} - \% Area_{1min}}{10min - 1min}$$

Greeks

Pressure drop across the channel (Pa)

$$\Delta P$$

Voidage

$$\varepsilon$$

Viscosity (Pa.s)

$$\mu$$

Density (kg/m³)

$$\rho$$

Osmotic Pressure (Pa)

$$\Delta \pi$$

Transmembrane pressure (Pa)

$$\Delta P_{TM}$$

ABSTRACT

Research in the field of 3D printing and water industry, in particular, on the fabrication and evaluation of feed spacers produced via 3D printing, rapid prototyping or additive manufacturing (AM) techniques is presented in this thesis. Feed spacer is a mesh-like structure placed between membrane sheets to create channels for fluid flow in a spiral wound membrane module (SWM). It has an important role in the hydrodynamic conditions of a SWM, which serves to facilitate mass transfer in the feed channel by generating vortex and promoting mixing. The mass transfer is critical in reducing the concentration polarisation phenomenon in membrane processes, which is often associated with membrane fouling. However, the challenges of commercial feed spacers include the trade-off between mass transfer and pressure drop along the channel that leads to the rise in energy demand as well as their impact on membrane fouling. Many studies via computational fluid dynamics (CFD) simulations have shown that spacers with complex structures have great potential in enhancing the mass transfer. However, conventional method of spacer manufacturing by extrusion could not realise the complicated designs of spacers. In this work, the 3D printing technology is employed as a tool to fabricate novel feed spacers with structures that maximise the mass transfer while minimise the channel pressure drop.

It is nevertheless important to note that there are limitations in current AM technology. A link between the design and fabrication i.e. printability and surface finish properties of spacers was established. The printability of polypropylene (PP) which is the representative material of spacers was also investigated. The fabricated spacers were evaluated in terms of flux and pressure drop. Direct observation through the membrane (DOTM) technique was also used to study the impact of different 3D printed spacers on the critical flux of particles. Among the 3 broad classes of solid, liquid, powder based 3D printing techniques, the liquid based Polyjet technique was found to

give the most accurate representation of the intended design while the solid based FDM (Fused Deposition Modeling) technique produced spacers that showed the greatest deviation from the specifications. On the other hand, the improvement in mass transfer by the FDM printed spacer was unexpectedly the greatest among the three 3D printed spacers, due to the ‘randomness’ in the strand of spacer. In addition, the surface finish of the spacers was found to have an effect on the critical flux, specifically, the anisotropic surface finish of FDM and semi-anisotropic surface finish of Polyjet. Biofouling potential was discovered to be correlated to the surface roughness of samples. Among which, Polyjet and SLS printed samples have greater bacteria attachment due to their higher microscale roughness. Eventually, three design considerations for developing 3D printed novel spacers were recommended.

A series of existing (i.e., taken from the literatures), modified and innovative spacer structures, compared with commercial feed spacer, were examined to identify the basis form of spacer structure with the greatest potential. Further optimization of the selected structure was conducted to improve the spacer performance. With the primary structure made up of sinusoidal curves and secondary structures consisting cylindrical protrusions along the curve, the novel spacer S12 showed an improvement of 18% at power number, $Pn=10^6$, and 25% at $Pn=10^5$ in mass transfer compared to commercial spacer. With this optimal design, a smart multi-material spacer was developed by designing the primary structure with a rigid material and the secondary structures with flexible materials. The multi-material responsive spacer with Tangoblackplus as the flexible material was able to lower the flux decline due to bentonite fouling by 7.6% as compared to the commercial spacer and 5.2% when compared to the single rigid material spacer. This indicates that a spacer with flexible filaments has a beneficial effect on fouling reduction. The flexible properties of the selected section on the spacer allow dynamic movement under varying flow rate, which creates a “sweeping” effect

that disrupts the boundary layers and prevents foulants from accumulating near spacer filaments and on the membrane surface, thereby mitigating fouling. These favourable findings have contributed as one of the pioneering work in this interdisciplinary field.

CHAPTER 1 INTRODUCTION

This chapter provides the background, problem statement, objectives and scope of the thesis. The background discusses the implementation of spiral wound membrane module in membrane processes particularly in reverse osmosis process. The problem statement describes the roles of feed channel spacers in the membrane module, briefly explains the problems faced and proposes a solution with 3D printing technology. Subsequently, the objectives and scope of the research, followed by the organization and structure are introduced as an overview of the content of this thesis.

1.1 Background

Reverse Osmosis (RO) technology has wide applications in separation, concentration and recovery of valuable components in various industries, particularly the water desalination and reclamation industry. Despite its wide application, RO technology is confronted with challenges associated with high energy demand. The high energy demand arises from osmotic pressure, membrane resistance, concentration polarisation, pressure drop and fouling. In particular, concentration polarisation (CP) arises when solutes rejected by membrane accumulate near the membrane surface causing a higher concentration than the bulk concentration. The magnitude of CP is approximately an exponential function of the ratio of flux to mass transfer i.e. $CP = \exp(J/k)$. In addition, concentration polarisation is often associated with membrane fouling. Therefore, it is important for membrane modules to have good fluid management in order to reduce the effect of concentration polarization and fouling.

RO processes adopt the spiral wound module (SWM) as the standard membrane module configuration. The SWM as seen in Figure 1.1, comprises several flat sheet membrane leafs made by gluing membrane sheets and permeate carrier together at three edges. Feed channel spacers were placed between the membrane leafs to separate the top layers of the membranes. The membrane leafs and feed spacers

were then wound around a central pipe punctured with holes for water collection [1].

Figure 1.1: Assembly of the different components of a spiral wound membrane module.

1.2 Problem statement

In a membrane module i.e. the spiral wound modules used in desalination process, feed channel spacers are sheets of plastic mesh sandwiched between adjacent membranes (Figure 1.1) [2]. These spacers are inserted for two purposes: creating a flow channel between membranes and promoting mixing to enhance the mass transfer, thus reducing the concentration polarization [3]. However the increase in mass transfer is often accompanied by the penalty of pressure drop [4]. Another concern associated with the long term use of spacers is the accumulation of micro-organisms on spacer surfaces, or fouling, which may lead to blockage of the flow paths and hence incurs more operational cost for desalination process. Therefore, the design criteria for spacers are: (1) the spacer should enhance mass transfer at a moderate pressure drop; and (2) the spacer should have anti-fouling property. To meet these two requirements, one popular school of thought is to increase the structural and functional complexity of spacers, because current spacers are extremely simple in both material and design (i.e. a polypropylene net).

There are several papers [5-11] on computational fluid dynamic (CFD) simulations of different spacer geometries to optimise flux and mass transfer. However, due to difficulties in fabricating complicated geometries of the spacer, these simulations of the direct impact of different complex spacer geometries on flux, mass transfer and fouling cannot be validated. Previous experimental efforts [2, 4, 12-14] mainly involved commercial feed spacers made via common extrusion method into diamond or ladder-shaped mesh with very few works experimented on complex spacer geometries, for instance, the triple layered spacer made by hand [15] which had an 27% improvement flux at the expense of a 25% higher pressure drop as compared to the two-layered spacer, multi layered spacer with twisted filaments made by selective laser sintering (SLS) which showed a 30% enhancement in Sherwood number at same power consumption when compared to the optimal non-woven spacer [16], staggered herringbone and helical spacers made by fused deposition modelling (FDM) which had also shown improvement in mass transfer when compared to ladder spacers [17].

Being a cause of fouling problems, biofouling studies on spacers have been conducted. Spacers were sputter coated with silver [18-20], copper [19-21] or gold [20] as antifouling agents to inhibit the growth of biofilms. Nonetheless, the results were not favorable due to the leaching of the coated compounds from the spacer [20], indicating the instability of the materials. Despite having limited experimental works to validate the effect of spacer geometries on fouling, with the introduction of additive manufacturing (AM) technologies, it can be optimistic that existing difficulties in fabricating novel spacer design via the common extrusion method can be overcome and incorporating antifouling materials within the manufacturing process may also be made possible.

In summary, the problem of this study is that optimization of feed spacers is necessary to reduce the cost and energy demand of the RO process, but the spacer

designs are restricted by geometrical constraints. To resolve this, AM technology is a good tool to fabricate the feed spacer with greater design freedom such that novel spacers with complex geometries that maximise mass transfer and minimise feed channel pressure drop and fouling can also be manufactured. It is nevertheless important to note that there are limitations in current AM technology. The minimum resolution of current 3D printers is limited to the range of hundreds of micrometres. Other features such as tolerance, reproducibility and surface finish of 3D printing systems are also of paramount importance for manufacturing feed spacers. Therefore, a link between the design and fabrication i.e. printability and surface finish properties of spacers has to be established. With the establishment of this link, it is then possible to look into the development and optimisation of novel spacers for enhancement of mass transfer at reduced pressure drop.

1.3 Objectives and scope

The objectives of this thesis are identified as:

- To analyse the current state-of-art of feed spacers and 3D printing, identify the problems and the research gap between membrane module design and 3D printing technology and propose potential solution to bridge the gap.
- To establish a link between design, fabrication and surface finish properties of spacers produced via 3D printing technology.
- To develop a novel spacer for SWM via 3D printing that maximises mass transfer while minimising pressure drop and membrane fouling, to reduce the energy demand of an RO process.

The scope of research to work on with respect to the objectives includes:

1. Providing an overview of the developments at the interface between 3D printing and membrane technology, focusing on the existing literature on the design of

membrane module components including feed spacers and membranes.

2. Systematically investigating the different 3D printing techniques that resulted in differences between the designed and actual spacer geometry, surfaces finish properties and their effects on spacer performance in terms of mass transfer, pressure drop, critical flux and biofouling.
3. Designing and optimization of novel spacer structure using Taguchi's method to enhance mass transfer and minimise pressure drop.
4. Development of a multi-material responsive spacer to reduce membrane fouling. Performance evaluation will be characterised by flux reduction over time under bentonite fouling.

1.4 Organisation

The following chapters of this thesis are organised according to the structure as illustrated in Figure 1.2 below.

Figure 1.2: Organisation and structure of thesis

CHAPTER 2   LITERATURE REVIEW: MEMBRANE MODULES, FEED CHANNEL SPACERS AND 3D PRINTING

This chapter gives an elaborated description of the spiral wound membrane module, the challenges faced in membrane processes, the feed channel spacers and 3D printing technology. The state-of-the-art in feed channel spacers and also 3D printed membrane module components including 3D printed spacers and 3D printed membranes are also presented. In addition, the role of 3D printing in membrane research is critically reviewed in this chapter, highlighting the potential and gap of 3D printing technology in fabricating future membrane modules.

2.1 Spiral wound membrane module (SWM)

The SWM configuration is largely employed by industrial applications due to its large membrane area to volume packing ratio. The SWM, as shown in Figure 1.1, comprises several flat sheet membrane glued at three sides to form membrane leafs with permeate spacers between the membrane sheets. The remaining opening side of the membrane leafs is connected to a central permeate collection tube. Feed spacers are inserted between two consecutive membrane leafs. The entire assembly is wound tightly around the central permeate collection tube and housed in an outer casing. The SWM geometry can be characterised by the number of membrane leafs, the leaf length, and leaf width, the feed channel height and permeate channel height which are defined by the height of the feed spacer and permeate spacer respectively.

During normal operation, pressurised feed water flows into the narrow channels of SWM filled with feed spacers along the axial direction parallel to the module. Solvent passes through the membrane, directed by permeate spacers and flows spirally in the radial direction to the central tube punctured with holes for collection as permeate. A more detailed flow path is illustrated in Figure 2.1. Feed solution flows along x direction, enters at $x=0$ and exits at $x=L$ across the entire length of the leaf

whereas permeate flows along y direction inside the membrane leaf starting from as far as $y=0$ and exits at $y=W$ to be collected in the central tube. Consequently, pressure loss in the axial direction is across the entire length, L of the membrane leaf due to the presence of feed spacer and pressure loss in the radial direction is across the entire width, W of the membrane leaf due to the presence of permeate spacer [22].

Figure 2.1: Detailed flow path across a single flat membrane leaf of the SWM (adapted from [22])

SWM elements are available in different sizes from 4, 6, 8 to 16 inches in diameter and 40, 60 inches in length. Typical industrial SWM elements have 8 in. diameter and 40 in. length. Usually, a number of these modules are connected in series and housed in a pressure vessel when in operation. The performance of the SWM can be affected by operating conditions, cleaning ability, geometry of the SWM and geometry of the feed spacers [22, 23]. Field et al. reported that the winding process during the SWM construction can also adversely affect the module performance [24]. In particular, SWM faces major challenges in:

- 1) Concentration polarisation and mass transfer

Concentration polarisation refers to the concentration of the solute at the membrane surface being higher than the concentration of the bulk feed solution. This is due to the

solutes rejected by the membrane accumulating at the membrane surface. The concentration build-up generates a diffusive flow of solute back to the bulk feed solution. Eventually, a steady-state condition will be reached (see Figure 2.2) in which the convective flow of the solute to the membrane $J.C$ will be equal to the sum of the solute that permeates through the membrane $J.C_p$ plus the solute that diffused back into the bulk feed $D.(dc/dx)$ [1]. The presence of concentration polarisation reduces the effective driving force across the RO membrane due to higher osmotic pressure at the membrane surface, and could possibly cause fouling. The effect of concentration polarisation can be reduced by enhancing mixing and increasing effective cross-flow velocity through the use of a feed spacer [25].

Figure 2.2: Illustration of concentration polarization across the RO membrane (adapted from [1])

2) High pressure drop

The feed spacers in SWM facilitate mass transfer and mixing of the feed flow. However, the trade-off is the high pressure drop along the channel due to greater resistances to fluid flow by the spacer. The relationship between pressure drop and spacer/channel geometry is addressed in Section 3.1.1.4(iii).

3) Biofouling

Biofouling occurs when unwanted microorganisms and algae grow on the feed spacer or membrane surfaces. The interaction between the spacer and membrane could lead to membrane fouling due to the ‘shadow effect’ of the spacer that can lead to accumulation of foulant on the membrane surface or the spacer itself can induce fouling problem [26].

4) Membrane damages

During the manufacturing process of SWM, the compression and winding of the membrane sheets causes the membrane to be susceptible to damages when pressing against the feed spacers. Feed spacers require a certain degree of stiffness to be able to maintain the separation between membrane leafs, however, a spacer that is too stiff will damage the membrane easily. This will affect the rejection properties of the membranes. As such, the spacer materials need to be softer and more flexible [27].

5) Smaller than expected channel height

Compression and tightening of the SWM causes the nesting of the adjacent feed spacer layers. As the feed spacers define the channel height by separating membrane leafs apart, the nesting of the feed spacer layers due to the tightening and compression leads to a decrease in the apparent feed channel height in the SWM, hence affecting the flow conditions within the SWM [27].

In general, feed channel spacers contribute to the above problems in a SWM and are one of the major concerns that should not be neglected in order to achieve good performance in a SWM. Section 2.2 below provides further information on feed channel spacers.

2.2 Feed channel spacers

Feed spacers are net-like structures usually made of low density polypropylene

filaments. Other types of plastics and metals that are chemically inert and thermally stable such as polyester, polysulfone, polyester, nylon, teflon, fiber glass, stainless steel, aluminum or brass can also be considered as spacer materials [28].

Commercial feed spacer consists of numerous repeating units of dual layer filaments constituting a net-like structure. In each unit cell, the first layer of filaments (bottom filaments) is placed parallel to each other at regular intervals specifically known as the mesh length, l_m . The second layer of filaments (top filaments) is welded at an angle known as the hydrodynamic angle, θ on top of the first layer. In addition, the angle that defines the orientation of the mesh with respect to the flow is also another parameter for considerations in experiments. Typical commercial diamond spacers have spacer thickness in the range of 28 mils to 34 mils (0.7mm to 0.9mm) and hydrodynamic angle at 90° . Commercial spacers are manufactured through extrusion of polypropylene filaments. The diameters of the spacer filaments are not uniform throughout and follow a characteristic shape portrayed in Figure 2.3. This undulating cross section may be due to an inherent error of the extrusion process. In this work, the spacer filaments were assumed to follow a circular cross section.

Figure 2.3: Image of a commercial spacer and its unit cell.

2.2.1 Characteristics of a spacer

Figure 2.4 illustrates a CAD model of the commercial net typed feed spacer. Following Da Costa's works [4], the geometric characteristics of the feed spacer used in this work can be represented mathematically based on a single unit cell. Typically, one unit cell of the spacer can be characterised by the design parameters, filament diameter d_f , hydrodynamic angle θ and mesh length l_m as described in the above section. Other characterisation parameters of a general net typed spacer such as voidage ε , hydrodynamic diameter d_h , volume V_{sp} and surface area S_{sp} of spacer can be derived from these design parameters.

Figure 2.4: Detailed view of one unit cell of the commercial spacer CAD model.

The voidage ε of the spacers in the feed channel can be defined by

$$\varepsilon = \frac{V_{tot} - V_{sp}}{V_{tot}} \quad (2-1)$$

Where the total volume of empty channel V_{tot} and total volume of the spacer V_{sp} are given by

$$V_{tot} = l_{m1} l_{m2} h_{sp} \sin \theta \quad (2-2)$$

$$V_{sp} = \frac{\pi}{4} (d_{f1}^2 l_{m2} + d_{f2}^2 l_{m1}) \quad (2-3)$$

The hydraulic diameter d_h of a spacer-filled channel was calculated based on the simplified equation derived by Schock and Miquel [4, 29],

$$d_h = \frac{4A}{P} = \frac{4(V_{tot} - V_{sp})}{S_{slit} + S_{sp}} = \frac{4\varepsilon}{\left(\frac{2}{h_{sp}} + (1 - \varepsilon)S_{vsp}\right)} \quad (2-4)$$

Where $S_{vsp} = \frac{S_{sp}}{V_{sp}}$, the specific surface of the spacer. The surface area of the spacer S_{sp}

is defined as

$$S_{sp} = \frac{1}{2} \left(2\pi d_{f1} l_{m2} + 2\pi d_{f2} l_{m1} \right) \quad (2-5)$$

Table 2.1 summarises the problems caused by feed spacers, the possible solutions to these problems, the desirable characteristics of a good spacer and the factors to consider in an experiment in order to identify the optimal spacer design.

Table 2.1: Summary of the problems caused by feed channel spacers, the possible solutions, targeted characteristics of a good spacer and the factors to consider in an experiment

	Problems of feed channel spacers in SWM	Possible solutions	Targeted characteristics of spacers	Factor(s) to consider	Test parameter
1	Low mass transfer and high pressure drop	Optimise spacer configuration	Able to enhance mass transport thus reducing concentration polarisation at membrane surface Able to reduce spacer resistance such that energy cost for membrane processes is reduced	Mass transport, pressure drop	Sherwood number, power number
2	Biofouling	Optimise spacer configuration, incorporate antifouling materials	Able to enhance shear stress or have antifouling properties	Formation of vortices to increase shear stress, surface finish, antifouling effect	Shear rate (factored in mass transport), flux, surface roughness, bacteria attachment tendency
3	Membrane damage during winding process	Explore softer materials	Have good compressive strength and not puncture membrane surface	Spacer stiffness	Young's modulus
4	Smaller than expected channel height after winding process	Optimise spacer configuration, explore other materials	Able to have the optimum support point density	Effective channel height	Apparent channel thickness after module fabrication

2.2.2 Prior works on conventional net-typed spacers

Optimising mass transfer in the SWM is critical in reducing the concentration polarization level in the RO process. However, there is a trade-off between mass transfer and pressure loss due to the form drag and viscous drag between fluid and spacers. Moreover, the spacer may provide localised dead spots with poor mass transfer that initiate fouling. Therefore, a better spacer design should maximise the mass transfer and minimise the pressure loss as well as fouling. Several research groups have been working to optimise the spacers. In general, the research works can be categorised into two main areas: (a) focused on improving the conventional net type spacer design by investigating the effect of spacer orientation and geometry (i.e. filament diameter, mesh length, spacer thickness) on mass transfer and spacer performance and coating antifouling agents to mitigate fouling; (b) focused on novel designs of spacers that can surpass the performance of conventional net type spacers. This section will review research area (a) while section 2.2.3 will review research area (b).

2.2.2.1 Pressure drop and mass transfer studies

As feed spacers greatly influence the hydrodynamic conditions in membrane modules, researchers have been studying the different characteristics of feed spacers in affecting mass transfer and pressure drop along the channel. Research on the influence of feed spacers on heat, mass transfer and pressure drop began as early as the 1960s. Glatzel and Tomaz reported that spacer orientation affected the heat transfer and pressure drop across spacer-filled channels [30]. Further analysis by Watson and Thomas discovered the presence of detached cylinders in the channel enhanced mass transfer by 240%. With that, they went on to evaluate different filament spacing of the cylinder rods and concluded that the optimum filament spacing was around 8-10 filament diameters [31]. In 1987, Schock and Miquels' work formed the basis of many

experimental studies when they proved that a flat channel test cell could be used to approximate and simulate hydrodynamic conditions in a SWM [29]. Schock et al. also defined important characteristics equations of spacers like porosity, hydraulic diameter and specific surface of spacer.

In 1991, Da Costa et al. introduced another important characteristic of spacer, hydrodynamic angle, to express the change in flow direction [12]. Grober mass transport equation that correlated with laminar flow was developed. However, Grober equation never took into account the effect of spacer orientation. Different spacer orientation and hydrodynamic angle were examined to see the effect on mass transfer, flux and pressure drop in UF conditions. In 1993, Da Costa et al. modified the Grober equation to include a correction factor for spacer geometry and established a mass transfer prediction model with less than 10% deviation [32]. Pertaining to the commercial net typed spacers, a semi-empirical model for pressure drop along spacer-filled channels was developed [4]. The pressure drop along channels was modelled to combine the effect of viscous drag force on the feed spacer and the channel walls, the kinetic losses attributed to changes in flow directions and the form drag on the spacer.

2.2.2.2 Fouling studies

Spacer characteristics under fouling conditions were first investigated with ultrafiltration of whey protein solutions [13]. It was discovered that spacer configuration could not eliminate fouling but only reduced fouling rate by decreasing concentration polarisation due to eddies formation that increased local shear rates and local velocities.

Majority of the researchers were interested in non-invasive fouling characterization methods to study the effect of spacers on membrane fouling. A direct microscopic observation technique known as “direct observation through the membrane” (DOTM), developed by Fane’ s team [33], was used by various research

groups [34-37] to study and visualise the interaction of the foulant particles on the membrane surfaces with and without a spacer. Neal et al. investigated the effect of spacer filament orientation in affecting the critical flux and particle deposition on membrane surfaces using DOTM and reported that the deposition pattern was closely tied to the spacer geometry [37].

Optical coherence tomography (OCT) was also a tool rising in popularity to characterise flow patterns and study biofilm formation in flow channels. Gao et al. applied Doppler OCT to characterise the fluid flow dynamics in spacer filled channels with varied spacer orientations, allowing visualization of the development of eddies and spatial variation of shear flow [38]. Following which, Gao et al. was also the first to use OCT to visualise two dimensional cross-section of the biofilm formation in a spacer-filled channels in 2014 [39]. In 2016, West et al. exploited the advantages of OCT in acquiring three dimensional datasets and managed to achieve 3D images of the biofilm formation in channels with small-meshed and wide-meshed spacers using OCT [40]. Subsequently, Liu et al. also used 3D OCT imaging to study the effect of spacer orientation on the membrane fouling by in situ visualisation of the cake layer formation in a spacer unit cell [41].

Besides studying the effect of spacer configuration on fouling, there were also a few research groups that looked into coating the conventional net-typed spacers with antifouling agents to mitigate biofouling. In 2009, Yang et al. applied nanosilver particles on membrane and spacers through surface modifications and discovered that silver-coated spacer had a great impact on reduction of microbial growth [18]. Shelby and co-inventors came up with a biocidal spacer for an RO filter that was sputter-coated with copper which led to lower biofoulants deposited on the membrane surface as compared to a conventional RO filter [42]. Hausman et al. grafted copper ions onto PP spacer and reported lower microbial cell attachment as compared to the virgin PP

material and a 25% lower flux decline during filtration [21, 43] In his later works, Hausman tested on silver-coated spacers and found that silver leaching caused an increase in colloidal fouling of dead cells when compared to copper-coated spacers [19]. In 2012, Araujo et al. studied feed spacers and membranes coated with functionalised polymers like polydopamine and polydopamine-g-PEG, feed spacers with copper, silver or gold coatings and a commercial biostatic feed spacer and stated that spacer and membrane modifications were not effective for biofouling control in long term and also reported leaching problems from the modified spacers [20, 44, 45]. In 2015, Wibisono et al. coated the spacer with hydrogel plasma mediated UV-polymerization and showed improvement in the antifouling properties of the spacers in bacteria attachment test [46].

2.2.2.3 Computational fluid dynamic (CFD) studies

Computer techniques that enable small scale resolution analysis of fluid flow and mass transfer phenomena increased in popularity in 2000s owing to the reduction in experimental time, costs and risks involved in running experiments. One of the commonly used numerical techniques to simulate flow is Computation Fluid Dynamics (CFD). Cao et al. [5] used CFD to simulate two dimensional flow across flow channels where spacers filaments were in different arrangement (see Figure 2.5, being cavity arrangement (spacer filaments touching same channel wall), submerged arrangement (spacer filaments suspended in channel) and zigzag arrangement (spacer filaments touching opposite channel wall). Eddies formations were observed in front and behind filaments. High shear regions were also found to propagate for a short distance downstream of filaments. Decreasing the distance between filaments to achieve an overlapping of the shear regions would enhance flux greatly but there would be a trade-off associated with pressure drop.

Figure 2.5: CFD simulation of different spacer filament arrangement (adapted from [5])

Karode and Kumar [47] conducted the first three dimensional CFD steady state simulations on the spacers used in Da Costa's work [2, 12] and concluded that their simulations and Da Costa's pressure drop model overestimated the experimental pressure drop values. The ratio of filament diameter to the inter-filament distance, the filament diameter and the angle between the spacer filaments were determined to be the main factors affecting the design of an effective spacer. The 3D CFD simulation was limited by the low spatial resolution and the exclusion of mass transfer in the study.

Schwinge et al. [48] examined the same spacer filament arrangement as Cao et al. [5] and found that the suspended filament arrangement showed the highest wall shear stress and thus highest pressure drop among the three spacer filament arrangement. Pressure losses were found to increase when Reynolds number and filament diameter increased and mesh length decreased. In the study of mass transfer enhancement by CFD [49], the zigzag arrangement of spacer filaments demonstrated

the highest mass-transfer enhancement to pressure loss ratio for any filament diameter. The Reynolds number at which flow transient to super critical for the three filament arrangement was also studied under unsteady flow condition [50].

CFD studies attempting to model flow and concentration polarisation in permeate and feed channels were first conducted by Wiley and Fletcher who emphasised the necessity of very fine mesh near the membrane wall to effectively simulate concentration polarisation effects [51, 52]. Following which were CFD studies to optimise design of spacers. Li et al. used CFD to design and optimise geometrical parameters of the spacers to improve mass transfer and minimise energy consumption [10, 53]. Saeed et al. studied the effect of filament spacing on the shear stress, mass transfer coefficient and the fouling propensity on the top and bottom surfaces of the membrane walls [54, 55]. Amokrane et al. investigated the impact of different cross sections of the spacer filament in elliptical, oval shapes, including tilting the spacers and found reduction in pressure drop when tilting the oval spacers at 20 degrees as compared to the conventional spacers [56].

In this section 2.2.2, prior works on conventional net typed spacers were reported. A short summary of the effect of various parameters of net-typed spacers on pressure drop and mass transfer investigated in this section is listed in Table 2.2.

Table 2.2: Microscopic analysis: effects of spacer parameters on pressure drop and mass transfer

Net typed Spacer Parameters	Effects on pressure drop	Effects on mass transfer (proportional to flux)	Ref.
Filament diameter d_f	Larger d_f increases the viscous drag on spacer surfaces and thus increase pressure drop despite the larger channel height.	Larger d_f will generate larger circulating regions thus a higher flux.	[13, 15]
Mesh length l_m	Shorter l_m increases the number of obstacles in the flow direction leading to higher pressure drop	Decreasing l_m will increase cross flow velocity thus flux will increase first to an optimum and start to decrease after that due to increased fraction of membrane area being blocked.	[4, 15]
Voidage ε	Lower ε at constant flow rate increases velocity in channel, thus pressure drop increases.	Lower ε increases velocity at membrane surface, lower concentration polarisation, thus mass transfer increases to a limit and drops due to increased fraction of membrane area being blocked.	[4]
Hydrodynamic angle θ	Increasing θ causes greater pressure drop as more energy is lost from greater changes in flow direction and greater form drag	Mass transfer is maximum when $\theta = 90^\circ$	[2, 13, 15]
Orientation of spacer filaments	Submerged arrangement has the highest pressure drop At low flow rates, pressure drop for zigzag arrangement approximate pressure drop for cavity arrangement At flow rates > 0.25 L/min, Pressure drop for zigzag arrangement greater than pressure drop for cavity arrangement	When transverse filament is facing membrane, the mass transfer is enhanced by formation of eddies in front of and behind each transverse filaments When axial filament is facing membrane, the mass transfer is enhanced by the increased velocity of flow.	[15]

2.2.3 Prior works on novel spacers

Research in area (b) on novel spacer designs began as early as 1980s [28, 57] but was restricted to simple modifications of the spacer or mainly through CFD simulations. This topic became popular only in 2000s with the onset of CFD simulations and 3D printing technologies to simulate and produce spacers with complicated geometries [14-17, 34, 58-66].

Liu et al. proposed a saw-tooth spacer design made by carving sequential right angled triangular geometries on a Plexiglas plate and was able to generate higher turbulent kinetic energy and higher shear rate to reduce membrane fouling [67]. Koutsou et al. came up with spacers with spherical nodes to create contact points to reduce dead zones instead of the usual contact lines in conventional spacers [68].

CFD simulated novel spacers with irregular cross sections have limited actual spacer prototypes probably due to the difficulties in making the complex spacers through conventional methods. In fact, the geometry of spacers is limited by their conventional manufacturing methods, such as molding or heat extrusion, resulting in difficulties in innovative modification of the geometry for further improvement in the performance. There is a need for a feasible technology to manufacture these innovative spacers for experimental testing and validation. 3D printing, also known as additive manufacturing or rapid prototyping, is a family of technologies that fabricate freeform objects layer by layer using a variety of materials, such as polymers [69], metals [70], composites [71] and even smart materials [72, 73]. This will be covered in greater details in section 2.3.

Recently, 3D printing has begun to emerge as a potential technology for researchers to freely fabricate novel spacers with complex geometries [74]. In 2016, Siddiqui et al. proposed to develop, characterise feed spacers by numerical modeling on the relationship between pressure drop and linear flow velocity, fabricating using

3D printing and testing them in membrane fouling simulators [75]. They tested on net typed spacers with different mesh length and hydrodynamic angles. In 2017, Haaksman from the same group introduced the use of computed tomography (CT) scans to capture accurate geometry of the spacers which may affect the flow characteristics in the channel. They also came up with a novel net-typed spacer with alternating strand thicknesses that reduces pressure drop [76].

Table 2.3 summarises prior literature and work on novel spacer designs and their fabrication methods, including comments by the authors on the fabricated spacer (if any).

Table 2.3: Summary of prior works on novel spacer design

Author	Novel spacer Geometry	Method of fabrication	Available prototype	Reason provided for selection of particular 3D method	Comment provided on the printability	Comment provided on the finishing quality	Comment provided on the material	Ref.
Sawada et al.	Corrugating spacers with protrusions	Vacuum forming of a synthetic resin sheet	Not stated					[57]
Schwinge et al.	Zigzag-shaped spacer	N.A	Yes					[14]
Geraldes et al.	Ladder-type structure	N.A	Yes					[77, 78]
Schwinge et al.	Triple layer spacer	Handmade and glued on grid paper	Yes					[15]
Hester et al.	Tortuous flow channel	Conventional extrusion or molding	Not stated					[63]
Ahmad et al.	Spacer filament with triangular, circular, square cross sections	N.A	CFD only					[79]
Li et al.	Multilayer spacers including spacers with helical bar winding around the cylindrical filament and twisted taped spacers	3D printing, SLS (powder-based sintering)	Yes	N.A	N.A	N.A	N.A	[16, 80]

Dendukuri et al.	Spacer filament with circular, concave, convex cross sections	N.A	CFD only						[7]
Balster et al.	Multilayer spacers including twisted taped spacers	3D printing. SLS (powder-based sintering)	Yes	N.A	N.A	N.A	N.A	N.A	[58]
Ranade et al., Karode et al.	Spacer filament with triangular, square, circular, concave, convex, hourglass cross sections	N.A	CFD only						[64, 81]
Ahmad et al.	Spacer filament with triangular, rectangular, circular cross sections	N.A	CFD only						[8]
Shrivastava et al.	Staggered herringbone spacer	3D printing. FDM (solid-based extrusion)	Yes	N.A	N.A	N.A	N.A	N.A	[17]
Farrell et al.	Spacer with dynamic element	N.A	CFD only						[61]
Gabriel et al.	Flat sheet spacer with upper and lower projections	Embossing or bonding the projections onto the surfaces of the sheet material.	Not stated						[62]
Larsen et al.	Spacer with porous surface and perforations	Conventional extrusion	Yes						[82]

Liu et al.	Static mixer	3D printing, SLA (liquid-based laser curing)	Yes	N.A	N.A	N.A	N.A	[65]
Dontula et al.	Undulating or zigzag path.	Pressing a sheet of material in a die	Not stated					[60]
Fritzmann et al.	Helical spacer	3D printing. Polyjet (liquid-based material jetting)	Yes	Able to produce spacers with complex geometries with a resolution of up to 16 μm .	Unable to produce channels with smaller dimensions. Will cause blockages in the gaps between spacers.	N.A	N.A	[83, 84]
Xie et al.	Plate type spacer with sinusoidal channels	Milling sinusoidal or straight channels into brass or plastic blocks.	Yes					[66]
Koutsou et al.	Spacer with spherical nodes at intersection.	Molding	Yes					[68]
Li et al.	Hairy spacer with dynamic threads	Threads were glued onto a strip to form a fiber array.	Conceptual design. No functional spacer was made.					[85]

Liu et al.	Saw-tooth spacer with right-angle triangular filaments	Right-angle triangular patterns were carved on a plate.	Yes					[67]
Siddiqui et al.	Spacers with similar undulating cross sections as commercial spacers but with modified angles and mesh size	3D printing. Polyjet (liquid-based material jetting)	Yes	Author gave a brief comparison on FDM, SLA and Polyjet spacer fabrication. Polyjet was selected as the most suitable and feasible 3D printing method for spacer fabrication.	FDM spacer strands were thicker and brittle. Polyjet has a higher resolution at lower cost compared to other current 3D printing methods.	Polyjet printed spacer had a smoother surface finish compared to the FDM spacer.	SLA spacers did not have good mechanical strength and material rigidity in water over time.	[75]
Haaksman et al.	Alternating strand design	LANXESS-ASD LANXESS and Conwed Plastics joint project	Yes					[76]

2.3 3D printing technology

3D printing is a layer by layer process to fabricate three dimensional freeform objects. Historically, 3D printing was also known as rapid prototyping, solid free-form fabrication, layered manufacturing and many others user-defined names [86]. In 2012, a common name for all these various technologies was officially finalised at “Additive Manufacturing (AM)” and defined in ASTM F2792-12a: Standard Terminology for Additive Manufacturing Technologies. However the name “3D printing” is still commonly used today, as favoured by the media and the public, but it often refers to low-end or low-cost printers.

2.3.1 Principle of 3D printing

All 3D printing technologies adopt a similar process chain, involving mainly three steps as illustrated in Figure 2.6. Firstly, a computer aided design (CAD) software eg. Solidworks, Rhino, AutoCAD is used to draw a 3D CAD model with actual dimensions. The CAD file is then converted into the .STL (stereolithography) format, repaired and verified to be error-free before transferring into the computer of the 3D printing machines to be sliced into cross-sections. Secondly, the user has to prepare the building parameters such as building orientation, creating support structures, physical and technological parameters before printing. Thirdly, the printed part is removed from the system and user will have to remove support material if any from the completed part. Secondary processing such as polishing and sanding can also be used to improve surface finish of the part.

In recent years, owing to the popularity of 3D printing, a number of researchers have associated two dimensional printing processes (e.g. dispensing, extruding or inkjet) or other layer-by-layer processes to 3D printing, but not strictly adhering to the typical AM process chain, in which 3D modeling or slicing of the model into layers is essential. From this point of view, layer-by-layer assembly

technology, rather than 3D printing, may be the correct term [86].

Figure 2.6: 3D printing process chain (adapted from[86])

2.3.2 3D printing processes

3D printing is not a single or universal technology. There are over 50 different AM technologies for processing different materials. According to ASTM F2792-12a, these AM technologies are classified into seven process categories: binder jetting, direct energy deposition, material extrusion, material jetting, powder bed fusion, sheet lamination, and vat photopolymerization [86]. Another simple method to group these technologies is based on the form of feed material, such as solid-based printers, liquid-based printers, and powder-based printers as shown in Figure 2.7.

Fused Deposition Modeling (FDM), a solid-based method has become one of the most popular 3D printing methods since 2009 when the patent for FDM expired [87]. It relies on heating the tip of a non-brittle filament to form a semi-liquid and then laying down the semi-liquid filament for bonding and cooling (Figure 2.7a). Stereolithography Apparatus (SLA), Digital Light Processing (DLP), Continuous Liquid Interface Production (CLIP) and Two Photon Polymerization (2PP) processes rely on UV lamp or UV laser (usually less than 1 W) to cure a liquid photopolymer in a vat into a solid. Solidification of a part is achieved layer by layer whereby the next layer is always bound to the previous layer upon slightly over curing. Similarly, the Polyjet technology also relies on the principle of UV curing, but the liquid

photopolymer is deposited onto a build platform in the form of droplets, and each individual droplet corresponds to a voxel that constitutes the 3D object (Figure 2.7b).

Figure 2.7: Three representative 3D printing technologies a) solid-based b) liquid-based and c) powder-based.

Compared to most photopolymer-based 3D printing technologies, Polyjet has a better resolution (except for 2PP) and is able to simultaneously print multiple types of materials, such as printing a combination of rigid plastics and soft rubbers [88]. Superfine inkjet technology was developed by SIJ Technology in Japan. This technology can produce ultrafine droplets of less than 1 μm in diameter, which is one tenth of the size ejected by conventional inkjet printers. Superfine inkjet technology has the second best resolution after 2PP. Selective Laser Sintering (SLS) uses a laser (usually 1 - 100 W) to scan and heat powder particles at a temperature near the melt point such that the surface of the powder particles softens to join together – a process called solid state sintering. Then a new layer of powder is spread over the previous

layer for laser scanning and the process repeats layer by layer until the part is complete (Figure 2.7c). There are materials which require reactive sintering or liquid phase sintering, however, the principle of using a laser to heat and join the material remains the same.

2.4 Potential of 3D printing in membrane/membrane module design

In membrane research, the basic requirements for 3D printers would be the resolution achievable and the candidate materials, such as polymer, ceramics, etc. Table 2.4 lists a number of 3D polymer printing technologies that could be relevant to membrane research and Figure 2.8 shows the typical achievable resolution by various 3D printing methods. The resolution of current 3D printers is far above nanometre scale, most of them work best in the range of hundreds of micrometres. Among the various options, 2PP and superfine inkjet offer the finest resolution ($< 1\ \mu\text{m}$). Based on the current status of 3D polymer printing technology, some initial roles can be proposed for 3D printing to play to fill in the research gaps faced by membrane researchers. As illustrated in Figure 2.8, the resolution range for membrane fabrication only marginally overlaps the resolution range of 3D printing technology at 0.1 to 10 μm . This means that 3D printing is not yet sufficiently advanced for direct applications in making membranes. While some of the methods (e.g., 2PP and superfine inkjet) may be able to fabricate large pore microfiltration (MF) membranes or substrates for composites, the current generation of 3D printers is far from being capable of making the rejection layers of reverse osmosis (RO), nanofiltration (NF), or ultrafiltration (UF) membranes. It should also be noted that the rate of fabrication tends to be inversely related to resolution, so fine structures would take longer to prepare. This would not be an issue in prototyping various architectures but would limit mass production.

Figure 2.8: The current limitation of 3D printing technology in membrane research.

It is worth noting that in addition to the resolution limits, other features such as tolerance, reproducibility and surface finish of 3D printing systems are also of paramount importance for manufacturing beyond prototyping. Currently, the tolerance for most 3D printers is a few hundred micrometres or more, if any fitting or sliding between the mating surfaces is required, it has to be carefully designed before printing. The reproducibility of 3D printing is generally high for professional and production machines due to fully automated operation and various automatic compensation factors in the software (especially for liquid resin-based 3D printers). In general, a high accuracy of model-to-part can be ensured when the printer is operated at optimal process parameters. However, this may be compromised in low end printers that are lower costs with limited tunable process parameters. The quality of surface finish depends on the machine resolution, printing orientation (staircase effect) and post-processing.

Table 2.4: Comparison of 3D polymer printing technologies in terms of resolution and materials.

3D Polymer Printing Technology		Example Printers		Layer Thickness	XY Resolution	Feed Material	Multi Material	Scale, Speed and Cost
Category	Process	System	Company					
Solid-based	FDM	Dimension/Fortus	Stratasys (US)	178 or 254 μm	250 μm	Polymer filament	Yes	- All polymer printing technologies are mainly used for prototyping and tooling, not yet mature for industrial scale manufacturing. - Speed mainly depends on part size, complexity and building orientation. In general, CLIP is the fastest and FDM is the slowest. - Cost effective for low volume production, currently no cost advantage for high volume (tens of thousand) production.
Liquid-based	SLA/ μ SLA	ProX/Projet	3D Systems (US)	20-150 μm	50 μm	Liquid photopolymer	No	
	DLP/CLIP	Perfactory CLIP Printer	EnvisionTech (Germany) Carbon 3D (US)	25-50 μm	30 μm	Liquid photopolymer	No	
	2PP	Photonic Profession GT	Nanoscribe (Germany)	< 1 μm	0.15 μm	Liquid photopolymer	No	
	Polyjet	Connex 500	Stratasys (US)	16 μm	25 μm	Liquid photopolymer	Yes	
	Superfine Inkjet	SIJ Printer	SIJ Technology (Japan)	< 1 μm	0.5 μm	Organic ink Metallic ink	No	
Powder-based	SLS	sPro EOS P 396	3D systems (US) EOS (Germany)	100 μm	500 μm	Polymeric fine powder	No	

** FDM: Fused Deposition Modelling; SLA: Stereolithography Apparatus; DLP: Digital Light Processing; CLIP: Continuous Liquid Interface Production; 2PP: Two Photon Polymerization; SLS: Selective Laser Sintering.

A more immediate role for 3D printing is to help validate various designs for membrane modules such as novel designs for feed channel spacers. Previously, the assessment of a significant range of spacer designs can only be studied via computational fluid dynamics (CFD), and actual physical testing of the new designs has been limited by the ability to fabricate novel prototypes. With the introduction of 3D printing technology, this problem should be overcome. A second role for 3D printing may lie in its capability of supporting the fabrication of freeform design, which could answer questions like what are the optimal designs for other membrane module components, such as anti-telescoping supports in the SWM. There may be other optimal forms of components that could be developed if there is no manufacturing constraint.

One challenge for 3D printing in making membranes and membrane module components is the selection of materials. The raw polymeric materials for 3D printing generally require either (1) a melting step to heat the solid polymer for extrusion through a nozzle, or (2) a UV curing step to polymerise the monomer; or (3) a sintering step to fuse the powder together, therefore the correct material form must be available for 3D printing. In general, all polymeric materials used for 3D printing need to be prepared in one of the following forms in a relatively large quantity: spool of polymer filament, photopolymer liquid resin, or polymeric fine powder. Additionally, not all technologies are capable of printing multiple materials in a single process. The exceptions are Polyjet technology and FDM technology, which may open up the possibility of printing novel membrane module designs comprising materials of different properties or functions. In addition to directly printing a part (e.g. feed channel spacer), 3D printing also provides an indirect approach, in which a negative mold or a master pattern is printed first, and then used to cast out the desired part [89-

91]. This indirect approach is suitable for materials that cannot be easily 3D printed. Other considerations, such as chemical stability (pH, chlorine resistance), mechanical strength, and thermal stability should also be considered during the selection of materials.

2.4.1 3D printing of feed spacers

The advent of 3D printing created a new alternative for ease of fabricating complicated geometry designs and this enthralled researchers to employ 3D printing as a tool to fabricate novel spacers (see Figure 2.9) without manufacturing restraint. The first 3D printed spacers were fabricated by Li et al. in 2004 via a powder-based 3D printing, Selective Laser Sintering (SLS) to study novel spacers in membrane modules as shown in Fig. 5 [16, 80]. Their spacer designs included (1) spacers with modified filaments that had helical ridges wound around the cylindrical rod, (2) spacer filaments that took on the design of a twisted tape (helical) and (3) multi-layered structures with three layers, i.e. the outer layers were made of non-woven spacer filaments and the middle layer can be either the same non-woven spacer filaments or design of a twisted tape filaments. The designs were created on the basis that longitudinal and transversal vortices could be generated near channel walls while minimising power consumption in the middle of the channel. The different flow patterns induced by the three designs and their effect on mass transfer were investigated through electrochemical limiting current experiments. The multi-layered structure with twisted tape filaments in middle layer were discovered to demonstrate 30% higher Sherwood number and at 40% power consumption of the optimal non-woven spacer. Li et al. also mentioned that mass transfer simulations obtained from CFD were difficult and inaccurate due to the complexity of the novel spacer designs [16].

In 2006, Balster et al. also looked into multi-layered spacer structures for improving mass transfer in electrodialysis (ED) process [58]. This study systematically investigated the effect of different geometrical parameters of single spacers, including filament types (helical vs. normal), filament diameters, mesh lengths and flow attack angles on mass transfer before narrowing down the designs to create the multi-layered structures. Although the authors never explicitly stated this, one can expect that the multi-layered designs reduce the contact area of spacer filaments with the membranes and thus decrease the spacer shadow effect. These spacers produced by SLS were applied in ED desalination processes. The rationale for the application in ED processes was to effectively investigate concentration polarisation preferable to UF and RO where the interpretation would be challenging due to possible coexistence of concentration polarisation and fouling. The spacer performances were determined through limiting current density measurements in a lab scaled ED system. The multi-layered structures with smaller spacer filament diameter in the middle layer were able to produce 20% higher mass transfer than conventional net type spacers.

Figure 2.9: Images of 3D printed spacers and membranes in prior studies. (a) modified filament spacer (b) helical spacer (c) multi-layered spacers. (d) staggered herringbone spacers. (e) microstructured spacer (f) static mixing spacer. (gi) printed channel. (gii) molded membrane.

Both Li et al. and Balster et al. worked on improving the net typed spacer structures [16, 58]. The first 3D printed non-net typed spacers, suggested for application in UF and RO, were invented by Shrivastava et al. in 2008 with a solid based 3D printing technique, Fused Deposition Modelling (FDM) [17]. Other than helical spacers, Shrivastava et al. experimented with asymmetric structures such as herringbones and laddered typed spacers to examine the spacer shapes in reducing concentration polarisation and to provide a design guide to optimise spacers. The extensions of Lvque equation were used to predictively model the novel spacer designs in affecting concentration polarisation. The authors' model was in agreement with CFD simulations results and electrochemical experiments for the laddered typed spacers and with comparably larger deviation for the helical and herringbones spacers. However, the validation of mass transfer using electrochemical experiments instead of UF and RO experiments remained a concern of Shrivastava because in the electrochemical experiments based on limiting current method, ions migration occurs due to potential difference in the electrodes [17]. Whereas in the membrane experiment, the mass transfer estimation is based on the concentration polarization phenomena arisen due to the accumulation of rejected solutes (which is not restricted to ions) on the membrane surface, resulting in solute back-diffusion from the membrane surface to the bulk solution. The concentration polarization modulus is a function of mass transfer and flux, which is not presence in the electrochemical system. Thus, mass transfer in membrane system cannot be completely represented by electrochemical system.

In 2013, Liu et al. invented a novel spacer inspired by static mixers for SWM module with a liquid based 3D printing technique, Stereolithography Apparatus (SLA) [65]. In order to provide mixing resembling that of a static mixer in a circular flow channel, the spacer were designed such that fluid flow were diverged and mixed from

the top sections of the flow channel to the bottom section through the static spacer elements [92]. A theoretical model was developed to predict the effect of the novel static mixing spacer on mass transfer and pressure drop which was subsequently validated by UF experiments. Despite having higher pressure drop than conventional spacers, under similar power inputs, the static mixing spacers exhibited better mass transfer at lower flow rates and comparable mass transfer at high flow rates.

Shortly after Liu et al., Fritzmann et al. fabricated novel microstructured dual layered spacers via Polyjet printing for air sparged submerged membrane systems [83]. The novel spacer structures were also designed based on Kenics static mixers and differed from conventional spacers such that clogging of foulants in high loading submerged membrane systems can be reduced [93]. Each layer of the spacer was made up of parallel helix filaments with the top layer nicely fitted onto the bottom layer at another twisted orientation so that no filaments would be perpendicular to the flow. Critical flux measurements carried out shown an increment of critical flux by 100% with the use of the novel spacers. The spacers were determined via Design of Experiments (DOE) to be the most effective factor to mitigate fouling, followed by elevated cross flow velocity and aeration rate. This result denoted the potential of the novel spacers in reducing energy consumption in air sparged submerged membrane systems. In 2014, Fritzmann et al. continued with investigations of these spacers in their influences on mass transfer and separation characteristics such as molecular weight cut-off (MWCO) and selectivity in ultrafiltration experiments [84]. The authors illustrated the significance of the spacer geometries in affecting molecular weight cut-off and selectivity, which could have great impact in fractionation processes using UF membrane. Considerable improvement in overall mass transfer and selectivity of the novel spacers as compared to the conventional spacers were also noted.

2.4.2 3D printing of membranes

The typical resolutions of the current AM machines are in the scale of microns which make them generally well fitted for spacer printing but not for membrane fabrication. AM technology is still not able to freely tune the pore structures in membranes which are in the nano scale. This makes it difficult to be used for porous membrane printing, e.g. UF membranes but it may not diminish the opportunities of AM technology in other membrane fields such as biomedical and microfluidics, i.e, 3D printed fluidic devices for drug release [94, 95].

In spite of the current limitations of 3D printing technology in terms of resolution, researchers have begun to adopt AM technology for membrane fabrication in recent years. Wessling and co-workers were the major active group in developing 3D printed membrane from liquid based 3D printing technique, Digital Light Processing (DLP) [96-98]. In 2014, they fabricated a polydimethylsiloxane (PDMS) membrane for gas-liquid contactor directly from DLP instead of using the conventional two-step approach where a sacrificial mould would have to be produced [97]. Despite having 15% lower gas permeability as compared to standard PDMS membrane, the freedom in optimising the geometry of the contactor interface was speculated to bring about improvement to current membrane contactors. Wessling and co-workers also used DLP to indirectly construct membrane with complicated geometries based on triple-periodic minimal surface (TPMS) which current membrane fabrication methods were unable to produce [96, 98]. Comparison of the TPMS membrane to the geometrically equivalent hollow fibre and flat sheet membranes demonstrated a higher heat and mass transfer and better flow characteristics, denoting the possibility of advancement in membrane science beyond geometrical restrictions.

Conventional ink-jet printing technology was also used to assist in membrane fabrication in 2015. Badalov et al. reported ink-jet printing assisted fabrication (PAF)

of patterned selective layers of thin film composite (TFC) membranes [99]. They explored the hybridization between ink-jet printing technology and the interfacial polymerization process that facilitated the formation of unique polyamide selective layers. A diamine monomer that contained fluorine was printed on an ultrafiltration membrane to impart functionality and facilitate the analysis of the rejection layer of TFC membrane. Improved performances in term of permeate flux and sodium chloride rejection was observed in the resultant PAF membranes.

A short summary of these prior studies on 3D printed spacers and membranes is listed in Table 2.5.

Table 2.5: Summary of prior studies on 3D printed feed spacers and membranes.

Design	Application	Method	Thickness	Experiments and Findings	Ref.
Multi-layer twisted filaments (Figure 2.9a,b,c)	Spacer-filled channels in membrane modules	SLS	Round: 1 mm Twisted: 4 mm	CFD and limiting current method for mass transfer coefficient measurements 30% improvement in Sherwood number at same power consumption	[16, 80]
Multi-layer spacer (Figure 2.9c)	Electro-dialysis desalination	SLS	Round: 0.8 - 4 mm Twisted: 4 - 6.1 mm	CFD and limiting current method for mass transfer coefficient measurements 20% improvement in mass transfer at same power consumption	[58]
Ladder, staggered-herringbone spacers (Figure 2.9d)	UF and RO	FDM	0.75 mm	CFD and electrochemical experiments for mass transfer coefficient predictions Predictive models were consistent with CFD simulations	[17]
Dual layered helical spacers (Figure 2.9e)	Submerged membrane systems with air sparging	Polyjet	4 - 10 mm	Critical flux measurements, UF constant flux measurements with Dextran feed 100% increased in critical flux for SMBR with air scouring. Significant improvement in overall mass transfer and selectivity.	[83, 84]

Plate and frame static spacer (Figure 2.9f)	Planar flow channels, SWM	SLA	3 mm	UF experiments with Dextran feed Overall performance was better than conventional spacers at lower flow rates	[65]
Moulded membrane (Figure 2.9g)	Gas-liquid contactors	DLP	1 mm	Gas transport experiments Printed PDMS membranes had same selectivity but 15% lower permeability. Printed TPMS membranes shown improvement in mass transfer despite small surface areas.	[96-98]

2.5 Bridging the gap between 3D printing technology and membrane/module design

3D printing creates a totally new tool for the optimization and fabrication of membrane module components and hence more complex and miniature structure could be rapidly prototyped, which is totally inaccessible by using conventional manufacturing approaches. Figure 2.10 summarises the historical milestones of 3D printing in membrane module design. However, several critical challenges need to be addressed before the 3D printing technology could be used for the fabrication of membrane module. In addition to resolution, the speed of 3D printing technology is still not high enough for large scale mass production of membrane module components. Moreover, limited materials are currently available for 3D printing of membranes and spacers, and high cost of materials might be one of the most challenging problems. Therefore, consideration for new strategies or alternative approaches to overcome these obstacles is urgently needed to realise the full potential of 3D printing technology for membrane module design.

Figure 2.10: Critical milestones of 3D printing in membrane modules design.

Fortunately, rapid and progressive developments in AM technology are further extending the potentiality of 3D printing in membrane science. In fact, a new AM technology, Continuous Liquid Interface Production (CLIP) was developed by Tumbleston and DeSimone et al. to produce thin membranes to study structure-property relationships [100, 101]. With this, the structure of the membranes including membrane thickness, smoothness, and integrity can be potentially designed by the computer, simply by inputting the parameters into the system. As such, it may also be possible to look into 3D printing of profiled membranes for instance in Balster et al.'s work [102] where the spacer were integrated into the membrane by surface patterning for electro dialysis processes. Besides, this novel process allows the continuous polymerization of solid objects straight out of the photopolymer vat, significantly reduces the printing time of conventional 3D printers with a resolution below 100 μm by 25 to 100 times. In near future, the advent of 4D printing which adds the new dimension of time into the traditional 3D printing may also be a potential application in the design of membrane module components.

Last but not least, AM technology also provides the freedom to design and manufacture components without geometrical constraints. Therefore, this advantage can be further extended to optimise other parts of the membrane modules and

hydrodynamic components such as turbulence promoters, air diffusers, flow distributors, membrane holders/packing and membrane test cells. As a matter of fact, Croft Additive Manufacturing Limited had already successfully manufactured 3D printed metal filters with optimised aperture sizes to reduce pumping power consumption [103]. The ease of fabrication using AM also allows novel module designs for spiral wound, tubular, plate-and-frame and hollow fibre that were not possible to be manufactured using conventional techniques. Figure 2.11 shows the potential segments of a SWM that could be optimised by AM technology. The anti-telescoping device, perforated central tube and element casing (green labels) are parts that could be fabricated easily with the current AM technology. The current research focus lies in the optimisation of feed spacers (blue labels) but with advancement in AM, it is possible to shift to challenging segments like membranes and permeate spacers (red labels). Moreover, other than direct application of AM in fabrication, AM can also be employed indirectly to produce tools for making membrane, devices for testing membranes. For instance, the fabrication of 3D printed microfluidic cross-flow device [88, 104], sacrificial moulds for intricate membrane geometries [96], integrated membrane stirrers [105] and possible novel spinnerets designs [106, 107] for more efficient hollow fibre membranes.

Figure 2.11: Potential applications of AM technology in membrane module design. The colours of the labels represent the difficulty of parts that could be fabricated with the current AM technology. Green labels = easy; blue labels = medium; red labels = difficult.

2.6 Summary

To summarise, all the above mentioned indicates the immense potential of 3D printing in feed spacers and membrane components design. At the current state, there are still limited numbers of publications on the use of AM technology in fabrication of spacers for membrane modules. In addition, despite the availability of various commercial AM techniques at present (Table 2.4), researchers have thus far only been using SLS, FDM, SLA or Polyjet to fabricate spacers. This might be attributed to the advantages offered by these techniques, i.e. non-toxicity and non-support removal for SLS, soluble support for FDM and Polyjet and good resolution of SLA. Future studies may explore other 3D printing techniques for spacer fabrication such as Digital Light Processing (DLP) and a new AM technology, Continuous Liquid Interface Production (CLIP) which have comparably good resolution albeit the small build size. Although 2PP and Superfine inkjet have excellent resolution at $<1\mu\text{m}$, they are extremely slow and hence at this stage not suitable for spacer fabrication which does not require great resolution. The ratings for suitability of the various 3D polymer printing techniques for different types of spacer are tabulated in Table 2.6.

Table 2.6: Rating of suitability of 3D polymer printing technologies for different types of spacer required.

(Factors considered include material, resolution, speed, size, and ease of post-processing).

Method Spacer Type	SLA/ μ SLA	DLP/ CLIP	2PP	Polyjet	Superfine Inkjet	FDM	SLS
Net design	√√	√√√	√√	√√√	√√	√√√√	√√√√√
Non-net design	√√	√√	√√	√√√	√√	√√	√√√
Transparent material	√√√√	√√√√	√√√	√√√√	√	√√	√
Multi-material	√	√	√	√√√√√	√	√√	√

Note: √: Limited √√: Low √√√: Moderate √√√√: High √√√√√: Excellent

Further study of AM techniques, for instance, Polyjet in its multi-material capability for functional design of spacers can also be considered. In the following chapters, several areas that can be explored in this interdisciplinary field will be covered, such as:

1) Relationship between design, fabrication and surface properties of spacers

From the literature review, it can be seen that majority of the work focuses on the spacer geometry and configuration, in fact, there were not much discussion on the surface finish. The surface finish may be an important factor that affects the spacer performance. Different 3D printing techniques may affect the precise geometry and surface properties of spacers, such as roughness and wetting characteristics, which may then influence the attachment of foulants (e.g. organic, biological, etc.) and further induce both spacer and membrane fouling. Therefore, knowing the relationship between design, fabrication and surface properties of spacers can be beneficial to ease the selection of a suitable 3D printing technique for spacer fabrication.

2) Spacer designs

The advantages of AM in fabrication of unique spacers with non-recurring patterns, multi-material and three dimensional spacers are still not yet fully exploited by researchers. In addition, the leaching problems and instability of antifouling coatings on spacers call for the need to explore newer possibilities to produce a spacer with good antifouling properties. The capabilities of 3D printing, in particular, the multi-material aspect, could potentially be applied during the design of the spacers to help achieve a new generation of spacers with improved performance.

CHAPTER 3   CAPABILITIES AND FEASIBILITIES OF 3D PRINTING IN SPACER FABRICATION

This chapter systematically investigated the capabilities and feasibilities of different 3D printing techniques in the printing of spacers. Part 1 of the chapter focuses on the different 3D printing techniques that resulted in differences in spacer geometry and surfaces finish and their effects in spacer performance. Part 2 of the chapter investigates the printability of net-typed structures with Selective Laser Sintering (SLS), using polypropylene materials as the representative material for commercial feed spacers.

3.1 Comparison of 3D printing techniques in membrane spacer fabrication

The bulk of the literature mentioned in Chapter 2 has simply used 3D printing as a tool to fabricate novel spacer designs. Among the 3D printed novel spacers listed in Table 2.3, it can be seen that each research group only reported using one type of 3D printing technique, and there are almost no existing studies that compare different 3D printing techniques for spacer fabrication and performance. An exception is Siddiqui et al. who gave a very brief comparison of FDM, SLA and Polyjet spacer fabrication in terms of their resolution and surface finish [75]. However it was not the focus of their study and there were no supporting experimental data provided to relate to spacer performance. Yet it is noteworthy that 3D printing can inadvertently modify the geometry and surface properties of the spacers. In addition, depending on the 3D printing technique used, the accuracy of replication may vary from the specified design. The selection of a suitable 3D printing technique is thus of utmost importance in the fabrication of 3D printed spacers. As such, Part 1 of this chapter systematically investigated the differences in spacer geometry and surfaces finish (i.e. morphology, surface roughness, contact angle and zeta potential), and their effects in spacer

performance (i.e. mass transfer, pressure loss, fouling tendency, critical flux and affinity towards bacterial adhesion) by different 3D printing techniques. Based on the results, design considerations for additive manufactured spacers were then recommended. Three different types of 3D printing techniques: (a) solid-based FDM; (b) liquid-based Polyjet; (c) powder-based SLS that were rated most suitable for fabrication of net type spacers design [74], were selected in this study. A commercially available feed spacer made from polypropylene (PP) was used as a reference and compared with 3D printed spacers of the same nominal geometry.

3.1.1 Materials and methods

3.1.1.1 Chemicals and materials

Polyamide 12 based white powder PA2200 (EOS GmbH Electro Optical Systems, Krailling/München, Germany) was used for printing the feed spacer in the EOSINT P395 Selective Laser Sintering (SLS) system (EOS e-Manufacturing Solutions). ABSplus™ (Stratasys Ltd., Israel) thermoplastic was used as model material for the feed spacers and SCA-1200 (Stratasys Ltd., Israel) as support material for solid based 3D printing in the Dimension Elite Fused Deposition Modeling (FDM) machine (Stratasys Ltd.). Acrylic based monomer VeroClear RGD810 (Stratasys Ltd.) was used as model material and SUP705 (Stratasys Ltd.) as support material for liquid based 3D printing in the Objet Eden 350V (Stratasys Ltd.). It shall be noted that the different materials used for fabrication were dictated by the respective commercial 3D printers. Solutes and particles used for preparing test solutions for mass transfer measurement and critical flux determination included Dextran T500 (Molecular weight 450,000-650,000 Da, Sigma-Aldrich) and polystyrene (latex) beads (Particle size 5 µm, Sigma-Aldrich), respectively. The Ultrapure water used in the current study was supplied from a Milli-Q system (Millipore Singapore Pte Ltd).

3.1.1.2 Fabrication of feed spacers and benchmark artifacts via 3D printing

i. Preparing benchmarking part

In 3D printing, a benchmark study is a systematic assessment of the strength and weakness of each 3D printing system when given a set of specific design features [86]. This is important for designing spacers with new features for improved performance. A benchmarking part, also known as a test artifact [108], was designed using Solidworks (SOLIDWORKS Corp.) to evaluate the capabilities of the different 3D printing processes quantitatively as shown by Figure 3.1. The features of the test artifacts were designed to demonstrate the various characterising parameters of the feed spacers, such as filament diameter, mesh length and hydrodynamic angle. The purpose was to 1) determine the dimensions of the smallest possible printable features, and 2) assess the geometric dimensional accuracies of the various features which may be associated with novel feed spacer designs. The smallest features created were 0.05 mm in length and subsequently adjusted in small increments of 0.05 mm up to 1.00 mm and thereafter in increments of 0.10 mm up to 1.50 or 2.00 mm. The features of the benchmarking parts are summarised in Table 3.1.

Figure 3.1: Benchmarking test part (a) CAD model (b) 3D printed parts (i) SLS (ii) FDM (iii) Polyjet

Table 3.1: Summary of the features demonstrated in the benchmarking parts

Characteristics of feed spacers	Feature(s) used to demonstrate	Purpose
Filament diameter	Thin walls (0.05 mm to 1.50 mm)	To test the minimum printable filament diameter and geometric accuracies
Mesh length	Thin gaps from (0.05 mm to 1.50 mm)	To test the minimum printable mesh length and geometric accuracies
Hydrodynamic angles	Thin walls at different angles from 0° to 160°	To test the geometric accuracies at different angles
Novel features	Central cylinder (wall and gaps) (0.05 mm to 1.00 mm)	To test the ability of the system to produce round and concentric structures
Vertical features	Pins, holes from (0.05 mm to 2.00 mm)	To test the minimum diameter of a vertically protruded or depressed structure

ii. Preparing 3D design of feed spacer

A 3D computer aided design (CAD) model of the feed spacer was drawn in Solidworks (SOLIDWORKS Corp.) The 3D model design was based on the commercial 28 mils (equivalent to 0.711 mm) polypropylene feed spacer extracted from DOW FILMTEC™ TW30-2540 elements. Slight modifications were made to the filament diameters of the commercial spacer, i.e., (1) the ideal design of the feed spacer was assumed to have uniform cylindrical filaments but were infeasible due to the inherent manufacturing error of the conventional extrusion method (2) the 3D printing machines used in the current study were not able to print an exact replica of the 28 mils commercial non-uniform cylindrical filaments that were robust and sturdy enough for use in the experiments. Therefore, the 3D model spacer was designed to replicate, as closely as possible, the commercial spacer with a uniform filament diameter of 0.4 mm, mesh length of 2.90 mm and hydrodynamic angle of 90°. The 3D model and geometrical characteristics can be found in Section 2.2.1.

iii. Fabrication via powder based printing: Selective Laser Sintering (SLS)

PA2200 powder were deposited evenly on the building platform of the EOSINT P395 SLS machine and heated to a temperature below the melting point. A carbon dioxide (CO₂) laser was used to sinter the powder according to the corresponding 2D cross sections at each layer height of the feed spacer. Unsintered powder remained as the support material for the build. The SLS processing parameters for PA2200 were based on the EOS part properties profile. The completed part was removed after allowing 24 hours of cooling to prevent warpage. The support materials were removed in an abrasive blasting machine and thereafter washed and soaked in ultrapure water to ensure stability of the printed spacer.

iv. Fabrication via solid based printing: Fused Deposition Modeling (FDM)

Catalyst software of the FDM Dimension Elite machine sliced the CAD file into thin cross sections where each layer was converted into toolpaths, indicating the extrusion path of the print head. ABS material in the form of a spool of filaments was fed into the print head of the FDM Dimension Elite machine and heated to its melting point. Soluble support material was first extruded to form a base for the model before the extrusion of ABS material according to the toolpaths arranged by the system at each layer of 2D cross sections. The support material was removed by soaking the entire printed part into hot alkaline solution until complete dissolution. The retrieved feed spacer was then soaked in ultrapure water to remove any residual chemicals.

v. Fabrication via liquid based printing: Polyjet printing

CAD models were orientated and placed on the build platform in Objet Eden 350V software. The 3D models can be printed with a matte surface or a glossy surface. The spacers were chosen to be printed with a glossy surface to reduce consumption of

support materials and for easier support removal. Photopolymeric materials VeroClear RGD810 was jetted out in droplets according to the 2D cross sections of the model and immediately cured by Ultra-Violet light. Support materials were generated to hold the overhanging structures. The process repeats for subsequent layers to form a 3D model. Support materials were removed using a water jet.

3.1.1.3 Surface analysis of feed spacers

The surface finish of the printed spacers and commercial PP spacer were observed under a scanning electron microscope (Jeol JSM 5600-LV, USA). However, the direct quantification of surface properties of spacers, such as roughness, hydrophobicity and surface charge, were not possible due to limitations in the analytical instruments, so samples with flat surfaces were prepared separately and used instead as an estimate. Each sample was washed with Milli-Q water three times before being dried under ambient air prior to measurements. The macroscale surface roughness of the 3D printed flat samples were measured using a stylus profilometer (Taylor Hobson Talysurf Series 2, UK) along X-axis and Y-axis for a measurement length of 10 mm. Meanwhile, the microscale roughness was measured by atomic force microscopy (AFM) (Park Systems NX10, Korea) with an aluminium coated cantilever tip (model PPP-NCHR-10M, NANOSENSORS, Switzerland) for an analysis area of 20 x 20 μm . Water contact angle of the flat samples were tested with a goniometer (DataPhysics Instruments GmbH, Germany) using the captive bubble method whereby specimens were submerged under deionised water and an air bubble with a volume of 5 μL was released and captured on the specimen surfaces. The captive bubble method was chosen instead of the sessile drop method due to the instability of the drop on the 3D printed surfaces in the latter method. Surface charge was measured using zeta potential analyser (Zetasizer Nano N, Malvern). The flat samples were cut into 3.8 mm X 5.0 mm pieces to fit the sample holder. Pre-rinsing with Milli-Q water was necessary

before mounting the sample. Tracer solution was prepared by diluting small amount of creamer powder into deionised water without pH adjustment. The measured pH of the tracer solution was around 6.8. All the data reported were average value of 3 replicates.

3.1.1.4 Performance evaluation of 3D printed feed spacers

i. Pressure drop and mass transfer measurements

The pressure drop and mass transfer study were conducted in a flat channel crossflow test cell with a channel length of 278 mm and width of 35 mm. Polysulphone UF membranes HFK131 (Koch Membrane Systems Inc.) with a nominal molecular weight cut off of 5000 Da were used. The active membrane area was $9.73 \times 10^{-3} \text{ m}^2$. Feed spacer replicates printed by either SLS, FDM or Polyjet were placed in the feed channel and a commercial net-type permeate spacer was placed in the permeate channel. Supporting inserts with varying thickness were used for adjustments such that the feed spacer height fitted the channel height. Dextran T500 (Sigma Co.) at 1 g/L was used as the feed solution.

The initial water flux of the membrane was measured with ultrapure water (Milli-Q System) before the start and after each run. In a typical run, fresh feed solution was circulated at the required flow rate and pressure for about 10 minutes for stabilisation at a temperature of 20°C. Permeate was collected and measured in terms of Total Organic Carbon (TOC) concentration. Measurements of channel pressure drop by pressure sensors were also taken. The details of the setup are illustrated in Figure 3.2. Ranges of transmembrane pressure (TMP) from 40-90kPa and flow rates from 0.4-1.5 L/min were used in these tests.

Figure 3.2: Schematic diagram of the cross-flow setup

ii. Mass transfer calculations

The filtration experiments with dextran T500 were conducted under test conditions of 0.4-1.5 L/min flow rate, 40-90 kPa TMP and concentration at 1g/L. Properties of dextran T500 were acquired from the literature [109],

Viscosity:

$$\mu = e^{0.019c - 5.98} \quad [Pa.s] \quad (3-1)$$

Density:

$$\rho = 1013 + 0.33c \quad [kg / m^3] \quad (3-2)$$

Diffusivity:

$$D = \left(0.1204 + 2.614 \left(\frac{c}{1000} \right) - 4.167 \left(\frac{c}{1000} \right)^2 + 2.132 \left(\frac{c}{1000} \right)^3 \right) 10^{-10} \quad [m^2 / s] \quad (3-3)$$

Osmotic Pressure:

$$\Delta\pi = \left(0.0867 \left(\frac{c}{1000} \right) + 2.98 \left(\frac{c}{1000} \right)^2 + 89.8 \left(\frac{c}{1000} \right)^3 \right) 10^5 \quad [Pa] \quad (3-4)$$

The mass transfer coefficients k can be obtained from the osmotic pressure model and the film model [12, 14]. The concentration of dextran T500 in kg/m³ is denoted as c . The membrane permeability coefficient L_p , transmembrane pressure ΔP_{TM} and the permeate flux J obtained from experiments were substituted into the following equation to get $\Delta\pi_w$, the difference in osmotic pressure of dextran T500 from the wall side to the permeate side of the membrane.

$$J = L_p (\Delta P_{TM} - \Delta\pi_w) \quad (3-5)$$

The concentration of dextran T500 at the membrane wall, c_w is then calculated from Equation (3-4). Finally, mass transfer coefficients k can be calculated from the film model using:

$$J = k \ln \frac{c_w - c_p}{c_b - c_p} \quad (3-6)$$

Where c_b refers to the concentration of the bulk feed solution and c_p refers to the concentration of permeate measured with a TOC Analyser (Shimadzu TOC-VCSH, Japan).

Mass transfer coefficient k can be expressed as the dependence of Sherwood number (Sh) with flow conditions in terms of Reynolds number (Re) and Schmidt number (Sc) [12].

$$Sh = \frac{k_{av} d_h}{D} = \alpha Re_h^\beta Sc^\gamma \left(\frac{d_h}{L} \right)^\delta \quad (3-7)$$

where α , β , γ and δ are constants related to the effects of hydrodynamics and geometry of the flow channel.

iii. Pressure loss measurements

The pressure drop across the channel can be expressed as

$$\Delta P \propto u^m \quad (3-8)$$

This relationship was also used to determine the flow regime in the spacer-filled channels. For $m=1$, the dominant flow regime in the spacer-filled channels is laminar flow whereas, for $m = 1.75$, high turbulence flow is dominant. From the experimental data, the values of m range from 1.50 to 1.65, indicating that all the spacers were operating in the upper transition regime.

The pressure drop across the channel can be related to the dimensionless Power number P_n which can be calculated to compare the energy consumption of different spacers.

$$P_n = \frac{\Delta P}{L} u_{eff} \left(\frac{\rho^2 h_{ch}^4}{\mu^3} \right) \quad (3-9)$$

where u_{eff} refers to the effective cross flow velocity (u/ε) and L refers to the channel length [4].

3.1.1.5 Fouling study – critical flux determination

The direct observation through the membrane (DOTM) technique [33] was used to observe particle deposition on the membrane surface and to determine the critical flux. Critical flux is defined as the flux above which foulants begin to deposit and below which there is no fouling [34]. The type of spacers used can influence the particle deposition rate and thus the critical flux. A higher critical flux reduces the fouling tendency due to improved hydrodynamics. The DOTM experimental setup includes having the lens of the microscope (Axiolab, Zeiss) positioned on the permeate side of a custom designed membrane module made of perspex to allow transmission of light through it. Anopore™ membranes (Anodisc, Whatman, UK) with a nominal pore

size of 0.2 μm were used as they were visually transparent when wetted. This enabled light transmission through the membrane such that deposition at the membrane surface could be observed from the permeate side. Images and videos were captured and recorded by the digital camera (Q-imaging, Canada) directly connected to a computer.

Experimental studies to determine the effect of spacer design on critical flux of latex particles with DOTM were conducted by the flux-stepping method [36]. Firstly, a peristaltic pump (Cole Parmer, USA) on the permeate side was used to maintain constant flux at 15 $\text{l/m}^2\text{h}$ for 10 min. If there were little or no deposition on the membrane surface during the 10 minutes observation, the flux was regarded as below critical flux level. Hence, the flux was incrementally stepped up by 15 $\text{l/m}^2\text{h}$ for each 10 minute interval until particles were observed to start depositing on the membrane surface. This would mean that the flux was near the critical flux and therefore, flux was stepped up in a smaller increment to carefully determine the critical flux value. Real time images were captured at the 1st and 10th minute for surface coverage analysis using image analysis software (Image-pro plus, Media Cybernetics). 5 μm latex beads at a concentration of 2 g/L were used as the feed solution at a linear velocity of approximately 0.2 m/s. The superficial linear velocity u is calculated by

$$u = \frac{Q}{\text{effective area}} = \frac{Q}{wh_{ch}} \quad (3-10)$$

where w is the width of the channel and h_{ch} is the height of the channel defined by the spacer heights and Q refers to the flow rate. The actual velocity, u_{eff} , will be given by u/ε .

At least five positions on the membrane were observed and recorded for each experiment and experiments were duplicated to identify the critical flux for each type of spacer. It was estimated that critical flux values reported were within $\pm 10 \text{ l/m}^2\text{h}$.

3.1.1.6 Bacteria attachment analysis

Model bacteria *Pseudomonas aeruginosa* was used in this study. The bacteria was first cultured in 5 g/L nutrient broth (BD Difco) solution with background salinity of 500 mg/L NaCl for 24 hours. One mL of the cultured bacteria was then transferred into 20 mL test solution containing 40 mg/L nutrient broth with the same background salinity. Three replicates of flat samples (3D printed by FDM, SLS and polyjet and commercial PP), with size of 3.8 x 5.0 mm, were prepared by soaking in 70% ethanol (Merck) for 1 hour and subsequently rinsed three times with Milli-Q water. Then, the flat samples were soaked in the test solution to allow for bacteria attachment for 48 hours in a shaker-incubator at 120 RPM and controlled temperature of 37 °C.

After 48 hours of incubation, the flat samples were removed and carefully rinsed three times in sterile saline solution to remove any loosely attached bacteria. They were then individually soaked in 1 mL of sterile saline solution and sonicated for 5 minutes to induce the dispersion of attached bacteria from the flat samples. Finally, the solution was vortexed (Vortex-Genie2) for 1 mL at maximum speed for 1 minute. The amount of bacteria was measured with a flow cytometer (Accuri C6, BD Diagnostics) using SYTO9 Green Fluorescent Nucleic Acid Stain (Cat No S34854, Molecular Probes).

3.1.2 Results and discussion

3.1.2.1 Benchmarking of 3D printing techniques

The geometric accuracy of the features on the benchmarking part printed via SLS, FDM and Polyjet were measured using digital callipers and stereo microscope. The results of the deviation of the printed dimensions to the model dimensions were plotted and are shown in Figure 3.3. Positive deviation refers to printed parts being larger than the designed value (expansion) and negative deviation means printed parts being smaller than the designed value (shrinkage). In general, most features with

protrusion (e.g. pins and walls) became smaller after printing due to the volumetric contraction of polymeric materials when solidifying from the liquid or semi-liquid state. Features with depressions (e.g. gaps and holes) tended to become larger if the feature involved a curvature (Figure 3.3a and 3.3b). However, this was also due to the contraction of polymers in the outward radial direction. 3D printing techniques have limited effects on the angled features. Among the examined features, circular walls and gaps were the most difficult to print with precision because the data points are the most scattered (see Figures 3.3a, b, c). In fact, this is one of the limitations when using a line by line strategy to print curves. The direct implication of these results for spacer feature design is that, in order for one to ensure a better part to model accurately, features with curvatures should be avoided and features with protrusions should be designed slightly larger to overcome the shrinkage effect. Comparison among the three 3D printing technologies, SLS, FDM and Polyjet showed that Polyjet, was more capable of producing smaller and more accurate features, followed by SLS then FDM. This result was in agreement with the capability of the 3D printing technologies listed in prior literature [74]. The smallest possible dimensions to be printed with less than 10% deviation are summarised in Table 3.2.

Figure 3.3: Deviation of actual dimensions from designed dimensions for SLS, FDM and Polyjet printed parts. (a) Holes and Pins (b) Circular gaps and walls (c) Gaps and walls (d) Angles and corresponding wall thicknesses

Table 3.2: Comparison of the dimensions at which the deviation of printed features of the spacer is less than 10%

Characteristics of feed spacers	Feature(s) used to demonstrate	Dimensions at which deviation <10% (mm)		
		SLS	FDM	Polyjet
Filament diameter	Thin walls from 0.05 mm to 1.50 mm	>1.30	>1.40	>0.60
Mesh length	Thin gaps from 0.05 mm to 1.50 mm	>1.30	>1.20	>0.70
Hydrodynamic angles	Thin walls at different angles from 0° to 160°	0° to 160°	0° to 160°	0° to 160°
Novel features	Central cylinder (wall and gaps) from 0.05 mm to 1.00 mm	Gaps: >1.00 Walls: >0.75	Gaps: >0.65 Walls: >1.00	Gaps: >0.60 Walls: >0.70
Vertical features	Pins, holes from 0.05 mm to 2.00 mm	Pins: >1.40 Holes: >0.6	Pins: >1.40 Holes: >0.95	Pins: >0.65 Holes: >1.20

3.1.2.2 Characterisation of 3D printed spacers

i. Geometric accuracy and characteristics

Feed channel spacers printed with SLS, FDM and Polyjet were measured with a stereo microscope and subsequently calculated in terms of deviation from the designed values to observe the effect of the different 3D printing techniques. The results plotted in Figure 3.4a matched well with the benchmark study in Section 3.1.2.1. The filament diameter demonstrated by the thin walls features gave a 20% deviation at the designed dimensions of 0.4 mm for SLS and Polyjet, whereas >100% deviation was observed for FDM. The mesh length and hydrodynamic angles demonstrated by the gaps and angled walls feature respectively were accurately printed for all three techniques at a designed value of 2.9 mm and 90°. The spacer thickness is a vertical dimension dependent on the machine layer thickness resolution. Polyjet has a layer thickness of 16 µm whereas SLS and FDM have layer thicknesses of 100 µm and 238 µm respectively. Therefore, it is anticipated that the spacer thickness printed by Polyjet would have the lowest deviation compared to SLS and FDM. Filament diameter was discovered to be the designed parameter with greatest deviation for all three techniques, followed by spacer thickness. The cause of the larger deviation of the filament diameter as compared to spacer height was attributed to the combined error in the x, y and z direction for filaments in contrast to simply the z direction for the spacer height [110]. The strand eccentricity parameter e (Equation 3-11) introduced in Haaksman et al.'s work [76] was used to evaluate the printed spacers:

$$e = \sqrt{1 - \frac{b^2}{a^2}} \quad (3-11)$$

where b refers to the shortest semi-axis of the filament cross section and a refers to the longest semi-axis of the cross section.

Due to difficulties in obtaining the exact cross sections of the spacer filaments

without X-ray computed tomography, the strand eccentricity in Figure 3.4b were determined from the averaging of at least 10 sets of a and b values measured using a digital calliper within ± 0.08 mm from the attached and detached filaments of the different spacers. The strand eccentricity value ranges from 0 to 1, where a strand eccentricity value of 0 indicates that the cross section of the spacer filament is completely circular. From Figure 3.4b, FDM showed the greatest strand eccentricity, followed by Polyjet, SLS and the commercial spacer. This finding was further supported by the SEM images in Figure 3.5. In addition, the standard deviations of strand eccentricity indicated by the error bars showed that FDM had the largest strand eccentricity deviations, followed by SLS. This may be due to the differences in strand eccentricity of the attached (top) filaments and detached (bottom) filaments for FDM and SLS spacers as a result of the printing process. The magnitude of these standard deviations can be used as an indicator of the randomness of the 3D printed spacer geometry. The geometric characteristics of the printed spacers described in Section 2.2.1 are listed in Table 3.3.

Figure 3.4: Deviation of the characteristics of feed spacer fabricated by SLS, FDM and Polyjet (a) Dimensional deviation of printed values compared to designed values (b) Strand eccentricity

Figure 3.5: (i) Photo images (ii) SEM images of cross section (iii) SEM images of top view of (a) Commercial (28 mil) spacer (b) SLS printed spacer (c) FDM printed spacer (d) Polyjet printed spacer

Table 3.3: Geometric characteristics of spacers

Spacer	h_{sp} /mm	d_f /mm	l_m /mm	ϵ	S_{vsp}	Θ /°	d_h /mm	e	Standard deviation of e
Commercial	0.71	0.43	2.88	0.858	9302	90.0	0.831	0.236	0.0570
SLS	0.82	0.48	2.93	0.851	8386	90.0	0.923	0.460	0.120
FDM	0.90	0.84	2.81	0.562	4762	90.0	0.521	0.810	0.131
Polyjet	0.71	0.46	2.91	0.838	8658	90.0	0.794	0.694	0.0445
Design	0.70	0.40	2.90	0.876	10000	90.0	0.856	0	-

ii. Surface finish

Figure 3.5 shows the morphological comparison of the filament junction of the commercial spacer with 3D printed spacer replicates. The FDM fabricated spacer had a smooth surface but each strand of cylindrical filament was observed to be printed out in several layers resulting in a flat cross section thus deviating to a greater extent from

the design. Parallel grooves can be observed on the surfaces of FDM printed spacer due to the printing process. Polyjet and SLS printed spacers were able to produce a cylindrical filament without much deviation from the design.

Table 3.4 summarises the results obtained from surface roughness, contact angle and zeta potential measurements of commercial PP, SLS, FDM and Polyjet printed flat samples. The macroscale surface roughness was taken along the X-X axis and Y-Y axis for each printed specimen. In comparison, Polyjet had the lowest surface roughness in the X-X axis, followed by SLS then FDM printed specimen. All 3D printing techniques produced rougher surfaces at the macrostructure level (i.e. μm range) compared to commercial PP. The ratio of the X-X and Y-Y macroscale roughness provides an indication of the surface anisotropy. The FDM spacer has a very anisotropic surface with a ratio of ~ 15 whereas all other spacers have a ratio closer to unity (1.1 to 1.5). As seen in the SEM images (Appendix Figure A1), the cause of the different surface roughness in x and y directions were the parallel grooves along the printed parts, hence a greater roughness was detected across the parallel grooves than along the grooves for Polyjet and especially FDM printed specimen. This varying surface finishes in x and y directions of the 3D printed samples indicated significant anisotropy in the case of FDM spacers, a lower level of anisotropy for Polyjet spacers and the lowest level of anisotropy (almost isotropic) for SLS and commercial spacers because of the homogeneity. Similar anisotropic characteristics of FDM, Polyjet and SLS parts were reported in prior work [111-113].

Table 3.4: Surface roughness, contact angle and zeta potential of commercial PP, SLS, FDM and Polyjet printed flat samples (n = 3)

	Macroscale Ra (μm)*		Microscale Ra (nm)	Water Contact Angle ($^{\circ}$)	Zeta Potential (mV)
	X-X axis	Y-Y axis			
PP	0.01 ± 0.009	0.008 ± 0.001	4.5 ± 0.9	80.0 ± 2.3	-49.6 ± 5.4
SLS-PA12	12.1 ± 0.7	11.1 ± 0.6	158.3 ± 63.8	36.5 ± 3.5	-48.6 ± 6.1
FDM-ABS	16.6 ± 1.2	1.1 ± 0.4	17.4 ± 2.9	53.2 ± 2.5	-39.5 ± 2.0
Polyjet-Veroclear	1.9 ± 0.1	1.3 ± 0.1	$178.7 \pm 52.3^{\#1/}$	$32.7 \pm 3.3^{\#1/}$	-59.9 ± 8.6
			$188.0 \pm 30.1^{\#2}$	$38.2 \pm 2.3^{\#2}$	

*: refer to Appendix A1
 #1: matte surface of Polyjet
 #2: glossy surface of Polyjet

Interestingly, the roughness profiles appeared differently on the microscale level (i.e. nm range) measured using AFM (Table 3.4). The results showed that PP and FDM ($R_a = 4 - 18$ nm) were distinctively smoother compared to Polyjet and SLS ($R_a = 158 - 178$ nm). The roughness of the Polyjet printed surface might be due to incomplete removal of support materials or associated with the drop-wise jetting pattern of the machine leading to a patchy surface. Likewise, the sintered spherical powder particles increased the microscale roughness of the SLS printed surface. The AFM measurements (Table 3.4) agreed with the observations from the SEM images (Figure 3.5).

In addition, the wettability analysis of the 3D printed surfaces showed higher hydrophilicity for Polyjet, SLS surfaces ($CA = 32 - 38^{\circ}$) and FDM surfaces ($CA = 53^{\circ}$) compared to the commercial PP surfaces ($CA = 80^{\circ}$), while all the surfaces had measured zeta potential in the range of -40 to -60 mV. The surface finishes of the 3D printed spacers/surfaces were found to play a significant role in the bacterial adhesion, further details are provided in Section 3.1.2.5.

3.1.2.3 Filtration of dextran

i. Influence of 3D printed spacers on mass transfer and pressure loss

Filtration tests using dextran in the presence of different spacers were conducted. The mass transfer coefficients and pressure drops over the channel were presented in terms of dimensionless Sherwood number Sh and power number P_n at the same designed d_h values. As shown in Figure 3.6a, at the same Re , FDM, SLS and Polyjet spacers generated higher mass transfer as compared to the commercial spacer with FDM being the highest, followed by SLS and Polyjet printed spacers. The mass transfer trend of FDM, SLS, Polyjet and commercial spacers can be related to the model-to-part accuracy of the three 3D printing techniques. In particular, the performance of the FDM spacer can probably be attributable to the greater randomness of the filament diameter which deviates from the designed values (as indicated by the magnitude and standard deviation of the strand eccentricity: see Figure 3.4b). The FDM spacer also differs in having a lower voidage and smaller hydraulic diameter, but this is accounted for in the Re number used in Figure 3.6. The benefit of varying filament diameters mirrors the recent work of Haaksman et al. [76] where spacers with alternating thick and thin filaments were found to be effective in enhancing shear stress on the membrane surfaces. As shown in Figure 3.6b, the power consumption, represented by the power number, increased significantly with Re and the FDM spacers exhibited the highest power numbers (proportional to pressure drop) compared to the SLS and Polyjet spacers. This demonstrates the trade-off between mass transfer and pressure drop in which higher mass transfer typically leads to higher pressure drop. However, considering mass transfer at fixed power number $P_n = 10^6$ (see Figure 3.6c), there was an approximately 18% enhancement in Sh for FDM spacers, 10% for SLS and 3% for Polyjet spacers. It is also noteworthy that at $P_n < 4 \times 10^5$, an extrapolation of the FDM spacer data may lead to a lower mass transfer than the commercial spacer.

The mass transfer correlations for the 3D printed spacers listed in Table 3.5 were developed using the Sherwood relationship in Equation (3-7). As the spacers tested were replicates of the commercial spacer, the hydraulic diameter and length were fixed and thus δ were assigned the value zero and γ were set to 0.33 since the value is approximately constant for laminar and developing turbulent flow. Figure 3.7 provides the overview of the Sh vs Re for spacers of prior works with available mass transfer correlations and data from this work. The highest Sh numbers were obtained with the FDM spacers produced in this work.

Table 3.5: Mass transfer correlations for commercial, SLS, FDM and Polyjet spacers $Sh = \frac{k_{av} d_h}{D} = \alpha Re_h^\beta Sc^\gamma (\frac{d_h}{L})^\delta$

Spacer Types	α	β	γ	δ
Commercial	2.30	0.24	0.33	0.00
SLS	3.34	0.19	0.33	0.00
FDM	1.95	0.32	0.33	0.00
Polyjet	2.76	0.22	0.33	0.00

Figure 3.6: (a) Sherwood number versus Reynold's number (b) Power number versus Reynold's number (c) Sherwood number versus Power number (TMP = 90 kPa, $C_b = 1$ g/L)

Figure 3.7: Plot of Sherwood number versus Reynolds number for prior works and this work

3.1.2.4 Fouling study – Critical flux

Images taken via DOTM were analysed for surface coverage by particles at the first and tenth minute of corresponding constant flux using Image Pro Analyser (Media Cybernetics Inc. USA). Figure 3.8a illustrates the gradual increase in deposition of particles on the membrane surface during flux stepping. When comparing SLS, FDM and Polyjet printed spacers and commercial spacers, the apparent surface coverage of the foulants were lower at the same flux level. The surface coverage rate by latex particles was calculated,

$$\frac{dC}{dt} = \frac{\%Area_{10min} - \%Area_{1min}}{10min - 1min} \quad (3-12)$$

In this study, the critical flux was determined to be the corresponding permeate flux at which the threshold value of 0.03 %/min for surface coverage rate was reached. This threshold value was determined as the consistent point at which rapid increase in deposition occurs across all the experiments [35]. The surface coverage rate and critical flux in the presence of different spacers are shown in Figure 3.8b. In general, an increase in the surface coverage rate can be observed at higher operating flux. The

sigmoid shape of the coverage plot can be explained by the increasing and decreasing deposition of the particles. The accelerating part was due to the rapid increase in particles depositing over an uncovered area whereas the decelerating part was due to the particles depositing over an already covered region resulting in negligible or no detection in the increase of coverage area. The critical fluxes in the presence of different spacers are listed in the table (see Figure 3.8b, insert), with the FDM printed spacer showing the highest critical flux and followed by Polyjet, SLS and commercial spacers. The results here agree with the data in Section 3.1.2.3 where the FDM printed spacer has the greatest improvement in mass transfer thus alleviating the concentration polarization, reducing fouling tendency and increasing the critical flux of latex particles. Another possible reason may be due to the surface finish of the printed spacer. The anisotropic surface finishing of the printed spacer may affect the hydrodynamic conditions of the micro-environment, thus reducing the concentration polarization effect [114]. With reference to Figure 3.5 and Appendix A1, the FDM printed spacer displayed anisotropic surfaces, while Polyjet printed spacer was seemingly semi-anisotropic and SLS and commercial spacers were almost isotropic. Semi-anisotropic is defined as having surfaces with both isotropic and anisotropic surface finishing in this study. Although SLS printed spacer showed a higher critical flux of 83 LMH compared to commercial spacers of 73 LMH, statistically, the average value may be the same at a confidence level of 95% due to the larger deviation observed in the commercial spacer.

Figure 3.8: (a) DOTM analysis of surface coverage by 5 μm latex particles at different flux levels for (i) Commercial spacer (ii) SLS replicate, (iii) FDM replicate, (iv) Polyjet replicate. Image taken at 10th minute and observation area = 473 x 390 μm (b) Effect of spacer types on the coverage rate. (2 g/L latex particles at crossflow velocity of 0.2 m/s)

3.1.2.5 Bacterial attachment on surfaces

Biofouling is a serious problem in SWM which leads to increased energy requirements and reduced product water quality. The site of biofilms in the SWM can be either on the membrane or attached to the spacer matrix. The impact of the biofilms on performance will depend on operation [115, 116] but all surfaces in the flow channel will be susceptible. Therefore it is necessary to assess the affinity of 3D printed spacer/surfaces towards bacteria adhesion, as this is the initial process of biofilm development on surfaces.

As shown in Figure 3.9, the printed flat samples appeared to have greater affinity towards bacteria attachment. The amount of bacteria attached per unit area are 74.4×10^3 , 22.2×10^3 , and 132.7×10^3 Cells/cm² for SLS, FDM, and Polyjet printed samples, respectively. The results showed significant increase in the bacteria attachment on the 3D printed samples compared to the commercial PP sample, which had an average of 5.0×10^3 Cells/cm². The most likely explanation is that the bacteria attachment trend can be correlated to the surface roughness of the samples; as variable attachment profiles are expected on different roughness levels (i.e. macro, micro, and nano scale) [117]. In this study, it appears that the microscale roughness has greater impact on the bacterial attachment than the macroscale roughness (refer to Table 3.4 and Section 3.1.2.2 ii). In contrast, all the surfaces had similar zeta potential of -40 to -60 mV, while there was significant difference in the amount of attached bacteria. The role of surface charge was less important here due to suppressed electrostatic interaction by the elevated ionic strength in the presence of background salinity. Nonetheless, surface wettability, as measured by contact angle, provided interesting findings. The Polyjet and SLS printed surfaces were more hydrophilic (contact angle of $\approx 32.7^\circ/38.2^\circ$ and 36.5°) compared to FDM (CA = 53°) and commercial PP (CA = 80°) (see Table 3.4), however the bacteria attachment was the greatest. This observation

differed from the previously reported bacteria–surface interaction effect where hydrophobic surfaces are typically more prone to bacteria attachment [118]. One possible explanation is that the bacteria surface consists of both hydrophobic and hydrophilic components, and there are complex mechanisms which regulate the overall bacterial hydrophobicity [119]. Under current experimental condition, it is possible that the overall bacteria cell was hydrophilic, hence more bacteria adhered to the hydrophilic samples. Another explanation is that the bacteria attachment is simply controlled by the surface micro-roughness factor only.

The authors understand that biofilm development involves complex mechanisms and even more so in a SWM where the hydrodynamic conditions can be a major factor. In this study, simple bacteria attachment tests were performed on a bench-scale to compare the impact of different surface finishes. The results suggested that bacteria attachment analysis should be considered as an evaluation criteria when selecting spacer fabrication method.

Figure 3.9: Bacteria attachment on different flat samples (n=3). Numbers in [ ] are the magnitude of surface roughness (nm) [see Table 3.4].

3.1.3 Conclusion

From the benchmarking study, it can be concluded that Polyjet was able to give the most accurate representation of the intended design while FDM produced features that showed the greatest deviation from the specifications. In the spacer performance study, all 3D printed spacers by FDM, SLS and Polyjet showed better performance in terms of mass transfer at fixed power consumption and critical flux than the commercial spacer. Despite having greatest deviation from the design, the improvement in mass transfer by the FDM printed spacer was unexpectedly the best among the three 3D printed spacers. This finding implies that spacer with random variation in filaments may be beneficial to mass transfer. Yet, as FDM cannot attain the required spacer design with precision, the recommended approach is to use Polyjet or SLS to fabricate spacer filaments with deliberated randomised geometry. However, due to difficulty in reproducing the randomised geometry of FDM printed spacer, this study has not yet tested this approach. In addition, the surface finish of the spacer was also found to have an effect on critical flux, in particular, the anisotropic surface finish of FDM and semi-anisotropic surface finish of Polyjet.

3.2 Fabricating polypropylene spacers using selective laser sintering (SLS)

The spacer, together with the membrane leafs will eventually be rolled up around the central permeate tube forming the spiral wound membrane modules (SWM) as shown in Figure 1.1. The roll-up generates compressive forces and tightening of the spiral will result in further compression of the spacers [120]. As such, the spacer material has to be both flexible and stiff with high tensile modulus of elasticity. Polypropylene (PP) is the commercially used material for feed spacers due to its low cost, flexibility and excellent chemical resistance properties. Currently, only the powder form of PP can be used in 3D printing. Therefore in Part 2 of this chapter, selective laser sintering (SLS), a powder based 3D printing technique will be employed to fabricate net-typed structures similar to that of a commercial feed spacer using polypropylene powder in this study. As the processing parameters for solid type structures and net-typed structures are different, the optimal processing parameters for printing of net-typed structures using polypropylene materials will be investigated. This work serves as the initial step to explore the suitability of SLS method for printing PP materials which is the representative material of spacers such that more complex structures can be printed in the future.

3.2.1 Materials and methods

3.2.1.1 3D CAD models

Three types of 3D CAD models as shown in Figure 3.10 were created using Solidworks (SOLIDWORKS Corp.). First, a single layer T cross at thickness of 100 μm was created to investigate the optimum powder temperature for sintering of PP powder without any warpage. Second, a square specimen was created to determine the appropriate energy density required for successful printing of PP materials for several uninterrupted continuous layers. Third, a tensile bar was modified to embed the net-typed structure of the spacer in the middle section to examine the mechanical strength

of the printed net-typed structure and thus providing insights to the mechanical strength and stiffness of the printed PP spacer. The purposes for the three CAD models will be explained further in Section 3.2.2.

Figure 3.10: CAD models a) T-cross b) square specimen c) net-typed tensile

3.2.1.2 Equipment and material

SLS is a powder-based additive manufacturing technique, commonly used for the fabrication of polymer parts. The SLS machine used in this paper is the EOSINT P395 SLS machine from EOS which was illustrated in Figure 2.7c. The printing procedure is exactly as described in Section 3.1.1.2.iii. The material used was PP powder from Diamond Plastics GmbH (Laser PP CP2) with an average particle size of 60 μm and density of 0.92 g/cm^3 .

3.2.1.3 Process parameters

To fabricate the net-typed structures similar to that of a commercial feed spacer, optimising the SLS process is critical. Therefore, the SLS process parameters required to obtain the desired spacer characteristics in term of mechanical strength were investigated. The SLS process parameters include layer thickness, orientation, powder bed temperature, scan pattern, and energy density (laser power, scanning speed, scanning distance).

i. Layer thickness and orientation

In order to increase the accuracy of the printed spacers, layer thickness of 0.100 mm, which was the limit of the EOS SLS machine, was selected for printing the spacers. The net-typed structures were oriented such that fine features were positioned flat top down to ensure printability. The orientation and layer thickness are important factors to look into since spacers have fine features and typical commercial spacers with thickness in the range of 28 mils to 34 mils (0.7 mm to 0.9 mm) are considered very thin for 3D printing.

ii. Powder bed temperature

Powder bed temperature refers to the temperature of the powder on the SLS building platform. This temperature is usually set as high as possible but below the melting point of the powder so that less energy is required for the laser to heat up the powder particles during the sintering process. This parameter affects the temperature gradient between the printed part and its surrounding powder. High temperature gradient could result in distortion of parts [121, 122]. The PP powder was first tested for the melting temperature and glass transition temperature using Differential Scanning Calorimetry (DSC) before printing (Figure 3.11). The melting point of the PP powder was determined to be around 163 – 165 °C. Hence, the powder bed temperature range was set between 150 °C and 160 °C in this study.

Figure 3.11: DSC analysis of Polypropylene powder.

iii. Scan pattern

The EOSINT P395 SLS machine requires different parameters setting for different types of scan lines as seen in Figure 3.12. The scan lines present in a solid structure are the hatch lines and contour lines. Among the two, the preeminent scan path in solid parts is the hatch lines hence process parameters for contour lines were kept constant while hatch lines were studied in depth. Whereas for the fabrication of net-typed structures was similar to that of a commercial feed spacer, which has millimetre scale dimensions as low as 0.4 mm, the type of scan lines present was the edge lines. Therefore, the edge line settings were investigated to obtain the optimal parameters for fabricating the net-typed structures.

Figure 3.12: a) Solid square specimen and b) net-typed structure similar to a feed spacer. i) 3D model ii) scan lines of the 3D model at 0.3 mm layer height

iv. Energy density

Continuous printing for several layers may fail when subsequent scanning over the same area causes the sintered part to warp. The recoater would not be able to function properly when hindered by the warped parts and the build would fail. The warping effect can be attributed to the energy density of the laser. The energy density E_L is defined as the energy input per unit volume and is given by the following equation:

$$E_L = \frac{P_L}{v_s h_s d_L} \quad (3-13)$$

where P_L refers to the laser power, h_s is the hatch distance, v_s is the scanning speed and d_L is the layer thickness. These parameters of energy density were varied in order to achieve complete bonding of the powder layers and optimal mechanical properties with flexibility and no warpage [70]. In this study, the parameters setting for the solid structure (square specimen) listed in Table 3.6 were first investigated to

determine the appropriate energy density for printing the PP material. Laser power and scan speed were studied in higher levels as these were the two most significant factors that affected the physical properties of the printed structures. Subsequently, the best parameters for the solid structure were used for SLS processing of the solid sections in the net-typed tensile bars. The parameters for the contour lines were fixed at laser power of 22 W and scanning speed of 3000 mm/s for all runs.

For net-typed structures, edge laser power and edge scan speed values were selected such that the calculated edge energy density would spread over the range from 0.24 J/mm³ to 2.27 J/mm³ for total of 16 runs in increasing energy density. The details of parameters are listed in Table 3.7.

Table 3.6: Process parameters setting for solid structures

HATCH				
Runs	Laser Power (W)	Scan Speed (mm/s)	Scan Distance (mm)	Energy density (J/mm³)
H1	12	6000	0.25	0.08
H2	15	6000	0.25	0.10
H3	18	6000	0.25	0.12
H4	21	6000	0.25	0.14
H5	24	6000	0.25	0.16
H6	27	6000	0.25	0.18
H7	30	6000	0.25	0.20
H8	33	6000	0.25	0.22
H9	12	4500	0.25	0.11
H10	15	4500	0.25	0.13
H11	18	4500	0.25	0.16
H12	21	4500	0.25	0.19
H13	24	4500	0.25	0.21
H14	27	4500	0.25	0.24
H15	30	4500	0.25	0.27
H16	33	4500	0.25	0.29

Table 3.7: Process parameters setting for net-typed structures

EDGE				
Runs	Laser Power (W)	Scan Speed (mm/s)	Scan Distance (mm)	Energy density (J/mm³)
E1	3	300	0.25	0.400
E2	5	300	0.25	0.667
E3	7	300	0.25	0.933
E4	9	300	0.25	1.200
E5	11	300	0.25	1.467
E6	13	300	0.25	1.733
E7	15	300	0.25	2.000
E8	17	300	0.25	2.267
E9	3	500	0.25	0.240
E10	5	500	0.25	0.400
E11	7	500	0.25	0.560
E12	9	500	0.25	0.720
E13	11	500	0.25	0.880
E14	13	500	0.25	1.040
E15	15	500	0.25	1.200
E16	17	500	0.25	1.360

3.2.1.4 Measurement of dimensional accuracy and tensile testing

The dimensions of the printed net tensile bars for each run were first measured for the filament diameter and thickness for at least three different positions along the gauge length using a digital calliper. The printed net tensile bars were then tested for the tensile strength in the Shimadzu universal testing machine. The measurement for each run was repeated at least thrice until consistent results were achieved. The Young's modulus was calculated using the linear portion of the stress-strain curve for each run.

3.2.2 Results and discussion

3.2.2.1 Powder bed temperature optimisation

The optimal powder bed temperature was determined to be 157 °C in the temperature search test conducted. Curling occurred when the powder bed temperature was too low, causing a high thermal gradient between the sintered part and the unsintered powders. On the other hand, caking occurred when the powder bed temperature was too high, leading to the agglomeration of powder particles when powder particle surface started to melt. For this test, 9 CAD models of T-shape crosses, each with single layer height of 0.100 mm, were uniformly positioned on the building platform of the SLS machine. The building platform temperature was initially set at 153 °C then adjusted in small increments (1 - 2 °C) after noting the number of crosses that curled up after laser sintering. At temperature of 153 to 156°C, curling was observed at several positions especially in the areas along the edge due to uneven heat distribution across the building platform. After increment to 157 °C, no more curling was observed. Hence, the optimal temperature was determined to be 157 °C.

3.2.2.2 Selection of SLS parameters for the solid structures

The square specimens fabricated using the parameters in Table 3.6 examined the appropriate energy density to sinter the PP materials for several layers without

warping. The parameters for Runs H1 to H13 were able to produce solid parts with sufficient strength for proper handling and no breakage was observed upon retrieval from the powder bed; the higher the energy density, the greater the strength of the sintered solid parts. Runs H14, H15 and H16 with higher laser power and lower scanning speed led to larger sintering area, which caused over-sintering and partial melting of powder particles. As such, Run H13 with the greatest strength was set as the hatch line parameters for the solid grip section of the net tensile bars. However, during sintering of the edge lines parameters in Table 3.7, it was observed that the solid grips sections tended to warp and this disrupted the building process. This might be due to the difference in the energy density of the solid parts (0.21 J/mm^3) and the net-typed structures (0.24 J/mm^3 to 2.27 J/mm^3). There might be a need to study the compatibility of the hatch and edge lines parameters settings to build a part incorporating both solid and net-typed structures in future. Despite the fact that Run H15 resulted in the over-sintering of the square specimen, it was found that Run H15 was compatible with Run E1 to E16. The initial over-sintering might be due to the larger thickness of square specimens at 2 mm causing greater overlapping of scan paths as compared to the thinner net-typed tensile bars at 0.7 mm. Thus, Run H15 was used for SLS processing of the solid grip sections in the net-typed tensile bars.

3.2.2.3 Evaluation of printed parts

Figure 3.13 shows the images of the printed net tensile bars for each run. Run E9 with an energy density of 0.24 J/mm^3 was insufficient to sinter and fuse the PP powder particles together. As a result, no physical parts were produced for Run E9. It was observed that as the edge energy density of the run increased, the dimensional accuracy of the net-typed spacer structure in the middle portion of the tensile bars reduced.

Figure 3.13: EOS SLS printed PP net tensile bars

The Young's modulus reflects the stiffness of the spacer. A low Young's modulus value would mean low resistance of the material to elastic deformation under load whereas a high Young's modulus would mean having high stiffness. Although there was no study on the specific tensile strength and Young's modulus required for a feed spacer, the feed spacer material must at least be flexible enough to be wrap around a tube. The printed PP net-typed structure for each run showed brittle failure with little or no elongation and hence were concluded as still unacceptable when compared to the commercial feed spacer. The desirable results of the net tensile structures were small dimensional variation, high ultimate strength and considerable young's modulus. Hence, dimensional variation, ultimate strength and Young's modulus against edge energy density (Figure 3.14, 3.15) were plotted for the 16 runs. In Figure 3.14, the Young's modulus and ultimate strength both showed positive relationship with the edge energy density. The correlation between Young's modulus and energy density could be explained by the mechanical property of porous materials, i.e., Young's modulus increases linearly when porosity decreases [123]. Consider the net-typed structure of the tensile bar as a porous material, when energy density increases, it

resulted in the bonding of more materials in a defined envelope hence decreasing the porosity of the printed parts. In addition, as the edge energy density increased, the ultimate strength of the printed net-typed tensile bars also increased.

Figure 3.14: Edge energy density vs. Young's modulus vs. ultimate strength

Figure 3.15: Edge energy density vs. Young's modulus vs. dimension deviation a) spacer height deviation b) filament diameter deviation

It could be observed that the dimensional variations for printable and handle-able PP net-typed structures were very high with the least being around 40% as shown in Figure 3.15. The spacer height deviation might be due to the first and last layer of the printed parts and had no correlation with Young's modulus. The first layer of the

print was thicker as a result of larger sintering depth that penetrated slightly into the bottom supporting powder. Although this effect might not be significant in higher parts, this was apparent in very thin parts of millimetre scale. Furthermore, the thicker last layer of the print might be attributed to the layer thickness fixed by the recoater, i.e., the last layer would have a fixed layer thickness of 100 μm although the actual last layer of the CAD model might be less than 100 μm . A larger than expected spacer height would decrease the amount of membrane area that could be packed into the spiral wound membrane module, thereby lowering the production yield of clean water.

In comparison, the filament height deviation was much larger than the spacer height deviation. Given that the cause of deviation in spacer height was 40% to 100% in the z direction, the filament diameter was affected by the x, y and z directions. The totality of the deviation in all 3 directions would justify the larger filament diameter deviation at 100% to 300% as compared to the spacer height deviation. The results in Figure 3.15 also demonstrated that the dimensional deviation correlated with the Young's modulus via porosity. Higher deviation led to lower porosity of the printed net-typed structures and hence higher Young's modulus. Dimensional inaccuracy of the filament diameters would lead to either larger or smaller than expected filament diameter and thickness which would affect the flow dynamics in the membrane modules. The effects of the filament size are still debatable because on one hand, larger filament diameters may lead to lower voidages, hence increasing the velocity at membrane surface and enhancing mass transfer. On the other hand, it would also block a larger fraction of the membrane causing lower flux [4, 15]. Generally, dimensional deviations can be reduced by using compensation factors taking into account the laser beam offset and possible linear scaling factors in the x and y direction. However, it may be ineffective for this particular net-typed structure as the laser beam diameter (0.5 mm) was already larger than the filament diameter (0.4 mm).

3.2.3 Conclusion

Powder bed temperature search test and parameters optimisation test were conducted to determine the optimal building temperature and process parameters to print PP materials. Both PP solid structures and net-typed structures were successfully printed via SLS. PP net-typed spacer prototypes were evaluated for ultimate strength, Young's modulus and dimensional accuracy i.e. spacer heights and filament diameters. It was found that the higher the energy density used, the higher the Young's modulus and ultimate strength of the printed net-typed tensile bars due to the mechanical property of porous materials, i.e., Young's modulus increases linearly when porosity of the net-typed structure decreases from over-sintering. The desirable results of the net tensile structures were small dimensional variation, high ultimate strength and considerable Young's modulus. However, the Young's modulus of the PP material tended to be correlated to the accuracy of the dimensions of the net-typed spacer prototypes. This raw PP powder might not be suitable for direct printing of feed spacers with the current setting of process parameters. However, pre-treatment of this PP powder or exploring advanced printing strategies may be investigated in future to improve the mechanical properties.

3.3 Summary

In summary, Chapter 3 of this thesis has targeted to establish a link between design, fabrication and surface properties of spacers. To achieve this, the capabilities and feasibilities of 3D printing in spacer fabrication, in particular, the design printability, surface finish and the representative material (PP) printability of spacers were investigated. Eventually, three design considerations for developing 3D printed novel spacers are recommended.

(1) Geometric printability.

The printability of spacer features varies significantly for different 3D printing techniques. Not all 3D printing techniques can print the same design feature with the same precision. Polyjet has the highest precision for both protrusions and depressions features and FDM has the lowest overall precision.

(2) Model to part accuracy.

Not all design features can be additively manufactured with accuracy. A larger dimensional deviation would lead to a misrepresentation of the intended design. Spacer performance may also be incidentally affected by the deviation.

(3) Surface finish.

The surface finish of spacers fabricated by different 3D printing techniques can be smooth, rough, isotropic or anisotropic. The microstructures may have an effect on the hydrodynamic conditions in the micro-environment and thus affecting the concentration polarization. In addition, the tendency of bacteria attachment can also be influenced by the surface finish.

The implication of this research is that factors to be considered in spacer fabrication by 3D printing technique or other methods shall not be limited to the geometry parameter, the accuracy and surface finish associated with the fabrication

methods are equally important. For instance, post-treatment of 3D printed parts may be necessary to reduce the surface roughness as it was found to be a critical factor.

A summary of the suitability of different 3D polymer printing technologies for spacer fabrication considering the accuracy and improvement in spacer performance, is rated in Table 3.8. Nevertheless, it is noteworthy that photocurable resins used in Polyjet are sensitive to light and heat and may degrade over time. On the other hand, materials used in SLS and FDM such as nylon and ABS are more durable than photopolymers. Therefore, the long term usage of photopolymer spacers is suggested to be investigated in future against nylon and ABS spacers. For large scale production of spacers via 3D printing methods, other factors such as the speed of production and the type and cost of materials would also need to be taken into account. Alternatively 3D printing can be used to facilitate preparation of a wide range of novel prototype structures allowing optimisation of spacer design.

Table 3.8: Rating of suitability of 3D polymer printing technologies for different performance in net design spacers versus commercial spacers

Method Performance	Commercial	SLS	FDM	Polyjet
Accuracy of geometry	√√	√√√	√	√√√√
Pressure loss minimisation	√√√√	√√√	√	√√
Mass transfer enhancement	√	√√√	√√√√	√√
Critical flux enhancement	√	√√	√√√√	√√√
Bacteria attachment reduction	√√√√	√√	√√√	√

Note: √: Limited √√: Low √√√: Moderate √√√√: High

CHAPTER 4   NOVEL SPACER STRUCTURES

This chapter focuses on the development and optimization of a novel spacer for SWM via 3D printing to maximise mass transfer while minimising pressure drop and membrane fouling. Part 1 of this chapter examines a series of existing, modified and innovative spacer structures against commercial feed spacers to identify the basis form of spacer structure with the greatest potential. Part 2 of this chapter covers the optimization of the selected structure to improve its performance in mass transfer and pressure drop.

4.1 Evaluation of existing, modified and innovative spacer structures

Three categories of novel spacer structures were tested in this work. The spacer designs were selected to replicate and compare the performance of the 3D printed spacers to the commercial spacer. Novel spacer designs in literature including the zigzag spacer [14] and milled sinusoidal channels spacers [66] that have shown great potential in achieving better performance than commercial spacer were modified and tested. Protrusions were added into the sinusoidal channels to improve shear rate at the concaving part of the sinusoidal wave by introducing dynamic movements. More details of the dynamic protrusions will be covered in Chapter 5. A new design, the saddle design was also proposed in this work considering the potential of sinusoidal/saddle surfaces in generating steady vortices [124, 125]. The CAD models and design parameters of the spacers that were fabricated and tested are shown in Figure 4.1.

Types of spacer tested	Commercial Replicate	Zigzag Spacer	Sinusoidal Spacer	Saddle Spacer
Spacer CAD model				
Design Parameter	- Filament diameter - Mesh length - Hydrodynamic angle	- Peak width - Axial length between bend	- Amplitude - Wavelength - Protrusion length	- Amplitude - Wavelength

Figure 4.1: CAD models and design parameters of the spacers

4.1.1 Materials and methods

UF membranes made of polyethersulfone from GE Osmonics (GE MW) with a nominal molecular weight cut off of 5000 Da were used. The active membrane area was $1.2672 \times 10^{-2} \text{ m}^2$. The same fabrication methods, FDM, Polyjet and SLS were employed to fabricate spacers in this work. All the other chemicals, materials and experimental procedures used in this study were the same as that in Section 3.1.1.

4.1.2 Results and discussion

4.1.2.1 Dimensional accuracy

Dimensional measurements with the digital caliper were conducted to determine the accuracy of 3D printed spacers. The dimensional errors of FDM, Polyjet and SLS fabricated spacers are listed in Table 4.1. Similar to results reported in Section 3.12.2(i), FDM fabricated spacers showed the largest percentage error compared to the designed CAD model while Polyjet and SLS fabricated spacers both demonstrated close adherence to the design. The accuracy of FDM was limited by the extrusion nozzle size and thus was not used in the fabrication of saddle and sinusoidal flutter spacers.

Table 4.1: Dimensional accuracy of 3D printed spacers. a) replicate b) zigzag spacer c) sinusoidal flutter spacer d) saddle spacer

a)		Filament diameter/mm			Mesh length/mm			Hydrodynamic Angle/ °			Height/mm		
Spacer type	AM technique	Designed	Actual	% error	Designed	Actual	% error	Designed	Actual	% error	Designed	Actual	% error
Replicate	FDM	0.40	0.89	121.75	2.90	2.81	3.02	90	89.0	1.11	0.7	0.9	28.57
	Polyjet		0.64	58.85		2.91	0.34		90.0	0.00		0.7	1.43
	SLS		0.47	17.70		2.97	2.50		90.3	0.33		0.8	17.14
Commercial	-	-	0.40	-	-	2.90	-	-	90.0	-	-	0.7	-

b)		Peak width / mm			Axial bend length / mm		
Spacer type	AM technique	Designed	Actual	% error	Designed	Actual	% error
zigzag	FDM	1.73	1.48	14.45	10.39	9.85	31.21
	Polyjet		1.41	18.50		10.55	9.25
	SLS		1.60	7.51		10.58	10.98

c)		Amplitude / mm			Wavelength / mm		
Spacer type	AM technique	Designed	Actual	% error	Designed	Actual	% error
Sinusoidal flutter	Polyjet	6.00	6.10	1.67	24.00	23.90	0.42
	SLS		6.20	3.33		24.20	0.83

d)		Amplitude / mm			Wavelength / mm		
Spacer type	AM technique	Designed	Actual	% error	Designed	Actual	% error
saddle	Polyjet	0.38	-	-	3.00	2.88	4.00
	SLS		-	-		2.72	9.33

4.1.2.2 Fouling studies- critical flux determination

From Figure 4.2, it was observed that there was negligible deposition below critical flux whereas deposition became apparent near critical flux at 85 l/m²h for the commercial spacer. A higher flux exacerbated latex particle deposition to cover an extensive area of the membrane surface. The effect of spacer types on the coverage rate was compared and is shown in Figure 4.3.

Figure 4.2: DOTM images of 5 μ m latex particles deposition when using the commercial spacer a) below critical flux at 65 l/m²h, b) Near critical flux at 85 l/m²h, c) Above critical flux at 113 l/m²h d) Above super critical flux at 165 l/m²h (i) at the first min of image (ii) at the tenth min of image

Figure 4.3: Effect of spacer types on the coverage rate. (2 g/L 5 μ m latex at cross flow velocity of 0.2 m/s)

Both Polyjet and SLS fabricated spacer replicates demonstrated higher critical flux than the commercial spacer at the threshold value of 0.03 %/min coverage rate indicated by the dotted line in Figure 4.3, indicating that latex particles deposited at a slower rate on the membrane surfaces. SLS fabricated spacers were discovered to perform better than Polyjet fabricated spacers with the higher critical flux. These two findings are in agreement with critical flux experiments reported in Section 3.1.2.4. A summary of the critical fluxes at the threshold coverage rate of 0.03 %/min for each type of spacer is listed in Table 4.2. Among the novel spacer designs, the saddle and zigzag design demonstrated higher critical flux at 85-100 l/m²h but also with higher percentage error due to irregular flow distribution in these two types of spacers.

Table 4.2: Summary of the critical flux for different spacer types

Spacer Types	At threshold of 0.03 %coverage /min
	Critical Flux (L/m ² h)
Commercial	93.5 ± 17.4%
Polyjet Replicate	94.3 ± 4.3%
SLS Replicate	118.7 ± 10.8%
Novel Spacer Designs	
Polyjet Sinusoidal Flutter	67.7 ± 17.5%
SLS Sinusoidal Flutter	69.0 ± 2.1%
Polyjet Alt Saddle	87.5 ± 28.3%
Polyjet Zigzag Spacer	102.5 ± 51.7%

4.1.2.3 Pressure drop and mass transfer performance

The pressure drop along channels was measured by a digital pressure gauge. According to Da Costa [4], pressure drop along the channels can be attributed to viscous drag on spacer, form drag, kinetic losses due to change in flow direction and viscous drag on channel walls. Figure 4.4 compares the pressure drop along channels for different type of spacers. The saddle spacer portrayed the largest pressure drop as a result of the closely knitted tortuous flow path which increased the viscous drag on spacer and kinetic losses due to continual changes in flow directions. The conventional net type design exhibited the second largest pressure drop. Following next with lower pressure drop were the zigzag and sinusoidal flutter design. It was also noticed that the pressure drop behaviour of Polyjet and SLS replicates matched that of the commercial spacer. SLS fabricated spacers led to slightly higher pressure drop in contrast to Polyjet printed spacer. This is in accordance with results reported in Section 3.1.2.3. Subsequently, considering the trade-off between pressure drop and flux behaviour shown in Figure 4.5, SLS zigzag and SLS sinusoidal flutter both performed better than the commercial spacer with higher flux and lower pressure drop.

Figure 4.4: Pressure drop along the channels for different spacer types. (TMP = 20 kPa and $C_b = 1$ g/L)

Figure 4.5: Flux versus transmembrane pressure (TMP) for different spacers. ($Q = 1.0$ L/min and $C_b = 1$ g/L)

The mass transfer and pressure drop results were subsequently plotted in the dimensionless form represented by Sherwood number and Power number. Using the commercial spacer as the benchmark for comparison of 3D printed replicates and novel spacer designs, the spacers fabricated were considered to bring about an improvement if the Sh were higher than the commercial spacer at a fixed Pn value. From Figure 4.6, SLS replicate and both SLS and Polyjet sinusoidal flutter have shown improvement and better performance than the commercial spacer when Pn is more than 10^5 . Increasing pressure drop increased the mass transfer for all of the spacer designs except for the saddle design. The saddle design demonstrated slight decrease in mass transfer with increasing pressure drop. This was an interesting observation that implied the possible elimination of trade-off which needed to be further validated with CFD modelling.

Figure 4.6: Plot of Sherwood number against Power number for different spacers. ($Q = 1.0$ L/min and $C_b = 1$ g/L)

4.1.3 Conclusion

A series of existing, modified and innovative spacer structures from prior literature was fabricated by 3D printing technology and tested against commercial feed spacers and its replicate, to preliminarily identify the basis form of spacer structure with the greatest potential. SLS, Polyjet sinusoidal flutter and SLS replicate have shown improvement in terms of higher flux and lower pressure drop. The sinusoidal flutter designs proved to generate higher flux, lower pressure drop and higher mass transport in contrast to the commercial spacer. Therefore, the sinusoidal design was eventually selected for further investigation by varying the design parameters to obtain the optimal design.

4.2 Structure optimisation of sinusoidal spacers

Having selected the basis form of spacer structure with the greatest potential to surpass the performance of commercial spacer, this part of Chapter 4 focuses on the optimization of the geometry of the sinusoidal spacer to improve its performance in mass transfer and pressure drop. Two sequential stages of optimization were conducted to reduce the number of runs. Stage 1 optimisation is for pinpointing the optimal spacer amplitude and protrusion length to maximise mass transfer while Stage 2 optimisation is to identify the optimal spacer wavelength to minimise pressure drop.

4.2.1 Stage 1 optimisation via Taguchi's method: To improve mass transfer

Taguchi's method was chosen to find the optimal parameters of the novel spacer in order to optimise performance characteristics. Uncontrollable and controllable factors were introduced in the Taguchi's method for parameter design in order to ensure the design of the spacer could perform consistently and were robust to variation caused by uncontrollable factors such as the feed concentration and the cross flow velocity in the feed channel. In this work, two controllable factors pertaining to the geometry of the spacer were selected, i.e. the ratio of the wave amplitude to the mesh length of the spacer unit cell and the ratio of the protrusion length to the mesh length. Two uncontrollable factors, the Reynolds range and the feed concentration, which could possibly cause deviation to the spacer performance, were chosen. The factors with different levels and their corresponding parameter values are summarised in Figure 4.7. The objective of this parameter design was to find the best run under the different combinations of the levels of controllable factors, such that (1) the response value, i.e, the Sherwood number would be maximised, (2) the value of the response would be very stable with minimal influence by the uncontrollable factors.

Figure 4.8 shows the unit cell of the spacers produced under the different combinations of the levels of controllable factors, denoted by the run number S1 to S9.

The commercial spacer and the slit (empty channel) were also included in the run to act as a benchmark for the mass transfer performance of the spacers. For each run, $n=10$ observations were taken under different levels of uncontrollable factors.

Figure 4.7: Parameter design for sinusoidal spacers (a) Schematic diagram of a unit cell of sinusoidal spacer. (b) Parameter design table

Figure 4.8: Unit cell of the spacers from S1 to S9

4.2.1.1 Materials and methods

All the spacers were printed using Polyjet as Polyjet offers multi-material printability which was required in the following study in Chapter 5. Fabrication methods and material are the same as that in Chapter 3. The determination of the effective membrane area of S1 to S12 is illustrated in Appendix A2. The surface area of the spacers S_{sp} was obtained from the properties of the drawn CAD model from SOLIDWORKS software. The geometrical characteristics of the 3D printed spacers are listed in Table 4.3.

Table 4.3: Geometrical characteristics of spacers

Spacer	Effective membrane area (m ²)	m _{sp} (g)	V _{sp} (10 ⁶ m ³)	S _{sp} (m ²)	ϵ	d _h (m)
S1	0.00766	3.31	2.79	0.0120	0.721	0.000866
S2	0.00766	3.37	2.85	0.0146	0.716	0.000799
S3	0.00766	3.38	2.85	0.0156	0.715	0.000777
S4	0.00927	3.23	2.73	0.0125	0.728	0.000862
S5	0.00927	3.54	2.98	0.0151	0.702	0.000773
S6	0.00927	3.55	3.00	0.0160	0.700	0.000752
S7	0.00912	3.34	2.82	0.0136	0.718	0.000824
S8	0.00912	3.55	3.00	0.0163	0.701	0.000747
S9	0.00912	3.65	3.08	0.0172	0.692	0.000720
S11	0.00732	3.21	2.71	0.0135	0.730	0.000839
S12	0.00817	3.29	2.78	0.0130	0.722	0.000843
Commercial	0.00973	N.A.	N.A.	N.A.	0.876	0.000856
Slit	0.0100	N.A.	N.A.	N.A.	1.00	0.00379

4.2.1.2 Results and discussion

(i) Effect of wave amplitude on spacer performance (S1, S4, S7)

The three spacers S1, S4, S7 were compared against the commercial spacer in the ultrafiltration of dextran molecules in order to study the effect of wave amplitude on the spacer performance. The mass transfer coefficients and pressure loss along the channel for the different spacers were presented in terms of dimensionless Sherwood number Sh and power number Pn. The detailed calculations for Sh and Pn are provided in Section 3.1.1.4.

Figure 4.9: Pressure drop and mass transfer performance for S1, S4 and S7. (a) Sherwood number versus Reynold's number (b) Power number versus Reynold's number (c) Sherwood number versus Power number (TMP = 100 kPa, Dextran T500 feed = 1 g/L)

Comparing S1, S4, S7 at Reynolds range less than 70 as shown in Figure 4.9a, S7 demonstrates the highest mass transfer followed by S4 and lastly S1. These results coincided with Xie et al.'s work which reported that among the different amplitude of sinusoidal channels that they tested, the flux performance of the spacer with higher amplitude was the best while the sinusoidal channels with amplitude=0 gave the lowest permeate flux [66]. When compared to the commercial spacer, at $Re < 50$, S4 and S7 had a higher mass transfer than the commercial spacer while the performance of S1 is similar to that of the commercial spacer. At $50 < Re < 120$, only S7 performed better than the commercial spacer. At $Re > 120$, the mass transfer of the commercial spacer overtook the three spacers eventually.

Generally, as Re increases, the power number increases exponentially. The spacer with the highest amplitude has a more tortuous path that provides a greater resistance to water flow. As such from Figure 4.9b, it can be observed that S7 had the highest power number, signifying the greatest pressure loss along the channel as compared to the other spacers. S4 had a slightly higher pressure loss than the commercial spacer. S1 with most of the filaments being parallel to the flow provided the least flow resistance and thus had the smallest power number as compared to the commercial which has filaments placed at an angle to the flow. A good spacer should be able to achieve a high mass transfer at a low pressure drop. From the Sh vs Pn plot in Figure 4.9c, the performance of the S4, S7 spacers were better than the commercial spacer with higher mass transfer at lower power number.

(ii) Determination of the best design-Marginal graph method

From the mass transfer and pressure drop experiment using dextran T500, the results for all the runs are tabulated in Table 4.4. To identify the best run from the parameter design table, the marginal graph method was used to analyse the results from all the runs such that the SN ratio was maximised and the mean response $\bar{y}$ was

optimum.

The mean response $\bar{y}$ over the n observations for each run can be calculated from:

$$\bar{y} = \frac{\sum_{i=1}^n y_i}{n} \quad (14)$$

The variation of the observations in each run was measured by the signal-to-noise ratio SN . In this case where a larger Sherwood number as the response value was favorable, the SN can be expressed as:

$$SN_L = -10 \log_{10} \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right) \quad (15)$$

A larger SN indicates a smaller variation and thus a more robust and stable run.

Table 4.4: Results from Taguchi's method

Run	Outer Array		Response y										$\bar{y}$	SN_L
	A	B	30	50	70	100	150	30	50	70	100	150		
			1	1	1	1	1	3	3	3	3	3		
S1	1	1	249.6	305.4	348.9	401.7	471.5	262.4	340.9	405.0	486.1	598.3	387.0	43.9
S2	1	2	270.8	310.1	339.1	372.8	415.2	284.3	360.0	420.6	496.0	598.3	386.7	44.1
S3	1	3	313.0	358.8	392.7	432.3	482.3	329.3	413.9	481.2	564.5	676.8	444.5	45.3
S4	2	1	298.9	335.5	362.0	392.4	430.0	247.6	295.0	331.0	374.1	429.8	349.6	43.5
S5	2	2	257.3	291.0	315.6	343.9	379.3	249.2	309.0	356.0	413.7	490.8	340.6	43.2
S6	2	3	304.3	345.8	376.1	411.2	455.1	298.0	355.5	399.4	451.8	519.8	391.7	44.5
S7	3	1	330.0	378.4	414.1	455.7	508.1	323.2	401.0	462.3	537.4	637.7	444.8	45.4
S8	3	2	289.3	345.1	387.5	438.2	504.0	314.1	382.3	435.2	499.2	583.4	417.8	44.9
S9	3	3	315.4	363.3	398.8	440.3	492.8	315.3	389.4	447.5	518.5	613.1	429.4	45.1
Commercial			246.2	313.8	368.2	436.2	528.9	N.A.	N.A.	N.A.	N.A.	N.A.	378.7	46.7
Slit			150.3	161.9	170.1	179.2	190.1	N.A.	N.A.	N.A.	N.A.	N.A.	170.3	40.6

Figure 4.10 shows the marginal graphs for $\bar{y}$ and SN values of Factor A and B plotted using the experiment results. The x-axis of each marginal graph represents the three levels, i.e. 1, 2, 3 of each uncontrollable factor. The value on the y-axis was calculated from the average of $\bar{y}$ values or SN values of the runs in which the factor was of the same level. Take for example the marginal graph for SN and $\bar{y}$ of Factor B

at level 1, the y-axis value for SN and $\bar{y}$ can be respectively calculated using $(SN_{S1} + SN_{S4} + SN_{S7})/3$ and $(\bar{y}_{S1} + \bar{y}_{S4} + \bar{y}_{S7})/3$. From the marginal graph on mean response $\bar{y}$, in order to obtain the maximum $\bar{y}$, the factors should be set as A3 B3. Similarly, from the marginal graph on SN ratio, in order to obtain the maximum SN, the factors should be set as A3 B3. Since both factor settings are the same, the combinations of A3 B3 which corresponds to Run S9, will result in the maximum SN and maximum $\bar{y}$ simultaneously. Therefore, Run S9 is identified as the best spacer design that gives the highest Sherwood number with minimal variation among the nine spacer design tested.

Figure 4.10: Marginal graphs to identify best run. (a) $\bar{y}$ for factor A (b) SN for factor A (c) $\bar{y}$ for factor B (d) SN for factor B

(iii) Pressure drop and mass transfer performance for S1 to S9

It is important to note that the above Taguchi's optimisation method only considers the response of the Sherwood number which represents the mass transfer of the spacers. Yet, it is also known that there is a trade-off between mass transfer and pressure drop. Figure 4.11 shows the plot of the pressure drop and mass transfer performance of the 9 spacers, S1 to S9 against the commercial diamond spacer. The yellow zone in Figure 4.11c indicates the favorable zone with high Sh and low Pn for the spacer to perform in. After taking into account the pressure drop represented by power number of the spacers (see Figure 4.11b), Run S9 is no longer the best design. The high mass transfer of Run S9 was nullified by its high pressure loss as shown in Figure 4.11. Run S3 emerged as the best performing spacer with an improvement of 7% in Sh as compared to the commercial spacer at $Pn = 10^5$. Nonetheless, at $Pn > 2 \times 10^5$, Run S3 and all the other spacers are performing worse than the commercial spacer. Based on typical seawater RO conditions with feed side pressure drop < 0.6 bar/m, Reynold number < 200 and an approximate feed concentration at 35000 ppm NaCl, the estimated maximum allowable power number for seawater RO operations is 10^6 . Therefore, if the power number is fixed at 10^5 and even lower, the mass transfer of most of the spacers would still be better than the commercial spacers.

Figure 4.11: Pressure drop and mass transfer performance for S1 to S9. (a) Sherwood number versus Reynold's number (b) Power number versus Reynold's number (c) Sherwood number versus Power number (TMP = 100 kPa, Dextran T500 feed = 1 g/L)

4.2.2 Stage 2 optimisation via Taguchi's method: To reduce pressure drop

Stage 1 optimization reported in Section 4.2.1 was able to narrow down the the spacer geometry variation in amplitude and protrusion length to improve the mass transfer performance. However, the improvement in spacer performance was not as great due to the relatively higher pressure drop. To further enhance the mass transfer considering the trade-off in pressure drop, a Stage 2 optimization of the spacer designs (see Figure 4.12) was carried out, targeting to reduce the pressure drop while maintaining the high mass transfer of the novel spacers by increasing the wavelength (Factor E) of the two selected best designs, i.e., Run S9 from Stage 1 Taguchi's method and Run S3 from the Sh vs Pn plot.

Response					
Sherwood number					
Controllable Factor	Levels				
	1	2	3		
A: Amplitude/Length A/L	0	-	$1/3=0.33$		
E: Wavelength (mm)	5	10			
Uncontrollable Factor			Levels		
C: Reynolds range	30	50	70	100	150

Figure 4.12: Parameter design table for Stage 2 optimisation

4.2.2.1 Results and discussion

Similar to Section 4.2.1.2 (ii), the results from ultrafiltration of dextran are tabulated in Table 4.5 and the marginal graphs for factor A and E were plotted and are shown in Figure 4.13. The results from the Stage 2 Taguchi's method concluded that the factors A3 E2 provided the highest response value and SN ratio, indicating that Run S12 was the best spacer design. This conclusion is found to be in accordance with the experiment plot of Sh against Pn in Figure 4.14 after considering the pressure drop of the spacer. S12 showed an improvement of 18% at power number, $Pn=10^6$, and 25% at $Pn=10^5$ in mass transfer compared to the commercial spacer. If extrapolated to $Pn=10^4$, the improvement in Sh for S12 could go up to 33%.

Table 4.5: Results from Stage 2 Taguchi's method

Run	Outer Array C		Response y							$\bar{y}$	SN _L
	A	E	30	50	70	100	150				
S3	1	1	313.0	358.8	392.7	432.3	482.3	395.8	47.7		
S9	3	1	315.4	363.3	398.8	440.3	492.8	402.1	47.8		
S11	1	2	280.3	335.5	377.6	428.2	493.9	383.1	47.2		
S12	3	2	327.8	407.2	470.2	548.1	653.0	481.3	48.9		

Figure 4.13: Marginal graphs to identify best run. (a) $\bar{y}$ for factor A (b) SN_L for factor A (c) $\bar{y}$ for factor E (d) SN_L for factor E.

Figure 4.14: Plot of Sherwood number against Power number for S3, S9, S11 and S12. (TMP = 100 kPa, Dextran T500 feed = 1 g/L)

4.2.3 Conclusion

To conclude Section 4.2, two sequential stages of Taguchi's method for parameter design were conducted to optimise the sinusoidal spacer design derived in Section 4.1. Stage 1 Taguchi's method allowed us to narrow down the design parameters to obtain the best parameter values to enhance mass transfer. Pressure drop was found to be a limiting factor in the enhancement of mass transfer. Stage 2 Taguchi's method allowed us to focus on reducing pressure drop while maintaining the parameters values obtained from first stage, to further enhance the mass transfer while reducing pressure drop. Eventually, Run S12 was determined to be the best spacer design that surpassed the performance of the commercial spacer.

4.3 Summary

To summarise, Chapter 4 focused on the development and optimisation of novel spacer structure to improve mass transfer and pressure drop. In Part 1 of this chapter, the commercial replicate, zigzag spacer, sinusoidal flutter spacer and saddle spacers were investigated for their performance in mass transfer and pressure drop through ultrafiltration of dextran and fouling tendency in critical flux measurements using DOTM. The sinusoidal spacer emerged as the design with the greatest potential and thus was selected to undergo further optimisation of the structure.

In Part 2 of Chapter 4, the Taguchi's method was used to design the parameter of the selected sinusoidal spacer and to ultimately identify the best spacer design that would give us a high Sherwood number as the response value. Stage 1 optimisation looked into varying the amplitude and wavelength of the sinusoidal spacer to improve the mass transfer. From Stage 1 optimisation, Run S9 was identified as the best spacer design in this stage that gave the highest Sherwood number with minimal variation among the nine spacer designs tested. When taking into account pressure drop, Run S3 overtook Run S9 as the best performing spacer in Stage 1 with an improvement of 7% in Sh as compared to the commercial spacer at $Pn = 10^5$. Nonetheless, this improvement was minimal, consequently, Stage 2 optimisation was carried to reduce the pressure drop of the two potential designs S9 and S3 by varying the wavelength of the sinusoidal design. Ultimately, in terms of mass transfer and pressure drop performance, Run S12 was determined to be the overall best spacer design that surpassed the performance of the commercial spacer with an improvement of 18% at power number, $Pn=10^6$, and 25% at $Pn= 10^5$ in mass transfer.

CHAPTER 5   SMART MULTI-MATERIAL SPACERS

This chapter focuses on the development of a smart multi-material spacer fabricated via 3D printing to improve hydrodynamic conditions between the fluid and the membrane surface. A range of materials with different Shore hardness were used to print the optimal spacer design identified in Chapter 4 and thereafter evaluated for their performance in reducing membrane fouling.

5.1 Technical aspects of the spacer design

The smart multi-material spacer investigated in this work took the structure and dimensions of the overall best spacer design S12 obtained in Chapter 4. However, one thing to note was that this smart multi-material spacer was not just limited to the geometry of S12, it might also be applicable to other spacer geometries. To be specific, the technical aspects of the smart multi-material spacer are described below:

(i) Structure

The unit cell of the smart multi-material spacer is shown in Figure 5.1. There were two levels of structure in this invention: (1) primary structure; and (2) secondary structure. Multiple unit cells of the spacer can be combined to form a feed spacer of desired size. For the primary structure, it was designed in sinusoidal curves which could promote the mixing or vortices on the membrane surface and hence decreased the concentration polarization. The primary structure might also be in any wavy, corrugating or zigzagging patterns. There were also bridging filaments that would connect the unit cells together to form a whole spacer. The secondary structure was on the primary structure. In this design, the secondary structure could be a rod-like structure or vortex generator-like structures on the sinusoidal curve (see Figure 5.2). The micro structure might have generally circular, elliptical, rectangular or helical cross sections etc. The positions of the secondary structure could be along the centre, upper or bottom part of the primary structure cross-sections as shown in the side view

cross section in Figure 5.1.

Figure 5.1: The structure of novel spacer in one unit cell

Figure 5.2: Possible designs of the multi-material responsive spacer

(ii) Dimensions

The primary structure can be characterised by amplitude (A), diameter (D), wavelength (λ) and length (L) between the sinusoidal curves on the primary structure. The secondary structure can be characterised by diameter (d_f), length (L_f) of the rod on the secondary structure and the interval (w) or number (n) of secondary structures, and

as shown in Figure 5.1. One of the advantages of using CAD design is that these dimensions could be changed easily and the design could be rapidly prototyped via AM technology. For this particular study, the technical details of these parameters followed that of Run S12 in Chapter 4 as listed in Table 5.1.

Table 5.1: Design dimensions for the novel spacers fabricated for experimental use.

Spacer	Primary Structure				Secondary Structure		
Parameter	A (mm)	D (mm)	λ (mm)	L (mm)	d_f (mm)	L_f (mm)	w (mm)
Dimension	1.0	1.0	10.0	3.0	0.4	2.10	2.50

(iii) Materials

The primary structure of the spacer serves as the base material unit with rigid components while the secondary structures serve as the soft material unit with flexible components. The base material unit and the soft material unit were printed simultaneously into the intended 3D configuration of the spacer by photopolymerisation of photopolymer. Objet500 Connex3 (Stratasys Ltd) was used to print the multi-material spacers. The material units are acrylic based photopolymer with a wide range of Shore hardness under ASTM D2240 type A and type D scales. Type A scales were used for measurement of softer polymers whereas type D scales were for harder polymer. The higher the Shore hardness, the harder and more inflexible the materials. Also, these materials are acrylic based photopolymer with a wide range of tensile strength and elongation at break. Tensile strength was used for measurement of the strength of hard polymers whereas elongation at break was used for measurement of the elasticity of soft polymer. The higher the tensile strength, the more rigid and more robust the materials while the larger the percentage of elongation at break, the more flexible and more elastic the materials. Different mechanical properties in a single spacer can be achieved by selecting materials of different Shore hardness or different tensile strength and elongation at break for the primary structures and

secondary structures.

To compare the effectiveness of the smart multi-material spacers in reducing membrane fouling, a single material rigid spacer of the same design and multi-material spacers were both studied under the same experiment conditions. Table 5.2 shows the list of materials with a range of Shore hardness for the secondary structure that were used in this study. Veroclear was used as the rigid primary structure for all the spacers while the secondary structure were respectively printed with Veroclear, DM-9095, DM-9070, DM9050 and Tangoblackplus. The spacer with Veroclear as both primary and secondary structures was the single material rigid spacer which acted as a control in the bentonite fouling experiment.

Table 5.2: Shore hardness scale of different materials for the secondary structure

Shore Hardness Scale		Extra Soft		Soft		Medium Soft		Medium Hard		Hard		Extra Hard			
Materials	Shore A Shore D	10	20	30	40	50	60	70	80	90	100				
Veroclear															
DM-9095															
DM-9070															
DM-9050															
Tangoblackplus															

5.2 Bentonite fouling

The spacers were printed with a length of 278 mm, width of 35 mm, height of 1 mm and placed in a flat channel test cell. The same experimental setup as described in Chapter 3 was used. One difference is that in this experiment, a peristaltic pump, instead of a gear pump, was used to create pulsating flow through the spacer, which brought about dynamic movement of the protrusions. The angular movement of the protrusion, θ_p was recorded down with a video camera at a speed of 60 fps (see Figure 5.3). Bentonite suspension at 3 g/L and molecular weight of 180.1 g/mol was used as the feed solution to simulate accelerated fouling condition. An average transmembrane pressure (TMP) of 50-60 kPa was used in the experiment.

Figure 5.3: Images of the angular movement of secondary structure of the multi-material spacer

Figure 5.4 plots the angle of protrusion in each frame over a period of 2.5 seconds. Only DM-9050 and Tangoblackplus showed differences in the angular movement of the protrusion under an average flow rate of 0.8 L/min. This indicates that the hydrodynamic forces at 0.8 L/min were not yet strong enough to cause greater angular movement of the protrusions.

Figure 5.4: Plot of angles of protrusion against frame number at 60 fps

Figure 5.5: Flux reduction over time due to membrane fouling

From Figure 5.5, all the 3D printed novel spacers achieved a lower flux decline rate (i.e., rapid fouling in the first 10 mins) and higher stabilised flux as compared to the commercial spacer. This further affirms the exceedingly good performance of the S12 geometry in reducing membrane fouling in addition to the enhancement of mass transfer at low pressure drop reported in Chapter 4. When compared to the single rigid material spacer Veroclear, all the smart multi-material spacers with protrusion made from DM-9095, DM-9070, DM9050 and Tangoblackplus demonstrated lower flux decline rate and higher stabilised flux due to bentonite fouling. In particular, the dynamic movements under pulsating flow of protrusions made from DM9050 and Tangoblackplus showed the best performance in fouling control. The flexible properties on the selected section of the spacer allows dynamic movement under varying flow rates, which created a “sweeping” effect that disrupt the boundary layers and prevented foulants from accumulating near spacer filaments and on the membrane surface, thereby mitigating fouling. The greater flux drop due to fouling by single

material static spacer, Veroclear, might be due to localised dead spots with poor mass transfer that initiated fouling. This problem was alleviated with the smart multi-material spacer which created a “sweeping effect” using flexible sections of the spacers.

5.3 Summary

To summarise, this chapter has studied the invention of a spacer with more than one type of materials (flexible and rigid materials) that could respond to varying flow rate. The benefits of the proposed spacer included reduced fouling and energy demand through reduction of membrane fouling. Membrane fouling could cause severe flux decline and hence required higher transmembrane pressure to maintain the same flux. Severe membrane fouling might require intense chemical cleaning or membrane replacement, which further increased the operating costs of a desalination plant. The results from this study indicated that a spacer with flexible filaments had a beneficial effect on fouling reduction.

CHAPTER 6   CONCLUSION AND FUTURE WORK

This chapter summarises all the work carried out for the completion of this thesis. Future works in relation to this project are also proposed.

6.1 Conclusion

The key contributions of the research are elaborated as follows:

(i) Analysis of current state-of-art, problems, potential solution and research gap

The role of 3D printing in membrane research has been critically reviewed for the first time in this field, highlighting the research gap and potential of 3D printing technology in fabricating future membrane modules and its components.

(ii) Establishing the link between design and fabrication of spacers with 3D printing technology

The first detailed discussion on the link between design, fabrication and surface properties of the 3D printed spacers were presented. The effect of different 3D printing techniques resulting in spacer geometry and surfaces differences and their effect in mass transfer, pressure loss and fouling tendency were evaluated. Design recommendations for 3D printing of spacers were provided. The randomness, represented by the strand eccentricity, of the spacer geometry and the microscale surface roughness of the spacers were found to have substantial impact on the mass transfer performance and biofouling potential of the spacers respectively.

The printability of the representative material of feed spacers, polypropylene (PP), for spacer prototypes via selective laser sintering (SLS) was investigated through the optimisation of SLS process parameters. Net-typed PP spacers were successfully fabricated. However, the Young's modulus of the PP material was found to be correlated to the accuracy of the spacer dimensions. Chemical pre-treatment of the

virgin PP powder was suggested to overcome the problem of low Young's modulus and high dimensional inaccuracy.

(iii) Development and optimisation of novel spacer structure to improve mass transfer and pressure drop

Different spacer designs from literature were successfully 3D printed with adequate resolution and evaluated for their performance in mass transfer, pressure drop and critical flux behaviour. The sinusoidal flutter spacer was identified as the basis form of spacer structure with the greatest potential to surpass the commercial diamond spacer and thus was selected to be further optimised via Taguchi's method. Stage 1 optimisation managed to eliminate the different levels of combinations of spacer design based on high mass transfer while Stage 2 optimisation looked into minimising pressure drop. Eventually, Taguchi's method pinpointed S12 as the best spacer design in Chapter 4, which showed an improvement of 18% in Sherwood number at power number, $Pn = 10^6$, and 25% at $Pn = 10^5$ compared to commercial diamond spacer.

An overall comparison of the spacer works in Chapter 3 and Chapter 4 were summarised in the plot of Sherwood number against Power number in Figure 6.1. Both C3-FDM and C4-S12 had comparable excellent performance as compared to the commercial spacers. Based on the results in Chapter 3, at $Pn = 10^6$, FDM printed spacer had the largest enhancement in Sh at approximately 18%, 10% for SLS and 3% for Polyjet spacers. Despite being printed with Polyjet, S12 from Chapter 4 was able to achieve a similar 18% improvement in Sh as compared to the commercial spacer at the same power number. S12 was therefore expected to attain more than 18% enhancement if printed with FDM or SLS. However, as summarised in Table 3.8, due to the low model to part accuracy of FDM, the second best alternative would be SLS. Therefore, in this section pertaining to the development of novel spacer structure, the conclusion that can be drawn from this thesis work was that S12 was the best spacer design and

the current best 3D printing technique that could produce great spacer performance with good precision would be SLS.

Figure 6.1: Overall plot of Sherwood number against Power number for spacer works in Chapter 3 and Chapter 4. (C3 refers to Chapter 3 while C4 refers to Chapter 4.)

(iv) Innovative spacer material to reduce fouling

The multi-material capability of 3D printing technology was first explored in this field. Conventional spacers and the novel spacers mentioned in Chapter 2 are static spacers. In this section of the thesis work, a multi-material spacer taking on the structure and dimensions of S12, which was the optimal design determined in Chapter 4, was invented. It comprised a range of hard-soft materials such that specific sections of spacer could have flexible (i.e., protrusions) or rigid (i.e., main structures or filaments that provide spacing between membrane leafs and define the height of the flow channel) properties. The multi-materials responsive spacer with Tangoblackplus as the flexible material allowed dynamic movements of the protrusions under varying crossflow rate, which created a “sweeping” effect that disrupted the boundary layers

and prevented foulants from accumulating near spacer filaments and on the membrane surface, thereby mitigating fouling. The flux decline of an accelerated membrane fouling by bentonite particles was found to be lowered by 7.6% as compared to the commercial spacer and 5.2% when compared to the single rigid material spacer. This indicated that a spacer with flexible filaments had a beneficial effect on fouling reduction. However, further optimisation work would be required to improve the dynamic spacers for fouling control.

All these favourable findings have provided a number of insights to the research and development of the water industry, especially to those sectors closely watching the development of 3D printing technology. More importantly, in this work, the synergy between 3D printing technology and membrane module design has been revealed. The main conclusion is that there is a huge potential for the design of membrane module components via 3D printing technology. This interdisciplinary field has shown steady growth over the last ten years. In the era where additive manufacturing of objects or structures will alter various industries, when 3D printing technology advances further in terms of resolution, speed and materials, membrane module design will be one of its most important applications to provide a sustainable water processing and desalination for the future. In this work, a first glance of systematic considerations in designing, fabricating and optimising of 3D printed membranes components, specifically feed spacers, has been explored and many future applications will be explored in due course.

6.2 Future work

6.2.1 Antifouling spacers

Prior biofouling studies on spacers which mostly involved coating of the spacers with silver, copper or gold particles as antifouling agents to inhibit biofilm growth has been proven ineffective in the long term due to leaching of the coated compounds from the spacers, indicating the instability of the materials. The preferable method of making a biocidal spacer was to disperse the biocidal agent into the melted polymeric material, mix homogeneously, combine with resin and extrude out as a biocidal feed spacer. This extrusion method impregnates and inhibits the migration of biocidal agent, resulting in a more lasting antifouling performance of the feed spacer [42]. AM technology is a possible tool that can be explored to incorporate antifouling agents during the manufacturing process of the spacer, which may provide high stability.

In fact, a preliminary study on the development of an antifouling resin by incorporating nanosilver particles in the commercial 3D printing resin material was conducted in this work. An antifouling resin was developed by doping nanosilver powder into the original transparent high resolution photopolymer Plasclear which is the commercial material available for the Digital Light Processing (DLP) printer (ASIGA PLUS 39, USA). A series of tests were conducted to investigate the curing characteristics of the antifouling resins. These tests include exploring the optimal process parameters of the each type of resins, such as exposure time, intensity, energy density and curing depth. Ultimately, 5 mm by 5 mm square specimens were printed using the commercial photopolymer Plasclear doped with 1 wt% nanosilver powder with particle size less than 100 nm. These 3D printed samples with and without 1 wt% nanosilver and commercial polypropylene (PP) material were tested for bacteria attachment. Model bacteria *Pseudomonas aeruginosa* was used in this study. Two

replicates of flat samples (commercial PP, Plasclear and Plasclear-1wt%Ag as seen in Figure 6.2, with size of 5.0 x 5.0 x 0.7 mm, were soaked in the test solution to allow for bacteria attachment. The amount of bacteria attached was extracted and was measured with a flow cytometer. The results in Figure 6.2 showed significant decrease in the bacteria attachment on the Plasclear-1wt%Ag as compared to the Plasclear sample, showing that the incorporation of nanosilver powder in the photopolymer before printing was effective in reducing the bacteria attachment on the sample surfaces. The slightly lower attachment on the commercial PP might be due to a lower surface roughness as compared to the 3D printed samples.

Figure 6.2: Bacteria attachment on different flat samples (n=2).

This preliminary study showed that it was possible to incorporate nanoparticles in the resin for 3D printing. However, the printing process was not yet optimised in this work and the specimens appeared to be slightly overcured. To achieve good antifouling properties, there is a further need to study the dosage concentration, dispersion method and process optimisation of DLP systematically and also a need to investigate the

printability of this antifouling resin in fabricating spacer prototypes. The leachability of the nanosilver from the resin is also another area that can be explored in future work.

6.2.2 Responsive spacers

In this work, the responsiveness of spacers to hydrodynamic forces (pulsating flow) by having multi-materials with a range of flexibility was introduced as an innovative approach to reduce membrane fouling. For future work, a functional spacer that may be responsive to other external stimulus can be explored. For instance, two functions are described as follows.

(i) Magnetic forces

Magnetic nanoparticles including ferrite nanoparticles or iron oxide nanoparticles etc. can be incorporated into the resin material, allowing the encapsulation of magnetic particles in the feed spacer filaments via UV photopolymerisation during the printing process. Under the effect of magnetic field, specific sections of the feed spacer printed with photoliable magnetic composite material will be able to respond to the magnetic field and move. As a consequence, a ‘sweeping’ effect can be created to disrupt the boundary layers to mitigate fouling.

(ii) Electric forces

Piezoelectric materials including zinc oxide, aluminum nitride, polyvinylidene fluoride, lithium tantalite, polyvinylidene fluoride, lanthanum gallium silicate, potassium sodium tartrate, barium titanate etc. can be incorporated into photoliable polymer solution [126]. Photopolymerisation during printing process enables the piezoelectric materials to be encapsulated in the feed spacers. Under shear stresses caused by the fluid flow in the channel, piezoelectric polymer will be able to convert compressive or tensile stresses to electric charges and vice versa. An applied electric field will change the shape of the piezoelectric composite feed spacer, creating a feed spacer responsive to electric field.

In addition to piezoelectric materials, photoliable conductive polymer including ionic liquids can also be used as the 3D printing material to fabricate spacers with conductive filaments that can respond to electric field [127].

These responsive spacers may be a better way of reducing membrane fouling by generating vortices and recirculation of bulk feed near the membrane surfaces as compared to current static spacers that result in localised dead zones.

REFERENCES

- [1] M. Mulder, Basic Principles of Membrane Technology Second Edition, Kluwer, 1996.
- [2] A.R. Da Costa, A.G. Fane, Net-type spacers: Effect of configuration on fluid flow path and ultrafiltration flux, *Industrial and Engineering Chemistry Research*, 33 (1994) 1845-1851.
- [3] M.W. Svetlana Popović, Turbulence Promoters in Membrane Processes, *Journal of Membrane Science*, Virtual Special Issue (2010).
- [4] A.R. Da Costa, A.G. Fane, D.E. Wiley, Spacer characterisation and pressure drop modelling in spacer-filled channels for ultrafiltration, *Journal of Membrane Science*, 87 (1994) 79-98.
- [5] Z. Cao, D.E. Wiley, A.G. Fane, CFD simulations of net-type turbulence promoters in a narrow channel, *Journal of Membrane Science*, 185 (2001) 157-176.
- [6] M. Shakaib, S.M.F. Hasani, M. Mahmood, CFD modeling for flow and mass transfer in spacer-obstructed membrane feed channels, *Journal of Membrane Science*, 326 (2009) 270-284.
- [7] D. Dendukuri, S.K. Karode, A. Kumar, Flow visualisation through spacer filled channels by computational fluid dynamics-II: Improved feed spacer designs, *Journal of Membrane Science*, 249 (2005) 41-49.
- [8] A.L. Ahmad, K.K. Lau, Impact of different spacer filaments geometries on 2D unsteady hydrodynamics and concentration polarization in spiral wound membrane channel, *Journal of Membrane Science*, 286 (2006) 77-92.
- [9] G.A. Fimbres-Weihs, D.E. Wiley, Numerical study of mass transfer in three-dimensional spacer-filled narrow channels with steady flow, *Journal of Membrane Science*, 306 (2007) 228-243.
- [10] F. Li, G.W. Meindersma, A.B. De Haan, T. Reith, Optimisation of non-woven spacers by CFD and validation by experiments, *Desalination*, 146 (2002) 209-212.
- [11] L. Song, S. Ma, Numerical studies of the impact of spacer geometry on concentration polarization in spiral wound membrane modules, *Industrial and Engineering Chemistry Research*, 44 (2005) 7638-7645.

- [12] A.R. Da Costa, A.G. Fane, C.J.D. Fell, A.C.M. Franken, Optimal channel spacer design for ultrafiltration, *Journal of Membrane Science*, 62 (1991) 275-291.
- [13] A.R. Da Costa, A.G. Fane, D.E. Wiley, Ultrafiltration of whey protein solutions in spacer-filled flat channels, *Journal of Membrane Science*, 76 (1993) 245-254.
- [14] J. Schwinge, D.E. Wiley, A.G. Fane, R. Guenther, Characterisation of a zigzag spacer for ultrafiltration, *Journal of Membrane Science*, 172 (2000) 19-31.
- [15] J. Schwinge, D.E. Wiley, A.G. Fane, Novel spacer design improves observed flux, *Journal of Membrane Science*, 229 (2004) 53-61.
- [16] F. Li, W. Meindersma, A.B. De Haan, T. Reith, Novel spacers for mass transfer enhancement in membrane separations, *Journal of Membrane Science*, 253 (2005) 1-12.
- [17] A. Shrivastava, S. Kumar, E.L. Cussler, Predicting the effect of membrane spacers on mass transfer, *Journal of Membrane Science*, 323 (2008) 247-256.
- [18] H.L. Yang, J.C.T. Lin, C. Huang, Application of nanosilver surface modification to RO membrane and spacer for mitigating biofouling in seawater desalination, *Water Research*, 43 (2009) 3777-3786.
- [19] R. Hausman, I.C. Escobar, A comparison of silver- and copper-charged polypropylene feed spacers for biofouling control, *Journal of Applied Polymer Science*, 128 (2013) 1706-1714.
- [20] P.A. Araújo, D.J. Miller, P.B. Correia, M.C.M. Van Loosdrecht, J.C. Kruithof, B.D. Freeman, D.R. Paul, J.S. Vrouwenvelder, Impact of feed spacer and membrane modification by hydrophilic, bactericidal and biocidal coating on biofouling control, *Desalination*, 295 (2012) 1-10.
- [21] R. Hausman, T. Gullinkala, I.C. Escobar, Development of copper-charged polypropylene feedspacers for biofouling control, *Journal of Membrane Science*, 358 (2010) 114-121.
- [22] J. Schwinge, P.R. Neal, D.E. Wiley, D.F. Fletcher, A.G. Fane, Spiral wound modules and spacers: Review and analysis, *Journal of Membrane Science*, 242 (2004) 129-153.
- [23] A. Saeed, Effect of feed channel spacer geometry on hydrodynamics and mass transport in membrane modules, in, Curtin University of Technology, 2012.

- [24] R.W. Field, F.A. Siddiqui, P. Ang, J.J. Wu, Analysis of the influence of module construction upon forward osmosis performance, *Desalination*, 431 (2018) 151-156.
- [25] W.S.W. Ho, *Membrane Handbook*, Springer US, Boston, MA, 1992.
- [26] J.S. Vrouwenvelder, D.A. Graf von der Schulenburg, J.C. Kruithof, M.L. Johns, M.C.M. van Loosdrecht, Biofouling of spiral-wound nanofiltration and reverse osmosis membranes: A feed spacer problem, *Water Research*, 43 (2009) 583-594.
- [27] A.J. Karabelas, M. Kostoglou, C.P. Koutsou, Modeling of spiral wound membrane desalination modules and plants – review and research priorities, *Desalination*, 356 (2015) 165-186.
- [28] J.L. Feimer, T.-J. Chen, D.L. Smith Jr, D.T. Bray, D. de la Cruz, Spiral wound element for separation, in, United States Patent No. 5275726 A, 1994.
- [29] G. Schock, A. Miquel, Mass transfer and pressure loss in spiral wound modules, *Desalination*, 64 (1987) 339-352.
- [30] W. Glatzel, M. Tomas, The effect of turbulence promoters on heat transfer and pressure drop in plate heat exchanger, CSIR Special Report CHEM, 53 (1966).
- [31] J. Watson, D.G. Thomas, Forced convection mass transfer: Part IV. Increased mass transfer in an aqueous medium caused by detached cylindrical turbulence promoters in a rectangular channel, *AIChE Journal*, 13 (1967) 676-677.
- [32] A.R. Da Costa, *Fluid Flow and Mass Transfer in Spacer-filled Channels for Ultrafiltration*, University of New South Wales, 1993.
- [33] H. Li, A.G. Fane, H.G.L. Coster, S. Vigneswaran, Direct observation of particle deposition on the membrane surface during crossflow microfiltration, *Journal of Membrane Science*, 149 (1998) 83-97.
- [34] R.W. Field, D. Wu, J.A. Howell, B.B. Gupta, Critical flux concept for microfiltration fouling, *Journal of Membrane Science*, 100 (1995) 259-272.
- [35] H.J. Tanudjaja, W. Pee, A.G. Fane, J.W. Chew, Effect of spacer and crossflow velocity on the critical flux of bidisperse suspensions in microfiltration, *Journal of Membrane Science*, 513 (2016) 101-107.
- [36] Y. Zhang, A. Fane, A. Law, Critical flux and particle deposition of bidisperse suspensions during crossflow microfiltration, *Journal of Membrane Science*, 282

(2006) 189-197.

[37] P.R. Neal, H. Li, A.G. Fane, D.E. Wiley, The effect of filament orientation on critical flux and particle deposition in spacer-filled channels, *Journal of Membrane Science*, 214 (2003) 165-178.

[38] Y. Gao, S. Haavisto, C.Y. Tang, J. Salmela, W. Li, Characterisation of fluid dynamics in spacer-filled channels for membrane filtration using Doppler optical coherence tomography, *Journal of Membrane Science*, 448 (2013) 198-208.

[39] Y. Gao, S. Haavisto, W. Li, C.Y. Tang, J. Salmela, A.G. Fane, Novel approach To characterising the growth of a fouling layer during membrane filtration via optical coherence tomography, *Environmental Science & Technology*, 48 (2014) 14273-14281.

[40] S. West, M. Wagner, C. Engelke, H. Horn, Optical coherence tomography for the in situ three-dimensional visualization and quantification of feed spacer channel fouling in reverse osmosis membrane modules, *Journal of Membrane Science*, 498 (2016) 345-352.

[41] X. Liu, W. Li, T.H. Chong, A.G. Fane, Effects of spacer orientations on the cake formation during membrane fouling: Quantitative analysis based on 3D OCT imaging, *Water Research*, 110 (2017) 1-14.

[42] I. Shelby, Cross-flow filtration apparatus with biocidal feed spacer, in, United States Patent No. 20090314713 A1, 2009.

[43] R. Hausman, T. Gullinkala, I.C. Escobar, Development of low - biofouling polypropylene feedspacers for reverse osmosis, *Journal of Applied Polymer Science*, 114 (2009) 3068-3073.

[44] P.A. Araújo, J.C. Kruithof, M.C.M. Van Loosdrecht, J.S. Vrouwenvelder, The potential of standard and modified feed spacers for biofouling control, *Journal of Membrane Science*, 403-404 (2012) 58-70.

[45] D.J. Miller, P.A. Araújo, P.B. Correia, M.M. Ramsey, J.C. Kruithof, M.C.M. van Loosdrecht, B.D. Freeman, D.R. Paul, M. Whiteley, J.S. Vrouwenvelder, Short-term adhesion and long-term biofouling testing of polydopamine and poly(ethylene glycol) surface modifications of membranes and feed spacers for biofouling control, *Water Research*, 46 (2012) 3737-3753.

[46] Y. Wibisono, W. Yandi, M. Golabi, R. Nugraha, Emile R. Cornelissen, A.J.B. Kemperman, T. Ederth, K. Nijmeijer, Hydrogel-coated feed spacers in two-phase flow cleaning in spiral wound membrane elements: A novel platform for eco-friendly

biofouling mitigation, *Water Research*, 71 (2015) 171-186.

[47] S.K. Karode, A. Kumar, Flow visualisation through spacer filled channels by computational fluid dynamics I.: Pressure drop and shear rate calculations for flat sheet geometry, *Journal of Membrane Science*, 193 (2001) 69-84.

[48] J. Schwinge, D. Wiley, D. Fletcher, Simulation of the flow around spacer filaments between narrow channel walls. 1. Hydrodynamics, *Industrial & engineering chemistry research*, 41 (2002) 2977-2987.

[49] J. Schwinge, D. Wiley, D. Fletcher, Simulation of the flow around spacer filaments between channel walls. 2. Mass-transfer enhancement, *Industrial & engineering chemistry research*, 41 (2002) 4879-4888.

[50] J. Schwinge, D. Wiley, D. Fletcher, A CFD study of unsteady flow in narrow spacer-filled channels for spiral-wound membrane modules, *Desalination*, 146 (2002) 195-201.

[51] D.E. Wiley, D.F. Fletcher, Computational fluid dynamics modelling of flow and permeation for pressure-driven membrane processes, *Desalination*, 145 (2002) 183-186.

[52] D.E. Wiley, D.F. Fletcher, Techniques for computational fluid dynamics modelling of flow in membrane channels, *Journal of Membrane Science*, 211 (2003) 127-137.

[53] F. Li, W. Meindersma, A. De Haan, T. Reith, Optimisation of commercial net spacers in spiral wound membrane modules, *Journal of Membrane Science*, 208 (2002) 289-302.

[54] A. Saeed, R. Vuthaluru, H.B. Vuthaluru, Impact of feed spacer filament spacing on mass transport and fouling propensities of RO membrane surfaces, *Chemical Engineering Communications*, 202 (2015) 634-646.

[55] A. Saeed, R. Vuthaluru, H.B. Vuthaluru, Investigations into the effects of mass transport and flow dynamics of spacer filled membrane modules using CFD, *Chemical Engineering Research and Design*, 93 (2015) 79-99.

[56] M. Amokrane, D. Sadaoui, M. Dudeck, C.P. Koutsou, New spacer designs for the performance improvement of the zigzag spacer configuration in spiral-wound membrane modules, *Desalination and Water Treatment*, 57 (2016) 5266-5274.

[57] S. Sawada, M. Shishido, Spiral wound type membrane module, in, *United States*

Patent No. 4,834,881 (1989).

[58] J. Balster, I. Pünt, D. Stamatialis, M. Wessling, Multi-layer spacer geometries with improved mass transport, *Journal of Membrane Science*, 282 (2006) 351-361.

[59] S. Chikura, S. Ishihara, M. Hirokawa, Y. Uda, Spiral type separation membrane element, in, United States Patent No. 8361318 B2, 2009.

[60] P.R. Dontula, Y. Tayalia, U.J. Bharwada, Feed spacer for spiral wound membrane element, in, United States Patent No. 13/316,011 (2011).

[61] K.J. Farrell, I. Heat Transfer Research, U.S.B.o.R.W.T.E.R. Team, W.D. Research, D. Program, Reduced Membrane Fouling Potential by Tailored Fluid/structure Interaction, U.S. Department of the Interior, Bureau of Reclamation, Technical Service Center, Water and Environmental Services Division, 2008.

[62] P. Gabriel, J. Suidureau, P. Johannsen, G. Reinhold, Spacer for Filter Modules, in, United States Patent No. 20080290031 (2005).

[63] J.F. Hester, B.E. Spiewak, P.D. Radovanovic, S.R. Reimann, R.S. Kody, Fluid separation membrane module, in, United States Patent No. 6986428, (2006).

[64] S.K. Karode, A. Kumar, Feed spacers for filtration membrane modules, in, United States Patent No. 6,989,097 (2006).

[65] J. Liu, A. Iranshahi, Y. Lou, G. Lipscomb, Static mixing spacers for spiral wound modules, *Journal of Membrane Science*, 442 (2013) 140-148.

[66] P. Xie, L.C. Murdoch, D.A. Ladner, Hydrodynamics of sinusoidal spacers for improved reverse osmosis performance, *Journal of Membrane Science*, 453 (2014) 92-99.

[67] J. Liu, Z. Liu, X. Xu, F. Liu, Saw-tooth spacer for membrane filtration: Hydrodynamic investigation by PIV and filtration experiment validation, *Chemical Engineering and Processing: Process Intensification*, 91 (2015) 23-34.

[68] C.P. Koutsou, A.J. Karabelas, A novel retentate spacer geometry for improved spiral wound membrane (SWM) module performance, *Journal of Membrane Science*, 488 (2015) 129-142.

[69] W.S. Tan, C.K. Chua, T.H. Chong, A.G. Fane, A. Jia, 3D printing by selective laser sintering of polypropylene feed channel spacers for spiral wound membrane

modules for the water industry, *Virtual and Physical Prototyping*, (2016) 1-8.

[70] H. Zhu, L. Lu, J. Fuh, Development and characterisation of direct laser sintering Cu-based metal powder, *Journal of Materials Processing Technology*, 140 (2003) 314-317.

[71] Y.H. Kok, X.P. Tan, N.H. Loh, S.B. Tor, C.K. Chua, Geometry dependence of microstructure and microhardness for selective electron beam-melted Ti-6Al-4V parts, *Virtual and Physical Prototyping*, 11 (2016) 183-191.

[72] J.E.M. Teoh, J. An, C.K. Chua, M. Lv, V. Krishnasamy, Y. Liu, Hierarchically self-morphing structure through 4D printing, *Virtual and Physical Prototyping*, (2016) 1-8.

[73] Y.Y.C. Choong, S. Maleksaeedi, H. Eng, P.-C. Su, J. Wei, Curing characteristics of shape memory polymers in 3D projection and laser stereolithography, *Virtual and Physical Prototyping*, (2016) 1-8.

[74] J.-Y. Lee, W.S. Tan, J. An, C.K. Chua, C.Y. Tang, A.G. Fane, T.H. Chong, The potential to enhance membrane module design with 3D printing technology, *Journal of Membrane Science*, 499 (2016) 480-490.

[75] A. Siddiqui, N. Farhat, S.S. Bucs, R.V. Linares, C. Picioreanu, J.C. Kruithof, M.C. van Loosdrecht, J. Kidwell, J.S. Vrouwenvelder, Development and characterisation of 3D-printed feed spacers for spiral wound membrane systems, *Water research*, 91 (2016) 55-67.

[76] V.A. Haaksman, A. Siddiqui, C. Schellenberg, J. Kidwell, J.S. Vrouwenvelder, C. Picioreanu, Characterisation of feed channel spacer performance using geometries obtained by X-ray computed tomography, *Journal of Membrane Science*, 522 (2017) 124-139.

[77] V.t. Geraldes, V. Semião, M.N. de Pinho, Flow management in nanofiltration spiral wound modules with ladder-type spacers, *Journal of Membrane Science*, 203 (2002) 87-102.

[78] V. Geraldes, V. Semião, M. Norberta Pinho, Hydrodynamics and concentration polarisation in NF/RO spiral-wound modules with ladder-type spacers, *Desalination*, 157 (2003) 395-402.

[79] A.L. Ahmad, K.K. Lau, M.Z. Abu Bakar, Impact of different spacer filament geometries on concentration polarization control in narrow membrane channel, *Journal of Membrane Science*, 262 (2005) 138-152.

- [80] F. Li, W. Meindersma, A. de Haan, T. Reith, Spacer for use in a membrane separation device and a membrane separation device comprising such a spacer, International Patent, WO, 112945 (2004) A1.
- [81] V.V. Ranade, A. Kumar, Fluid dynamics of spacer filled rectangular and curvilinear channels, *Journal of Membrane Science*, 271 (2006) 1-15.
- [82] K.V. Larsen, Spacer for membrane modules, a membrane module and uses thereof, in, United States Patent No. 11/884,044, (2006).
- [83] C. Fritzmann, M. Hausmann, M. Wiese, M. Wessling, T. Melin, Microstructured spacers for submerged membrane filtration systems, *Journal of Membrane Science*, 446 (2013) 189-200.
- [84] C. Fritzmann, M. Wiese, T. Melin, M. Wessling, Helically microstructured spacers improve mass transfer and fractionation selectivity in ultrafiltration, *Journal of Membrane Science*, 463 (2014) 41-48.
- [85] W. Li, K.K. Chen, Y.-N. Wang, W.B. Krantz, A.G. Fane, C.Y. Tang, A conceptual design of spacers with hairy structures for membrane processes, *Journal of Membrane Science*, 510 (2016) 314-325.
- [86] C.K. Chua, K.F. Leong, 3D Printing and Additive Manufacturing: Principles and Applications, Fifth Edition of Rapid Prototyping, World Scientific Publishing Company Pte Limited, 2017.
- [87] S.S. Crump, Apparatus and method for creating three-dimensional objects, in, United States Patent No. 5121329 A, 1992.
- [88] R. Haas, J. Gutman, N.C. Wardrip, K. Kawahara, W. Uhl, M. Herzberg, C.J. Arnusch, Glycosphingolipids Enhance Bacterial Attachment and Fouling of Nanofiltration Membranes, *Environmental Science & Technology Letters*, 2 (2015) 43-47.
- [89] Z.H. Du, C.K. Chua, Y.S. Chua, K.G. Loh-Lee, S.T. Lim, Rapid sheet metal manufacturing. Part 1: Indirect rapid tooling, *International Journal of Advanced Manufacturing Technology*, 19 (2002) 411-417.
- [90] W.Y. Yeong, C.K. Chua, K.F. Leong, M. Chandrasekaran, M.W. Lee, Indirect fabrication of collagen scaffold based on inkjet printing technique, *Rapid Prototyping Journal*, 12 (2006) 229-237.
- [91] J.Y. Tan, C.K. Chua, K.F. Leong, Indirect fabrication of gelatin scaffolds using

rapid prototyping technology, *Virtual and Physical Prototyping*, 5 (2010) 45-53.

[92] R. Thakur, C. Vial, K. Nigam, E. Nauman, G. Djelveh, Static mixers in the process industries—a review, *Chemical Engineering Research and Design*, 81 (2003) 787-826.

[93] V. Kumar, V. Shirke, K.D.P. Nigam, Performance of Kenics static mixer over a wide range of Reynolds number, *Chemical Engineering Journal*, 139 (2008) 284-295.

[94] K.B. Anderson, S.Y. Lockwood, R.S. Martin, D.M. Spence, A 3D printed fluidic device that enables integrated features, *Analytical chemistry*, 85 (2013) 5622-5626.

[95] J.L. Erkal, A. Selimovic, B.C. Gross, S.Y. Lockwood, E.L. Walton, S. McNamara, R.S. Martin, D.M. Spence, 3D printed microfluidic devices with integrated versatile and reusable electrodes, *Lab on a Chip*, 14 (2014) 2023-2032.

[96] T. Femmer, A.J. Kuehne, J. Torres-Rendon, A. Walther, M. Wessling, Print your membrane: Rapid prototyping of complex 3D-PDMS membranes via a sacrificial resist, *Journal of Membrane Science*, 478 (2015) 12-18.

[97] T. Femmer, A.J. Kuehne, M. Wessling, Print your own membrane: direct rapid prototyping of polydimethylsiloxane, *Lab on a Chip*, 14 (2014) 2610-2613.

[98] T. Femmer, A.J. Kuehne, M. Wessling, Estimation of the structure dependent performance of 3-D rapid prototyped membranes, *Chemical Engineering Journal*, 273 (2015) 438-445.

[99] S. Badalov, Y. Oren, C.J. Arnusch, Ink-jet printing assisted fabrication of patterned thin film composite membranes, *Journal of Membrane Science*, 493 (2015) 508-514.

[100] J.R. Tumbleston, D. Shirvanyants, N. Ermoshkin, R. Januszewicz, A.R. Johnson, D. Kelly, K. Chen, R. Pinschmidt, J.P. Rolland, A. Ermoshkin, E.T. Samulski, J.M. DeSimone, Continuous liquid interface production of 3D objects, *Science*, 347 (2015) 1349-1352.

[101] A.N. Sue Mecham, Rima Januszewicz, Benny D. Freeman and Joseph M. DeSimone, Continuous Liquid Interface Production (CLIP) of Precise Membrane Structures, in: 2015 North American Membrane Society Meeting, Boston, Massachusetts USA, 2015.

[102] J. Balster, D.F. Stamatialis, M. Wessling, Membrane with integrated spacer, *Journal of Membrane Science*, 360 (2010) 185-189.

- [103] M.B. Neil Burns, Darren Travis, Louise Geekie, Allan Rennie, Designing advanced filtration media through metal additive manufacturing, in: Chemical Engineering & Technology, 2015.
- [104] T. Femmer, A. Jans, R. Eswein, N. Anwar, M. Moeller, M. Wessling, A.J. Kuehne, High-Throughput Generation of Emulsions and Microgels in Parallelized Microfluidic Drop-Makers Prepared by Rapid Prototyping, ACS applied materials & interfaces, 7 (2015) 12635-12638.
- [105] T. Femmer, F. Carstensen, M. Wessling, A membrane stirrer for product recovery and substrate feeding, Biotechnology and bioengineering, 112 (2015) 331-338.
- [106] W. Nijdam, J. de Jong, C.J.M. van Rijn, T. Visser, L. Versteeg, G. Kapantaidakis, G.H. Koops, M. Wessling, High performance micro-engineered hollow fiber membranes by smart spinneret design, Journal of Membrane Science, 256 (2005) 209-215.
- [107] N. Widjojo, T.-S. Chung, D.Y. Arifin, M. Weber, V. Warzelhan, Elimination of die swell and instability in hollow fiber spinning process of hyperbranched polyethersulfone (HPES) via novel spinneret designs and precise spinning conditions, Chemical Engineering Journal, 163 (2010) 143-153.
- [108] S. Moylan, J. Slotwinski, A. Cooke, K. Jurrens, M.A. Donmez, An Additive Manufacturing Test Artifact, Journal of Research of the National Institute of Standards and Technology, 119 (2014) 429-459.
- [109] J. Wijmans, S. Nakao, J. Van Den Berg, F. Troelstra, C. Smolders, Hydrodynamic resistance of concentration polarization boundary layers in ultrafiltration, Journal of Membrane Science, 22 (1985) 117-135.
- [110] W.S. Tan, C.K. Chua, T.H. Chong, A.G. Fane, A. Jia, 3D printing by selective laser sintering of polypropylene feed channel spacers for spiral wound membrane modules for the water industry, Virtual and Physical Prototyping, 11 (2016) 151-158.
- [111] S.H. Ahn, M. Montero, D. Odell, S. Roundy, P.K. Wright, Anisotropic material properties of fused deposition modeling ABS, Rapid Prototyping Journal, 8 (2002) 248-257.
- [112] C. Majewski, N. Hopkinson, Effect of section thickness and build orientation on tensile properties and material characteristics of laser sintered nylon - 12 parts, Rapid Prototyping Journal, 17 (2011) 176-180.
- [113] M. Monzón, Z. Ortega, A. Hernández, R. Paz, F. Ortega, Anisotropy of

Photopolymer Parts Made by Digital Light Processing, *Materials*, 10 (2017) 64.

[114] I.V. Olga, V.B. Aleksey, Wetting, roughness and flow boundary conditions, *Journal of Physics: Condensed Matter*, 23 (2011) 184104.

[115] S.R. Suwarno, X. Chen, T.H. Chong, V.L. Puspitasari, D. McDougald, Y. Cohen, S.A. Rice, A.G. Fane, The impact of flux and spacers on biofilm development on reverse osmosis membranes, *Journal of Membrane Science*, 405–406 (2012) 219–232.

[116] J.S. Vrouwenvelder, C. Hinrichs, W.G.J. Van der Meer, M.C.M. Van Loosdrecht, J.C. Kruithof, Pressure drop increase by biofilm accumulation in spiral wound RO and NF membrane systems: role of substrate concentration, flow velocity, substrate load and flow direction, *Biofouling*, 25 (2009) 543–555.

[117] E. Preedy, S. Perni, D. Nipič, K. Bohinc, P. Prokopovich, Surface roughness mediated adhesion forces between borosilicate glass and gram-positive bacteria, *Langmuir*, 30 (2014) 9466–9476.

[118] M.C. van Loosdrecht, J. Lyklema, W. Norde, G. Schraa, A.J. Zehnder, The role of bacterial cell wall hydrophobicity in adhesion, *Applied and Environmental Microbiology*, 53 (1987) 1893–1897.

[119] T. Baumgarten, S. Sperling, J. Seifert, M. von Bergen, F. Steiniger, L.Y. Wick, H.J. Heipieper, Membrane vesicle formation as a multiple-stress response mechanism enhances *pseudomonas putida* DOT-T1E cell surface hydrophobicity and biofilm formation, *Applied and Environmental Microbiology*, 78 (2012) 6217–6224.

[120] J. Johnson, M. Busch, Engineering aspects of reverse osmosis module design, *Desalination and Water Treatment*, 15 (2010) 236–248.

[121] D. Pham, S. Dimov, F. Lacan, Selective laser sintering: applications and technological capabilities, *Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture*, 213 (1999) 435–449.

[122] M.C. Leu, S. Pattnaik, G.E. Hilmas, Optimisation of selective laser sintering process for fabrication of zirconium diboride parts, in: *Proceeding of International Solid Freeform Fabrication Symposium*. Austin, TX, 2010.

[123] J. Kováčik, Correlation between Young's modulus and porosity in porous materials, *Journal of Materials Science Letters*, 18 (1999) 1007–1010.

[124] L. Ding, W. Shi, H. Luo, Numerical simulation of viscous flow over non-smooth

surfaces, *Computers & Mathematics with Applications*, 61 (2011) 3703-3710.

[125] A. Niavarani, N.V. Priezjev, The effective slip length and vortex formation in laminar flow over a rough surface, *Physics of Fluids* 21 (2009) 052105.

[126] K. Kim, W. Zhu, X. Qu, C. Aaronson, W.R. McCall, S. Chen, D.J. Sirbulu, 3D Optical Printing of Piezoelectric Nanoparticle–Polymer Composite Materials, *ACS Nano*, 8 (2014) 9799-9806.

[127] A.R. Schultz, P.M. Lambert, N.A. Chartrain, D.M. Ruohoniemi, Z. Zhang, C. Jangu, M. Zhang, C.B. Williams, T.E. Long, 3D Printing Phosphonium Ionic Liquid Networks with Mask Projection Microstereolithography, *ACS Macro Letters*, 3 (2014) 1205-1209.

APPENDIX

A1

Figure A 1: SEM images of 3D printed flat solid parts. (a) SLS (b) FDM (c) Polyjet

A2

Determination of effective membrane area

As the spacers tested had different geometries, the areas on the membrane covered by the spacers were different. To determine the effective membrane area of the different spacers from S1 to S12, methylene blue dye was injected into the feed solution during a run with MQ water to stain the membrane area that was uncovered by the spacers. The unstained area, as illustrated in Figure A2, was then measured by digital microscope and imaging software to estimate the effective membrane area.

Figure A 2: Membrane stained by methylene blue