Development of Anti-fouling Piezoelectric Polyvinylidene Fluoride Membrane

Su, Yu Ping

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**DEVELOPMENT OF ANTI-FOULING PIEZOELECTRIC
POLYVINYLDENE FLUORIDE MEMBRANE**

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**INTERDISCIPLINARY GRADUATE SCHOOL
NANYANG ENVIRONMENT & WATER RESEARCH INSTITUTE**

2021

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POLYVINYLDENE FLUORIDE MEMBRANE**

SU YU PING

**Interdisciplinary Graduate School
Nanyang Environment & Water Research Institute**

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

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Su Yu Ping

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

08 August 2021

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Date

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Assoc. Prof. Chong Tzyy Haur

Authorship Attribution Statement

This thesis contains material from 1 paper published and 1 paper submitted in the following peer-reviewed journal(s) where I was the first author.

Chapter 3 is published as Yu Ping Su, Lee Nuang Sim, Xin Li, Hans G.L. Coster, Tzyy Haur Chong. Anti-fouling piezoelectric PVDF membrane: Effect of morphology on dielectric and piezoelectric properties, *Journal of Membrane Science* **620**: 118818 (2021). DOI: 10.1016/j.memsci.2020.118818.

The contributions of the co-authors are as follows:

- Assoc. Prof. Chong Tzyy Haur provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Sim Lee Nuang, Dr. Li Xin and Prof. Hans G.L. Coster
- I co-designed the study with Assoc. Prof. Chong and Dr. Sim and performed all the laboratory work at the Singapore Membrane Technology Centre. I also analysed the data.
- All microscopy, including sample preparation, was conducted by me in the Singapore Membrane Technology Centre and School of Civil and Environmental Engineering.
- Dr. Li provided guidance on the fabrication of flat sheet membranes.
- Dr. Sim and Dr. Li assisted in the interpretation of the data from the scanning electron microscopy and cross-flow filtration experiments.

Chapter 4 is submitted as Yu Ping Su, Lee Nuang Sim, Hans G.L. Coster, Tzyy Haur Chong. Incorporation of barium titanate nanoparticles in piezoelectric PVDF membrane. Submitted.

The contributions of the co-authors are as follows:

- Assoc. Prof. Chong Tzyy Haur proposed the initial research direction and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised together with Dr. Sim Lee Nuang and Prof. Hans G.L. Coster.
- I co-designed the study with Assoc. Prof. Chong and Dr. Sim and performed all the laboratory work at the Singapore Membrane Technology Centre.
- I performed all the membrane fabrication, conducted all the characterisation work and data evaluation.
- Assoc. Prof. Chong and Dr. Sim assisted in the interpretation of the data from membrane characterisation and filtration experiments.

08 August 2021

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Date

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Yu Ping Su, Lee Nuang Sim, Hans G.L. Coster, Tzyy Haur Chong (2021). “Incorporation of barium titanate nanoparticles in piezoelectric PVDF membrane.” Journal of Membrane Science 640: 119861

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LIST OF SYMBOLS

A_{α}	Absorbance value of α phase at 763 cm ⁻¹
A_{β}	Absorbance value of β phase at 840 cm ⁻¹
C_b	Concentration of solutes in bulk solution
C_m	Concentration of solutes at membrane surface
d_{33}	Piezoelectric coefficient
ΔP	Transmembrane pressure
Δt	Time delay
E_{AC}	Specific energy consumption for supplying AC signals
$E_{\Delta P}$	Specific energy consumption supplied to pump
f	Frequency
$F(\beta)$	Relative fraction of β phase
h	Film thickness
η_p	Pump efficiency
I_{Peak}	Peak current
J	Permeate flux
k	Boundary layer mass transfer coefficient
K_{α}	Absorption coefficient of α phase
K_{β}	Absorption coefficient of β phase
K_c	Cake filtration constant
K_i	Pore blocking constant
M	Concentration polarisation modulus
m_{dry}	Mass of dry membrane
m_{wet}	Mass of wetted membrane before pore draining
μ	Dynamic viscosity
P_{AC}	Power for supplying AC signals
ρ_w	Density of wetting liquid
ρ_m	Density of membrane
$\emptyset$	Phase angle
Q_f	Volumetric flow rate of feed

Q_p	Volumetric flow rate of permeate
R_{cake}	Cake layer resistance
R_f	Fouling resistance
$R_{\text{irremovable}}$	Irremovable fouling resistance
$R_{\text{irreversible}}$	Irreversible fouling resistance
$R_{\text{reversible}}$	Reversible fouling resistance
R_{mem}	Membrane resistance
R_{PB}	Pore blocking resistance
R_{total}	Total resistance to filtration
t	Filtration time
U	Rolling speed
V_{Peak}	Peak voltage
V_p	Volume of permeate
Y	Recovery

LIST OF ABBREVIATIONS

AC	Alternating current
AFM	Atomic force microscopy
APTES	(3-Aminopropyl)triethoxysilane
ATP	Adenosine triphosphate
BSE	Backscattered electron
CP	Concentration polarisation
DMF	N,N-Dimethylformamide
FESEM	Field emission scanning electron microscopy
FTIR	Fourier-transform infrared spectroscopy
HFM	Hollow fiber membrane
LDV	Laser doppler vibrometer
MBR	Membrane bioreactor
MF	Microfiltration
MW	Molecular weight
NF	Nanofiltration
NIPS	Non-solvent induced phase separation
NMP	1-Methyl-2-pyrrolidinone
NP	Nanoparticle
PFM	Piezo-response force microscopy
PVDF	Polyvinylidene fluoride
PZT	Lead zirconate titanate
RO	Reverse osmosis
TDS	Total dissolved solids
TEM	Transmission electron microscopy
TEP	Triethyl phosphate
TIPS	Thermally induced phase separation
TMP	Transmembrane pressure
TOC	Total organic carbon
UF	Ultrafiltration
VSEP	Vibratory shear-enhanced process

SUMMARY

Ultrafiltration (UF) is widely used in water treatment to remove turbidity and pathogens; in wastewater membrane bioreactor to retain biomass; in desalination for pre-treatment of seawater. One of the main challenges during UF operation is membrane fouling which limits the potential of UF technology. The occurrence of fouling is inevitable and usually results in an increase in operational costs due to several factors such as reduced membrane lifespan, increased energy demand, and increased chemical cleaning. Many fouling control methods are available for UF operation. An example would be commercially available vibratory shear-enhanced process (VSEP), a type of unsteady-shear methods. In comparison with VSEP, piezoelectric membrane serves as the source of agitation and potentially offers lower energy consumption as an anti-fouling strategy. However, previous studies on piezoelectric membranes mainly focused on enhancing the piezoelectricity of commercial membranes through electrical poling, and the optimal operating conditions for piezoelectric membrane to improve filtration performance. It is important to extend the research to cover the fundamental understanding between membrane properties and piezoelectricity and its impact on membrane fouling, as well as the long-term application of piezoelectric membrane.

In the first part of this study, piezoelectric flat sheet polyvinylidene fluoride (PVDF) membranes with different morphologies were fabricated by using different solvents via non-solvent induced phase separation (NIPS). The fabricated membranes were then electrically poled to enhance piezoelectricity and subsequently characterised in terms of morphology, piezoelectric properties, and mechanical properties. The effects of morphology on the filtration performance of piezoelectric PVDF membranes were also analysed. PVDF membranes, with finger-like morphology, had better dielectric and piezoelectric properties among all the fabricated membranes. Electrical poling aligned the dipoles of PVDF which enhanced piezoelectric properties of PVDF membranes and reduced finger-like cavities to drop-like cavities. For poled piezoelectric membranes under electrical signals, 25 to 46% significant improvement in critical flux, 66% reduction in rate of transmembrane pressure increase and approximately 3 times increase in filtration duration were observed.

In the second part of this study, different quantities of piezoelectric barium titanate (BaTiO_3) nanoparticles (NPs) were added during the fabrication of PVDF membranes

to enhance piezoelectricity of the membranes. Some of the BaTiO₃ NPs were modified by silane coupling agent to enhance dispersion and compatibility in PVDF membranes. The modified BaTiO₃ NPs, particularly 0.1 wt.%, were well-dispersed in the PVDF membranes than unmodified BaTiO₃ NPs, which had similar finger-like structures to neat PVDF membranes. The addition of BaTiO₃ NPs to PVDF membranes improved its dielectric strength, piezoelectric coefficient, and mechanical properties. Electrical poling of the membranes further improved their piezoelectricity. A linear correlation between piezoelectric d_{33} coefficient and critical flux was observed for poled piezoelectric membranes under the influence of applied electrical signals when colloidal silica was used as model foulant. In comparison with neat PVDF membranes, improvement in critical flux by up to 51% and extended duration of multiple filtration cycles by up to factor of 2 to 4 were observed for poled BaTiO₃-PVDF membranes under application of electrical signals

In the final part of this study, piezoelectric membrane was then implemented to filtration of real wastewater to evaluate long-term performance. The energy consumption to agitate the piezoelectric membrane through electrical AC signals and energy consumption to sustain transmembrane pressure were computed to assess the potential cost savings as compared with conventional VSEP method. The advancements of reversible, irreversible, and irremovable fouling were significantly lowered for piezoelectric membranes. The fouling pattern shifted from irremovable dominance of non-piezoelectric membrane to reversible dominance of piezoelectric membrane. The impacts of alternating current (AC) voltages and cross-flow velocities on fouling mitigation were also examined which demonstrated piezoelectric membrane under AC signals is more favourable as a fouling control strategy than increasing cross-flow due to better fouling mitigation for equivalent energy consumption. A possible synergy between piezoelectric effect and chemical cleaning was also noticed as less foulants were detected on the piezoelectric membranes at the end of the filtration cycles.

The findings of this study would provide a better understanding on the fundamental relationships among membrane properties, piezoelectric properties and filtration performance and offer valuable information for the future development of piezoelectric membrane as an energy efficient anti-fouling method.

CHAPTER 1

Introduction

1.1 Background

Water – an important element for life – is becoming increasingly scarce due to various stressors, such as climate change, population growth and industrialisation (Elimelech, 2006; Werber, et al., 2016). To tackle this issue, efficient and sustainable technologies to tap unconventional water sources such as wastewater (i.e., reclaimed water) and seawater (i.e., desalinated water) need to be developed (Shannon, et al., 2008). Membrane technologies provide an attractive method to increase water supply beyond what is obtainable from the natural hydrological cycle. In recent years, membrane technology is becoming key driver in desalination, reclamation, water and wastewater treatment due its unique features such as consistent product water quality, easy to scale-up (i.e., membrane system is modular), simple operation, small footprint, and relatively low energy consumption (i.e., compared to thermal based technologies for desalination) (Kang & Cao, 2014). In addition, membrane technologies are applied in various industrial applications such as clarification of fruit juice via ultrafiltration (Córdova, et al., 2020), carbon dioxide (CO₂) gas separation from blast furnace gas (Ramírez-Santos, et al., 2018), membrane bioreactor in wastewater treatment (Al-Asheh, et al., 2021), and seawater and brackish water reverse osmosis desalination (Curto, et al., 2021).

A membrane is a semi-permeable thin film between two phases with preferential transport of certain species over others. The most commonly used membranes in the water industry are pressure-driven membranes which can be categorised according to the pore size into microfiltration (MF, 100 nm to 10 µm), ultrafiltration (UF, 2 to 100 nm), nanofiltration (NF, 1 to 2 nm) and reverse osmosis (RO, non-porous) (Yang, et al., 2019). Among them, UF membrane, which is the focus of this thesis work, is used in water treatment to remove turbidity, pathogens, and natural organic matters; in wastewater treatment membrane bioreactor (MBR) to retain biomass; in desalination for

seawater pre-treatment. The main separation mechanism of UF is based on size exclusion, where certain species such as monovalent and multivalent ions are allowed to pass through while larger particles such as viruses and bacteria are retained. UF was developed in the late 1960s as a fractionation technique (Cheryan, 1986). In the 1970s, UF membranes were rapidly commercialised in chemical and pharmaceutical industries with the emergence of new materials (Li, et al., 2018). It was then implemented in the water treatment industry in the 1990s (Li, et al., 2018). Over the years, improvements are made in terms of membrane materials to achieve high productivity and selectivity, module designs to achieve high packing density and reduction in energy consumption to minimise costs (Anon., 2008)

However, one of the main concerns during UF operation is membrane fouling, which limits the potential of UF technology. Membrane fouling is defined as the deposition of unwanted materials such as colloids, organic molecules, bacteria etc., on the surface or inside the pores of membrane. The occurrence of fouling is inevitable and could be observed as a decline in flux or a rise in transmembrane pressure (TMP) with time of operation. Fouling usually results in an increase in operational costs due to several factors such as reduced membrane lifespan, increased energy demand, and increased chemical cleaning. Thus, to ensure the sustainability and competitiveness of membrane technology, efficient methods to control and minimise the extent of fouling are critical.

1.2 Problem statement

The prevention of membrane fouling before its occurrence is possible by the pre-treatment of feed water to reduce the foulant load entering the membrane system and the addition of anti-fouling chemicals. However, periodic membrane cleaning during long-term operation is still inevitable and needs be carried out routinely to remove foulants in order to recover the membrane productivity (D'Souza & Mawson, 2005).

Other approaches applied to mitigate membrane fouling include the surface modification of membrane to improve its anti-fouling properties, optimal membrane module design, and employment of unsteady-shear. Surface modification of membrane is possibly the most sustainable solution to achieve anti-fouling membranes (Asatekin, et al., 2007). The underlying idea of membrane modification is to enhance

hydrophilicity of the membrane by introducing hydrophilic groups or particles and thus the membrane is less susceptible to fouling. However, the stability of such hydrophilic groups or particles in polymeric membranes need to be improved for the long-term use of surface-modified membranes in actual applications. Well-designed membrane modules could enhance fluid hydrodynamic conditions and improve overall system performance dramatically (Yang, et al., 2013). However, there is limited literature covering membrane module designs because they are usually commercially developed in the form of patents. Unsteady-shear methods include gas sparging, vibrating membranes, particle fluidising and flow pulsations (Zamani, et al., 2015). However, the application of unsteady-shear methods is limited due to their unfavourable high energy demand. In unsteady-shear methods, most of the energy supplied is on the bulk fluid while unsteady shear is only required on the boundary layer above to membrane where the fouling occurs to provide anti-fouling effects. Many of the unsteady-shear methods have been developed for commercial full-scale applications. An example is vibratory shear-enhanced process (VSEP). It is an unsteady-shear method that has been commercialised for industrial applications by New Logic Research and has been used in different types of membrane modules spanning from microfiltration to reverse osmosis (Zouboulis & Petala, 2008; Ahmed, et al., 2010; Shi & Benjamin, 2011). In VSEP, the maximum achievable shear rate is approximately 10^5 s^{-1} which is significantly higher than gas sparging. However, one of the limitations of VSEP is its unattractive energy consumption, where specific power of 500 W.m^{-2} has been reported (Zamani, et al., 2015). Instead of oscillatory vibration employed by VSEP, a novel piezoelectric membrane which itself serves as a source of agitation during operation could potentially lower the energy consumption on “vibrating” the membrane (Coster, et al., 2011). The key distinction between VSEP and piezoelectric membrane is an external force is used to vibrate the entire membrane module in VSEP which explains the high energy consumption while piezoelectric membrane itself undergoes micro-vibration by applying electrical AC signals as shown in Figure 1.1.

Figure 1.1: Schematic illustrations of the membrane surfaces for (a) vibratory shear-enhanced process (an example of unsteady-shear methods) (Leong, et al., 2016) in which the entire membrane is vibrated by external source, and (b) piezoelectric membrane in which the membrane itself undergoes micro-vibration.

The state-of-the-art piezoelectric membrane leverages on its inverse piezoelectric effect to convert an applied electrical field to mechanical strain. During filtration, electrical signals were supplied to the piezoelectric membrane in which these electrical signals were transformed into mechanical expansions and contractions which potentially prevent the settling of foulants or disturb the foulants deposited on the membrane surface. This could minimise membrane fouling and extend the filtration operation before chemical cleaning is required. However, previous studies mainly focused on enhancing the piezoelectricity of commercial membranes through electrical poling, and the optimal operating conditions for piezoelectric membrane to improve filtration performance. The fundamental understanding between membrane properties and piezoelectricity and its impact on membrane fouling, as well as the long-term application of piezoelectric membrane have not been explored, which will be addressed in this thesis.

1.3 Objectives and outline

The overall objective of this study is to develop flat sheet polyvinylidene fluoride (PVDF) UF membranes possessing superior piezoelectric properties, fabricated via non-solvent induced phase separation (NIPS) method. The objectives and outlines of this thesis are:

- **Chapter 1: Introduction** – Highlight the background information on membrane technology (i.e., ultrafiltration, UF), membrane fouling, methods to control membrane fouling and novel piezoelectric membrane. The objectives and outlines of this thesis are also presented.
- **Chapter 2: Literature review** – This chapter is sectioned into five parts. The first part describes the fouling mechanisms and approaches to control fouling in membrane application. The second part introduces piezoelectric effect, the improvement in piezoelectricity through electrical poling, and the common piezoelectric materials. The third part reviews the properties of piezoelectric polymer PVDF which includes its crystalline phases, thermal stability, and chemical resistance. The fourth part covers the common fabrication methods and the principles of NIPS method. The last part of this chapter discusses on the past studies performed on piezoelectric membranes and the research gap that would be addressed in this thesis.
- **Chapter 3: Effect of morphology on dielectric and piezoelectric properties of PVDF membrane** – Flat sheet PVDF membranes with different morphologies were fabricated via the NIPS method using different solvents. The effects of different morphologies on the dielectric and piezoelectric properties of membranes were explored. The effect of electrical poling on improvement in the piezoelectric properties were established. The performance of piezoelectric PVDF membranes in fouling reduction were investigated and discussed.
- **Chapter 4: Incorporation of barium titanate (BaTiO₃) nanoparticles (NPs) in piezoelectric PVDF membrane** – Different quantities of piezoelectric BaTiO₃ NPs were added during the preparation of flat sheet PVDF membranes. Some BaTiO₃ NPs were modified by silane coupling agent which acts as dispersant and linking agent between PVDF and BaTiO₃. The effects of incorporating unmodified and modified BaTiO₃ NPs on the pore structure,

dielectric and piezoelectric properties, and filtration performance of the membranes were examined.

- **Chapter 5: Long-term application of piezoelectric membrane for wastewater filtration** – The piezoelectric membrane under the application of electrical AC signals were implemented in filtration of real wastewater to evaluate long-term performance. The energy consumption to agitate the piezoelectric membranes through AC signals was computed to assess the potential cost savings as compared to conventional method of vibratory shear enhanced process (VSEP).
- **Chapter 6: Conclusions and future work** – The key findings of this study and recommendations on future work are summarised in this chapter.

1.4 Significance of the research

The significant outcomes of this study are:

- I. A fundamental understanding between the membrane properties and piezoelectric properties of membrane and its impact on fouling is addressed. This will allow a systematic approach to scale up the membrane for commercial application in future work.
- II. This study demonstrates the long-term application of piezoelectric membrane for wastewater treatment and assess the energy consumption and potential cost savings. This will further advance the sustainability of membrane technology for water industry.

CHAPTER 2

Literature review

2.1 Membrane fouling

2.1.1 Introduction to membrane processes and fouling

Membrane is a selective barrier between two phases that allows certain components to pass through while retains the other components (Mulder, 1996). Pressure-driven membranes are the most common type of membranes used in water applications. There are generally four groups of pressure-driven membranes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). In this thesis work, the focus would be on UF pressure-driven membranes which is widely used to remove turbidity, pathogens, and natural organic matters in water treatment; retain biomass in wastewater treatment membrane bioreactor (MBR); pre-treatment in seawater desalination. However, one of the main challenges that limits the potential of UF technology is membrane fouling.

Figure 2.1: (a) TMP profile under constant flux operation and (b) flux profile under constant TMP operation.

Membrane fouling occurs when there is an accumulation of undesirable matters on the membrane surface or in the membrane pores. Membrane fouling leads to flux decline for constant pressure operation or transmembrane pressure (TMP) increase for constant flux operation as illustrated in Figure 2.1. Membrane fouling is often a result of concentration polarisation (CP) but there may be other possible causes (Matthiasson & Sivik, 1980).

2.1.2 Concentration polarisation

The phenomenon of CP is inherently related to membrane separation which occurs when there is an elevated concentration of solutes at the membrane surface than in the bulk solution due to the accumulation of retained solutes. This forms a concentration profile along the boundary layer as illustrated in Figure 2.2.

Figure 2.2: The concentration profile along the boundary layer at steady-state conditions (Mulder, 1996).

This results in a highly concentrated layer near the membrane surface which exerts a resistance towards mass transfer. The accumulation of solutes at the membrane surface could severely limit flux, leading to membrane fouling. Thus, membrane fouling is often associated with CP. Membrane fouling refers to the deposition and accumulation of undesirable foulants on membrane surfaces and membrane pores. Fouling is an inherent issue to membrane processes, limiting the potential for membrane applications. Based on boundary layer film model, CP modulus (M) is related to flux (J),

$$M = \frac{C_m}{C_b} = \exp\left(\frac{J}{k}\right) \quad (2.1)$$

where C_m and C_b are concentration of solutes at the membrane surface and in the bulk solution respectively, and k is the boundary layer mass transfer coefficient. This equation shows the two factors (J and k) and their origins that are responsible for CP. J is due to the membrane component while k is due to the hydrodynamics component. As shown in equation (2.1), the magnitude of CP is an exponential function of J divided by k . To maximise the overall energy saving, minimising the increase in energy associated with CP and fouling is the key. Intuitively, it is critical to enhance mass transfer to minimise CP at high J .

2.1.3 Fouling mechanisms

The blocking filtration laws were first proposed by Hermans & Bredée (1936) and subsequently developed by Gonsalves (1950). Blocking filtration laws illustrate the four different mechanisms of membrane fouling by colloidal particles as shown in Figure 2.3. The four fouling mechanisms are (i) complete blocking, (ii) standard blocking, (iii) intermediate blocking, and (iv) cake filtration.

Figure 2.3: Schematic diagram of the four different fouling mechanisms based on blocking filtration laws (Aslam, et al., 2015).

In complete blocking, each particle is assumed to be blocking the surface of membrane pores without overlapping other particles and hence water flow is decreased due to reduced area of membrane pores. In standard blocking, the deposition of particles inside the membrane pores causes the pore volume to be decreased proportionally to the

volume of accumulated particles. In intermediate blocking, there is a simultaneous accumulation of particles on the membrane surface and in membrane pores during filtration. In cake filtration, it is assumed that the particles that are larger in size as compared to the membrane pores would form a cake layer on the membrane surface.

Although blocking filtration laws were initially developed for filter with defined cylindrical pores, these laws have been demonstrated to be applicable in applications involving polymeric membranes with irregular pore structures (Hwang & Lin, 2002; Iritani, et al., 2007; Huang, et al., 2008). The blocking filtration laws have been applied in multiple studies for the fouling of porous membrane filtering solutions containing microorganisms (Xu & Chellam, 2005), proteins (Iritani, et al., 1995; Ho & Zydney, 2000; Palacio, et al., 2003), and natural organic matters (Yuan, et al., 2002). Also, these laws have been used for studies involving natural water (Iritani, et al., 1995) and wastewater (Suarez & Veza, 2000). It should be noted that the use of blocking filtration laws assumes no back-diffusion of the particles from the membrane surface to the bulk solution. Hence, this assumption restricts the applicability of these laws to unstirred dead-end filtration (Hermia, 1982). Recently, Kirschner et al. (2019) redeveloped these filtration laws to describe constant flux cross-flow filtration. They found out that a combined model of intermediate blocking and cake filtration agreed well with experimental data. However, complete blocking and standard blocking were considered inapplicable owing to conflicting assumptions and relevance respectively.

The total resistance to filtration can be expressed by equation (2.2), derived from Darcy's law (Broeckmann, et al., 2006),

$$R_{\text{total}} = \frac{\Delta P}{J \cdot \mu} \quad (2.2)$$

where R_{total} is the total resistance to filtration (m^{-1}), ΔP is the transmembrane pressure (Pa), J is the permeate flux ($\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), and μ is the permeate viscosity (Pa.s). The estimation of R_{total} could be modelled by the resistances-in-series approach whereby the total resistance of the fouled membrane can be quantified as the sum of the intrinsic membrane resistance (R_{mem}) and the fouling resistance (R_f) as shown in equation (2.3). R_f could be split into different contributions due to specific fouling mechanisms (equation (2.4)).

$$R_{\text{total}} = R_{\text{mem}} + R_f \quad (2.3)$$

$$R_{\text{total}} = R_{\text{mem}} + R_{\text{cake}} + R_{PB} \quad (2.4)$$

R_f could be expressed as the sum of the cake layer resistance (R_{cake}) and the pore blocking resistance (R_{PB}). The resistances characterising membrane fouling is often approximated by measuring the variations of TMP or permeate flux during filtration tests. The resistances are evaluated based on the following steps: (1) R_{mem} is computed by measuring the TMP under constant permeate flux of clean water; (2) R_{total} is determined based on the final TMP after the filtration cycle of foulant solution; (3) R_{PB} is estimated according to the TMP measurement at the beginning of the next filtration cycle after the membrane is physically and/or chemically cleaned; (4) R_{cake} is obtained by subtracting R_{mem} and R_{PB} from R_{total} .

2.1.4 Fouling control

Table 2.1 summarises the advantages and limitations of some fouling control strategies that could be categorised under pre-treatment, physical or chemical cleaning (i.e., operational methods), surface modifications and novel membrane materials, and unsteady-state shear methods. More details on some of the fouling control methods are described in the following sections.

2.1.4.1 Pre-treatment methods

A proper pre-treatment process before membrane filtration improves feed water quality that subsequently enhances permeate quality and reduces membrane fouling (Huang, et al., 2008). This would then decrease the frequency of cleaning and extend the lifetime of membrane. There are several pre-treatment methods depending on the chemical composition and properties of the feed water. These methods include adsorption, coagulation, chemical treatment, flocculation, and ozone oxidation. The selection of pre-treatment processes primarily affected by the nature of foulants present in the feed water.

The removal of organic matters, phosphorus and suspended solids could be achieved via coagulation and flocculation. The suspended solids are destabilised by coagulant, forming micro-flocs. In flocculation, these micro-flocs then agglomerate into particles that are large enough for their subsequent removal via sedimentation, floatation, or filtration. However, coagulation-flocculation processes are highly sensitive to variations in feed water quality. Thus, depending on the feed water, varying dosages of the

coagulant and flocculant chemicals are required. Furthermore, these conventional processes comprise of many steps and take up significant land area to accommodate the equipment (AlSawafthah, et al., 2021).

In adsorption pre-treatment, the foulants (i.e. adsorbate) are adsorbed on the surfaces of the adsorbents. These adsorbents are highly dispersive and have relatively high porosity resulting in large, exposed surface area. A commonly used adsorbent in coupled adsorption and UF processes is powdered activated carbon (PAC). Its commercial popularity is due to the good removal of certain contaminants because of its thermodynamically unstable surface, and the widespread availability of PAC. However, a change in charge of the adsorbent may occur if sufficient contact time and appropriate distance between the adsorbent and adsorbate are presented. This would lead to complication in the interactions between the membrane surface and adsorbent (Gao, et al., 2011).

Ozone, a powerful oxidising agent, preferentially oxidises electron-rich functional groups such as carbon double bonds and activated aromatic rings (Langlais, et al., 1991). Through oxidation by ozone, organic macromolecules can be oxidised into small molecules which are subsequently oxidised into inorganic matters. This could further decrease the concentration of fouling components and mitigate membrane fouling (Kumar & Ismail, 2015). Kim et al. (2008) studied the effect of hydrodynamic conditions and ozone dosage on the performance of the ozonation/ultrafiltration process used in natural water treatment. Their study showed that ozone dosage led to an increase in permeate flux over various operating conditions. Moreover, less fouling and better removal of total organic carbon (TOC) were observed after an increase in ozone dosage along with higher cross-flow and lower TMP applied to the system. However, there is an issue on the formation of bromate when ozonation is coupled with UF. Since bromate causes adverse health effects if ingested, the removal of bromate by UF and its effect on the permeability of UF membrane need to be examined.

2.1.4.2 Surface modification and novel membrane materials

Membrane fouling is caused by the interaction between the foulants and membrane surface. The foulants could either physically interact or chemically degrade the membrane surface (Rana & Matsuura, 2010). Among the surface characteristics of membrane, hydrophilicity and surface roughness were reported to be the two important

factors affecting membrane fouling (Louie, et al., 2006; Lee, et al., 2008). Membranes with hydrophilic and smooth surfaces are less susceptible to membrane fouling as compared to those with hydrophobic and rough surfaces. On a hydrophilic surface, water layer could be readily formed. Since most foulants are hydrophobic in nature, these foulants would repel away from membrane surface. There are several ways to enhance hydrophilicity and to reduce surface roughness such as surface modification and using novel membrane materials.

Surface modification is a very common approach to improve anti-fouling effect of membranes due to its simplicity (Cheng, et al., 2013; Jee, et al., 2016). The idea behind surface modification is to alter surface characteristics of the membranes, improving their resistance against fouling. For example, polyvinylidene fluoride (PVDF) membrane was coated with phospholipid analogue by grafting reaction and the phospholipid coating lowered flux decline in coated membrane during filtration of bovine serum albumin (BSA) solution as compared to uncoated membrane (Akhtar, et al., 1995); aluminium oxide (Al_2O_3) nanoparticles were incorporated in PVDF membranes via immersion precipitation which exhibited superior anti-fouling performance (L, et al., 2006); superwetttable PVDF membranes were fabricated by blending with PVDF-*graft*-poly(ethylene glycol) methyl ether methacrylate (PVDF-*g*-PEGMA) and these membranes demonstrated great improvement in flux and rejection (Wu, et al., 2020). Although many studies have been performed to explore anti-fouling effect of surface modification, most of these studies were only focused on specific foulants. Hence, the applicability of these membranes in complex water systems is greatly limited. Moreover, there might be some downsides after surface modification such as decreased water flux. Another disadvantage of surface modification is the use of chemicals during the process which poses environmental and human health issues.

In recent years, multiple studies on novel membrane materials have emerged such as nanoporous graphene (Cohen-Tanugi & Grossman, 2012), zwitterionic materials (He, et al., 2016), hybrid membrane (Dmitrenko, et al., 2019), and so on. Graphene, with a two-dimensional honeycomb sp^2 carbon lattice, is a multi-functional material that has benefits of chemical inertness and strong mechanical properties (Akbari, et al., 2016). Exceptional transport properties such as high permeability and high selectivity of graphene-based membranes in both liquids and gases have been reported (Kim, et al.,

2013; Joshi, et al., 2014; Huang, et al., 2014). Although graphene-based membranes have shown their potential in filtration applications, the challenge of manufacturing large area of such membranes for industrial scale-up need to be overcome (Mi, 2019). Zwitterionic materials, inspired by biological cell membranes, equally possess both positive and negative charged groups (Xuan & Liu, 2009). These materials have been recognised as promising anti-fouling materials because of the hydration shell formed by strong electrostatic attractions that are much stronger than hydrogen bonds. This hydration shell serves as an effective barrier against foulants by preventing foulants from directly contacting the surface (Chen, et al., 2005). The common methods to construct anti-fouling membrane surfaces with zwitterionic materials are surface grafting, surface segregation, biomimetic adhesion, and surface coating. However, to utilise membranes modified by zwitterionic materials in actual applications, there are certain issues that need to be addressed such as complex modification steps, high preparation cost, and long-term stability of anti-fouling layer (He, et al., 2016).

2.1.4.3 Operational methods

In addition to the pre-treatment methods or membrane modifications, the proper selection of operational methods could potentially minimise membrane fouling to a certain extent. Operating conditions such as cross-flow velocity, flux, temperature, and TMP could be adjusted to reduce fouling. At high cross-flow velocity, foulants on the membrane surface tend to be swept away due to the high shear rate and hence, the fouling layer is reduced. However, higher fouling at a higher flow rate has also been observed by many researchers (Kumar & Ismail, 2015). A membrane filtration system could be operated under one of the commonly used two modes: (1) Constant TMP or (2) constant permeate flux. A fixed permeate flux is ideal for operations that would require to meet the certain flux demand from upstream or downstream processes. Fouling could be controlled by operating below the critical flux whereby little or no fouling occurs (Field, et al., 1995; Howell, 1995). Although a relatively low flux causes a lower rate of fouling, additional membrane area would be required to achieve similar output which would then increase capital and operating costs. The critical flux can be determined by commonly used flux-stepping method. During flux-stepping, the flux is increased in steps, and TMP is recorded at each step (Kwon, et al., 2000). Above critical flux, fouling begins to occur as denoted by the increase in TMP, and the previous flux step is assumed to be the critical flux. The temperature control during filtration depends on the effects

of temperature on the mass transfer coefficient, solubility of the feed components, viscosity, and denaturation of the solutes. Hence, increasing the temperature can either decrease or increase the fouling of UF membranes. The minimisation of fouling during filtration also results in simpler cleaning of the membranes, prolonging the lifetime of polymeric membranes by avoiding the use of harsh chemicals during cleaning.

A fouled membrane could be cleaned physically, chemically, or biologically to reverse the effects of fouling and to achieve adequate flux and separation. Membrane cleaning has been extensively studied and there are several ways to clean a fouled membrane. Some of the widely used cleaning methods are rinsing, air scouring, and chemical cleaning.

Rinsing consists of backwashing and/or forward flushing, which are typically applied in succession. Frequent rinsing minimises aggregation of severe attachment of foulants on the membrane surface due to higher surface shear velocity from backwashing which reduces the effects of CP. Depending on the type of foulants, either backwashing or forward flushing may be more effective. Katsoufidou et al. (2008) discovered that backwashing cleaned sodium alginate fouling more effectively than humic acid fouling. Also, rinsing could be performed under an integrated mode of backwashing and forward flushing while some of the parameters, such as duration, cross-flow velocity and pressure, could be optimised. Liang et al. (2008) investigated different cleaning methods for UF membrane fouled by algae and concluded that 20 min backwashing with subsequent forward flushing as well as 4 h soaking of sodium hydroxide and sodium hypochlorite were beneficial for cleaning. Wang et al. (2008) recommended that a cross-flow velocity of 1.6 m.s^{-1} can effectively clean the fouled membrane while backwashing intervals and pressure showed minimal effect on the TMP. Since different water treatment plants have varying conditions, more trials have to be performed before applying optimised rinsing protocol as a fouling control method for UF membrane.

Air scouring provides sufficient surface shear for mass transfer to dislodge foulants from concentrating on the membrane surface. It is demonstrated that air scouring employed intermittently or continuously with rinsing is an effective cleaning strategy in filtration processes. The basis of air scouring method is to acquire high utilisation ratio by controlling the velocity, size, and direction of air bubbles. New technology or methodology is necessary for better air movement across liquid-solid phase surface to

achieve higher efficiency of air scouring. Psoch & Schiewer (2006) reported that a near complete fouling reduction in UF membrane could be achieved when repeated air scouring combined with sponge ball was performed. Despite that, there is insufficient studies on the fundamental mechanism of air scouring which is likely because of its complexity control during experiment.

2.1.4.4 Unsteady-state shear methods

Besides the foregoing fouling control operational methods, unsteady-state shear methods can be employed during filtration to mitigate fouling. Some examples of unsteady-state shear methods are gas sparging, particle fluidising, pulsations, and vibrating membranes. The energy consumption for the unsteady-state shear methods is listed in Table 2.1.

In gas sparging, unsteady-state shear stresses on membrane surface were induced by bubble motion and bubble wakes which promotes back-transport of foulants to the bulk flow and improves flux (Ducom, et al., 2002). Hence, gas sparging is more effective in removing reversible cake foulant layer than in the case of internal fouling (Mercier, et al., 1998; Hwang, et al., 2008). In particle fluidising, the improvement in flux could be explained by two main effects of (i) the reduction in concentration gradient due to mixing action of the particles and (ii) the vibration and cleaning of membrane surface due to mechanical action of the particles (Zamani, et al., 2015). Similarly, particle fluidisation is effective in removing cake layer from the membranes and preventing subsequent deposition of foulants on the membranes (Huang, et al., 2008). In pulsations, increased shear and oscillatory back-flushing are the two key mechanisms for enhancing permeate flux (Jaffrin, et al., 1994; Li, et al., 1998). The back-flushing effect is only prevalent in microporous membranes and not in non-porous membranes (i.e., RO membranes). In vibrating systems, unsteady-state shear is induced on the membrane surface to mitigate CP and fouling and is increasingly effective during turbulence flow when the amplitude and frequency of the vibration exceed a critical value (Genkin, et al., 2006). One of the challenges of vibrating systems is scaling-up due to the lack of understanding on the hydrodynamics involved (Jaffrin, 2008). An example of the vibrating systems is vibratory shear-enhanced process (VSEP). The concept of VSEP was proposed by Armando & Culkin (1992). Since then, it has been commercialised for industrial applications by New Logic Research. In VSEP, the maximum achievable

shear rate is approximately 10^5 s^{-1} , which is significantly higher than gas sparging. However, one of the limitations of vibrating membranes is its unattractive energy consumption, where specific power of 500 W.m^{-2} has been reported (Zamani, et al., 2015). Instead of the unsteady-state shear methods mentioned above, the use of piezoelectric membranes as fouling control has been suggested. These piezoelectric membranes capitalise on their inverse piezoelectric effects (i.e., electrical energy to mechanical energy) which self-agitate during filtration to produce unsteady-state shear. The focus of this work is to further extend the research on piezoelectric membranes, particularly on flat-sheet PVDF membranes.

Table 2.1: Some examples of fouling control strategies under pre-treatment, physical or chemical cleaning, surface modifications and novel membrane materials, and unsteady-state shear methods.

	Advantage(s)	Limitation(s)	Energy consumption	References
<i>Conventional pre-treatment methods</i>				
Acidification	<ul style="list-style-type: none"> - Inhibits scale formation due to pH reduction - Rejects boron at low alkaline levels 	<ul style="list-style-type: none"> - Increased tendency of corrosion at low alkaline levels - Prominent precipitation relevant issues at high alkaline levels 		(Goh, et al., 2018; Anis, et al., 2019)
Chlorination	<ul style="list-style-type: none"> - Removes bacteria and microorganisms - Reduces odours 	<ul style="list-style-type: none"> - Ineffective to remove protozoa and endospores - May compromise membrane integrity if high concentration of chlorine in feed 		(Jamaly, et al., 2014; Kavitha, et al., 2019)
Coagulation/flocculation	<ul style="list-style-type: none"> - Removes organic and colloidal foulants - Hinders biofouling 	<ul style="list-style-type: none"> - Inefficient in inhibiting scale formation - Presence of threshold concentration levels of coagulants and flocculants such that no significant damage on membranes 		(Goh, et al., 2018; Anis, et al., 2019)
Dissolved air floatation (DAF)	<ul style="list-style-type: none"> - Cost-effective method 	<ul style="list-style-type: none"> - Issues related to scraper 		(Jamaly, et al., 2014)

Media filtration	<ul style="list-style-type: none"> - Easy to install and require little land space - Suitable to treat feedwaters with high turbidity and high levels of suspended solids 	<ul style="list-style-type: none"> - Inefficient in inhibiting biofouling - Sensitive to changes in feedwater conditions 	(Anis, et al., 2019)
Ozonation	<ul style="list-style-type: none"> - Negligible change in feed in terms of odour and taste 	<ul style="list-style-type: none"> - Ozone must be generated on-site due to difficulties in storage and transportation - Challenging in monitoring ozone concentration 	(Jamaly, et al., 2014; Anis, et al., 2019)
Disinfection (i.e. UV)	<ul style="list-style-type: none"> - Easy implementation - Low cost 	<ul style="list-style-type: none"> - May lead to development of biofilm 	(Anis, et al., 2019; Kavitha, et al., 2019)
<i>Physical/chemical cleaning</i>			
Sponge ball cleaning	<ul style="list-style-type: none"> - Can be used to handle heavily polluted feedwaters (e.g., industrial wastewater) 	<ul style="list-style-type: none"> - Only applicable to tubular modules 	(Ezugbe & Rathilal, 2020)
Alternative flushing	<ul style="list-style-type: none"> - Effective in removing colloidal foulants 	<ul style="list-style-type: none"> - Requires optimisation of forward and backward flush times to prevent compromising of recovery efficiency 	(Miguel, et al., 2011)
Backwashing	<ul style="list-style-type: none"> - Satisfactorily restore flux back to pre-fouling state 	<ul style="list-style-type: none"> - Inappropriate in removal of irreversible fouling (i.e. clogging) 	(Ezugbe & Rathilal, 2020)
Chemical cleaning	<ul style="list-style-type: none"> - Easier to remove deposits due to reduction in affinity between foulants and membrane surface after use of chemical reagents 	<ul style="list-style-type: none"> - Selection of chemical reagents is extremely crucial so as not to damage membrane structure 	(Jiang, et al., 2017)

Surface modification and novel membrane materials

Physical surface modifications	- Suppress accumulation and adsorption affinity of foulants towards membrane surface by coating surface with protective lining	- Eventual deterioration of anti-fouling properties as coatings and membrane surface are bonded by weak van der Waals forces, hydrogen bonding, or electrostatic interactions	(AlSawafthah, et al., 2021)
Chemical surface modifications	- Impart desired functions by tailoring membrane surfaces using chemical reagents and interactions	- Fouling control is restricted to fouling occurred on membrane surfaces	(Kang & Cao, 2012; AlSawafthah, et al., 2021)
Novel membrane materials	- Previous studies have demonstrated enhancement in permeate flux, permeability, and hydrophilicity for novel membrane materials	- Yet to develop for commercialisation - Agglomeration of nanoparticles - Health and environmental risk associated with accidental discharge of nanoparticles	(Anis, et al., 2019)

Unsteady-state shear methods

Gas sparging	- Versatile method; can be employed to a broad range of superficial gas velocities - Easy to scale-up due to its simplicity and scalability	- Anti-fouling effects are limited at high gas flow rates due to slugging - Fibre spacing and geometry need to be carefully arranged to achieve even distribution of two-phase flow	6 W.m ⁻²	(Cui, et al., 2003; Zamani, et al., 2015)
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Submerged axial vibration	<ul style="list-style-type: none"> - Low energy demand relative to its high feasible enhancement factor - Directly influence on CP boundary layer 	<ul style="list-style-type: none"> - Flat-sheet membranes are not ideal to achieve anti-fouling effects of this method 	0.7 to 0.8 W.m ⁻²	(Li, et al., 2013)
Vibratory shear-enhanced process	<ul style="list-style-type: none"> - Significant flux enhancement - Reduced requirements of pre-treatment processes and a higher recovery 	<ul style="list-style-type: none"> - Limited to small-scale operations - Only applicable to plate-and-frame module design that is less suitable for high pressure operations 	500 W.m ⁻²	(Akoum, et al., 2005; Zamani, et al., 2015)
Particle fluidisation	<ul style="list-style-type: none"> - Low energy cost - Amenability for scale-up and continuous operation 	<ul style="list-style-type: none"> - Only applicable to certain module geometry for the movement of particles without any obstructions - Issues on membrane integrity, especially for membranes with thin skin layers 	0.1 to 0.2 W.m ⁻²	(Kim, et al., 2011; Zamani, et al., 2015)
Flow pulsation	<ul style="list-style-type: none"> - Cost-effective - Increased membrane lifespan 	<ul style="list-style-type: none"> - Minimal effect on streamlines near membrane surface where CP is happening - Negatively impact on fittings and piping 	-	(Huang & Chen, 2013; Zamani, et al., 2015)
Piezoelectric membrane	<ul style="list-style-type: none"> - Potentially low energy consumption because anti-fouling action caused by self-agitation of piezoelectric membrane 	<ul style="list-style-type: none"> - May not be effective in removing foulants that are deposited in membrane pores (i.e., pore blocking) 	80 to 120 W.m ⁻² (depending on frequency of AC signals)	(Darestani, et al., 2013)

2.2 Piezoelectricity

2.2.1 Dielectrics

Dielectric materials are electrical insulators, having energy gap of more than 3 eV (Anon., 2017). This large energy gap means that it is impossible to excite the electrons of dielectric material from the valence band to the conduction band. However, when a dielectric material is placed in an electric field, dielectric polarisation of the material occurs. Its positive charges are shifted towards the direction of electric field whilst its negative charges are deflected in the opposite direction. Hence, an induced dipole moment is formed. This is also known as electronic polarisation (P_e) which is independent of temperature but directly proportional to field strength. In a molecule with asymmetrical charge distribution between different atoms, a permanent dipole moment is produced. The permanent dipoles orientate in the direction of the electric field, causing polarisation. This is termed as orientational polarisation (P_o) which is dependent on temperature. The other mechanisms of polarisation are ionic polarisation (P_i) and surface charge polarisation (P_s) due to the displacement of ions and surface charges respectively. The total polarisation of a dielectric material could simultaneously involve all or some of the mechanisms of polarisation (Anon., 2017).

2.2.2 Piezoelectric effect

Piezoelectric effect could exist in two types – direct and converse. The direct piezoelectric effect was discovered in 1880 by the Curie brothers, Pierre and Jacques. In the following year (1881), Gabriel Lippmann realised the converse piezoelectric effect. A material that possesses direct or converse piezoelectric effect has the ability to transform mechanical strain into electrical charge or vice versa (Sodano, et al., 2004). Piezoelectric materials belong to a category of materials called ferroelectrics.

2.2.3 Electrical poling

One of the defining characteristics of ferroelectrics is that the material exhibits a local charge separation known as an electric dipole due to the orientation of its molecules (Sodano, et al., 2004). The remnant electrical polarisation in ferroelectrics could be orientated into a desired direction. When the material is heated to an elevated temperature and is exposed to strong electric field, the electric dipoles re-orientate themselves relative to the electric field. This process is known as electrical poling

(Wersing, et al., 2008). Once the material is cooled, the dipoles maintain in their orientation and the material is then said to be poled. The effect of electrical poling is permanent (Kawai, 1969). After electrical poling is completed, the material will exhibit piezoelectric effect. The orientation of the electric dipoles before, during and after poling is illustrated in Figure 2.4.

Figure 2.4: Alignment of electric dipoles (represented by arrows) before poling (left), during poling (centre), and after poling (right).

Conventional poling (AC or DC)

Corona poling

Figure 2.5: Schematic diagram of conventional poling (left) and corona poling (right) (Dias & Das-Gupta, 1996).

Generally, as depicted in Figure 2.5, there are two methods of poling: conventional poling and corona poling (Dias & Das-Gupta, 1996). In conventional poling, the sample is immersed in an insulated fluid at controlled temperature while being sandwiched by two electrodes and an electric field is applied across the electrodes for a period of time.

In corona poling, the sample is placed on a grounded electrode while it is charged by corona current.

2.2.4 Piezoelectric materials

The phenomenon of piezoelectricity could be found in roughly one-third of the existing materials (Safari & Akdoğan, 2008). Although many materials show piezoelectricity, only some are found to be useful in scientific fields. Piezoelectric materials can be generally grouped into the following five categories (Uchino, 2003):

- I. Single crystals: quartz, lithium niobate;
- II. Polycrystalline materials: barium titanate (BaTiO_3), lead zirconate titanate (PZT), zinc oxide (ZnO);
- III. Relaxator ferroelectrics: lead magnesium niobate-lead titanate, lead zirconium niobate-lead titanate;
- IV. Polymers: PVDF, poly(vinylidene difluoride-trifluoroethylene) (P(VDF-TrFE)), polymer-ceramic composites;
- V. Piezoelectric paper.

The piezoelectricity of PVDF was ascertained by Kawai in 1969. The science and technology of piezoelectric polymers has been dominated by the PVDF family ever since. Their strong molecular dipoles within the polymer chain and the resulting change of dipole density upon mechanical influence leads to the piezoelectricity in PVDF family. Kawai (1969) found that the polarising temperature of PVDF to be between 50 °C and 90 °C, and its piezoelectric effect did not decay after several months. Thereby, PVDF is an ideal material for piezoelectric membrane because of its intrinsic piezoelectric properties. Piezoelectric coefficient or piezoelectric modulus (d_{33}) quantifies the volume change when a piezoelectric material is subjected to an electric field, or the electric polarisation on application of stress. This coefficient is often used to assess the goodness of a piezoelectric material (Li, 2021). The d_{33} coefficient is related to three key properties of a material according to the following equation:

$$d_{33} = k_{33} \sqrt{\epsilon_0 k_3^T s_{33}^E} \quad (2.5)$$

where k is electromechanical coupling coefficient, k^T is relative dielectric constant at a constant stress, and s^E is elastic compliance at a constant electrical field (Li, 2021).

Some of the available methods to quantify d_{33} are Berlincourt d_{33} meter, piezo-response force microscopy (PFM), and laser doppler vibrometer (LDV). Referring to Table 2.2, the d_{33} of PVDF is reported between 24 and 34 pm.V⁻¹. Piezoelectric d_{33} coefficients of other piezoelectric materials are also listed in Table 2.2.

Table 2.2: Piezoelectric coefficient, d_{33} , of various piezoelectric materials (*Narita & Fox, 2017*).

	d_{33} coefficient (pm.V ⁻¹)
PVDF	24 – 34
P(VDF-TrFE)	25 – 40
PZT	225 – 590
BaTiO ₃	191
ZnO	12.4

Although d_{33} of piezoceramics are much larger than that of piezopolymers, piezoceramics are hard and brittle. One of the advantages of piezopolymers is their low acoustical impedance which makes them favourable for sensing in the environments like water, human tissue, and other organic materials (Toda & Thompson, 2010). Moreover, because of their flexibility, piezoelectric polymers and papers are great candidates in making piezoelectric films or substrates that could be manufactured by simple and low-cost fabrication techniques. Besides its intrinsic piezoelectric properties, PVDF is also a preferred material in membrane applications due to its outstanding properties such as chemical resistance and thermal stability which would be discussed in the next section.

2.3 Properties of polyvinylidene fluoride

PVDF is an addition polymer made up of 1,1-difluoroethene monomers, also known as vinylidene fluoride. Among the fluoropolymers, PVDF has exceptional mechanical properties and resistant to abrasion. Also, fluoropolymers are known to have excellent chemical and thermal stabilities, making PVDF an attractive polymer for a wide range of applications. Since PVDF can be easily dissolved in commonly used organic solvents, PVDF membranes can be fabricated via simple immersion precipitation method.

2.3.1 Crystalline properties of polyvinylidene fluoride

PVDF is a semi-crystalline polymer, containing 3 wt.% hydrogen and 59.4 wt.% fluorine (Dohany, 2000) as shown in Figure 2.6. The crystalline structure of PVDF leads to distinctive properties contributed by the spatial arrangement of CH₂ and CF₂ groups along the polymer chain (Liu, et al., 2011).

Figure 2.6: Chemical formula of PVDF.

The four known crystalline structures of PVDF are α , β , γ and δ . Among these crystalline structures, all-trans β phase is the primary contributor for the piezoelectricity of PVDF (Kochervinskii, 2003). Zhang et al. (2020) reported that PVDF membranes with mainly β phase demonstrated superior fouling resistance as compared to PVDF membranes with mainly α phase. However, PVDF that is processed by the commonly used melt or solution techniques consists of mainly non-piezoelectric α phase (Salimi & Yousefi, 2003). The α phase of PVDF has a molecular chain confirmation of trans-gauche (TGTG') which hydrogen and fluorine atoms are placed alternately on each side of the chain as illustrated in Figure 2.7. On the other hand, the molecular chain confirmation of all-trans β phase has the fluorine atoms aligned in the same direction which contributes to the piezoelectric effect of PVDF.

Figure 2.7: Conformation of α -PVDF (left) and β -PVDF (right).

The crystallinity of PVDF could be tailored by controlling the conditions during membrane fabrication. Wang et al. (2009) investigated the effect of coagulation bath temperature on the crystallinity of PVDF. They found that PVDF membranes fabricated at 60 °C contained mainly α phase PVDF while a mixture of α phase PVDF and β phase PVDF were formed for PVDF membranes fabricated at 15 °C. Besides conditions during membrane fabrication, many research work have been performed to study the formation of β phase of PVDF by different methods. These methods include the addition of additives (Nasir, et al., 2006), annealing (Neidhöfer, et al., 2004; Shaik, et al., 2017), crystallisation under high pressure (Hattori, et al., 1996), electrical poling (Ye, et al., 2006) mechanical stretching (Salimi & Yousefi, 2003) and polymer blending (Jr & Souza Nociti, 1995; Mohamadi & Sharifi-Sanjani, 2011). Among these methods, electrical poling is a common approach to convert crystalline structure of PVDF from α to β phase to impart piezoelectric properties to PVDF.

2.3.2 Chemical resistance of polyvinylidene fluoride

PVDF is generally resistant to various harsh chemicals such as acids, halogen-containing oxidants, hydrocarbons, ionic solutions, and aliphatic and aromatic solvents. There are several factors that could influence the chemical stability of PVDF membranes. They are the concentration of chemicals, duration of exposure, frequency of attack cycles, pressure, temperature, and mechanical strain applied.

However, the outstanding chemical resistance of PVDF does not apply to strong bases, esters, and ketones. This would become an issue of concern where PVDF membranes are used in applications that are often exposed to strong alkaline solutions or chemical cleaning involving alkaline solutions. The poor chemical stability of PVDF in alkaline solution was reported in several early studies (Komaki, 1979; Shinohara, 1979; Nguyen, 1985). The darkening of oxyfluorinated PVDF was observed by Shinohara (1979) upon hot alkaline treatment. This was a result of dehydrofluorination whereby carbon-carbon double bonds were formed. Yoshihide Komaki (1981) noticed when PVDF film was submerged in alkaline sodium hydroxide (NaOH) solution containing ethanol, the film shrank and became brittle. Similarly, Hoa & Ouellette (1983) observed the discolouration of PVDF samples in NaOH solution and suggested NaOH solution chemically attacked PVDF in α conformation.

2.3.3 Thermal stability of polyvinylidene fluoride

Generally, fluoropolymers have better thermal stability than hydrocarbon polymers due to the high electronegativity of fluorine atoms and large bond dissociation energy of C-F bonds in fluoropolymers. Several studies have demonstrated that the thermal degradation of PVDF is predominantly dominated by the loss of hydrogen fluoride and consequently led to the formation of carbon-carbon double bond (Nguyen, 1985; Madorsky, 1964; Lovinger & Reed, 1980). Lovinger and Reed (1980) proposed that the thermal degradation of PVDF occurred primarily in crystalline region instead of amorphous region as they observed the inhomogeneous discolouration of PVDF samples. In membrane application, Benzinger et al. (1980) observed no evident thermal degradation of commercial Kynar PVDF ultrafiltration membranes in spiral wound configuration when it was operated continuously at 85.6 °C for 7 months.

2.4 Non-solvent induced phase separation

2.4.1 Concept of phase separation

Phase separation is the process of transforming a polymer solution from liquid state to solid state in a controlled manner (Mulder, 1996). This phase change is usually initiated by the shift from one liquid state into two liquids, also termed as liquid-liquid demixing. In other words, a liquid polymer solution is precipitated into two phases: (1) a polymer-

rich phase that forms the membrane matrix; and (2) a polymer-lean phases that forms the membrane pores. The membrane morphology is subsequently fixed with solidification process.

There are several methods of phase separation that have been developed, namely (i) controlled evaporation of solvent from three component systems; (ii) non-solvent induced phase separation (NIPS); (iii) precipitation from vapor phase; and (iv) thermally induced phase separation (TIPS). Among these methods, NIPS and TIPS are most used in the fabrication of polymeric membranes. The choice of solvent used in phase separation would determine the eventual membrane properties and performance. Table 2.3 lists some of the solvents that are commonly used in phase separation and their respective boiling points.

Table 2.3: Hansen solubility parameters and boiling points of common solvents used in preparation of PVDF (Bottino, et al., 1991; Haynes, 2010).

Solvents	Dispersion parameter, $\delta_{d,P}$ (MPa ^{1/2})	Polar parameter, $\delta_{p,P}$ (MPa ^{1/2})	Hydrogen bonding parameter, $\delta_{h,P}$ (MPa ^{1/2})	Total solubility parameter, $\delta_{t,P}$ (MPa ^{1/2})	Boiling point (°C)
N,N-Dimethylacetamide (DMAc)	16.8	11.5	10.2	22.7	165.0
N,N-Dimethylformamide (DMF)	17.4	13.7	11.3	24.8	153.0
Dimethylsulfoxide (DMSO)	18.4	16.4	10.2	26.7	189.0
Hexamethyl phosphoramide (HMPA)	18.4	8.6	11.3	23.2	232.5
N-Methyl-2-pyrrolidone (NMP)	18.0	12.3	7.2	22.9	202.0
Triethyl phosphate (TEP)	16.8	11.5	9.2	22.3	215.5
Trimethyl phosphate (TMP)	16.8	16.0	10.2	22.3	197.2
Tetramethylurea (TMU)	16.8	8.2	11.1	21.7	176.5

2.4.2 Principles of NIPS method

NIPS is a process where the polymer solution is spread evenly on an appropriate support which is then immersed in a coagulation bath consisting of a non-solvent. The phase separation occurs when the solvent in polymer solution exchange with the non-solvent in the coagulation bath. NIPS is commonly used to fabricate industrial asymmetric membranes because of the simplicity of its process. Moreover, many commercial PVDF membranes are fabricated via NIPS process because PVDF could be easily dissolved in

commonly used organic solvents. Since PVDF is a semi-crystalline polymer, its phase separation behaviour is more complex than other amorphous polymers such as polysulfone (Wienk, et al., 1996).

The resulting morphology of the membrane is affected by parameters such as the composition of polymer solution, composition of coagulation bath, exposure time, humidity, and temperature. Also, membrane characteristics would be influenced by the thickness of the membrane which can be adjusted in the range of tens to hundreds of microns. NIPS process involves both aspects of kinetics and thermodynamics. The exchange rate of solvent and non-solvent and velocity of phase separation are associated to the kinetics, and it would greatly affect the structure of the membrane. The interactions among the polymer, solvent and non-solvent are related to thermodynamics. Free energy of mixing (ΔG_m) and solubility parameter theory can be used to examine these interactions. The thermodynamic stability of the mixture of polymer, solvent and non-solvent can be interpreted through a ternary phase diagram as shown in Figure 2.8.

The pure components and binary mixtures are represented by the corners and sides of the triangle in a ternary phase diagram, respectively. Any point within the triangle represents ternary mixture. The binodal and spinodal boundaries separate the triangle into three regions. The first region on the left of the binodal boundary represents the one-phase thermodynamically stable region, which can be subdivided in glassy, gel and solution regions. The second region between the binodal and spinodal boundary represents the metastable region, thermodynamically unstable in which no phase separation occurs. The third region on the right of the spinodal boundary represents a thermodynamically unstable region where phase separation occurs. In this region, the polymer solution spontaneously separates into a polymer-rich phase and a polymer-lean phase whose compositions are specified by the intercepts of the tie line with the binodal boundary.

Figure 2.8: Ternary phase diagram of polymer/solvent/non-solvent system (Baker, 2004).

The fabrication of membranes by NIPS can be summarised as follows:

- ❖ The exchange of solvent and non-solvent commences when the non-solvent is introduced into the polymer/solvent solution.
- ❖ The composition of the solution enters the two-phase region as the solvent and non-solvent are lost and gained respectively by the solution. Polymer precipitation takes place, forming polymer-rich and polymer-lean phases.
- ❖ The further exchange of solvent and non-solvent leads to the shift in the composition of the polymer-rich phase towards the polymer/non-solvent side and the membrane is formed.

2.5 Past studies on piezoelectric membranes

Thomas (1973) was among the first to realise that bulk crossflow induces fluid instabilities, which could considerably increase mass transfer of retained solutes away

from the membrane. Winzeler and Belfort (1993) further suggested that fluid instability at membrane-solution interface mitigate CP and fouling, which improves performance of pressure-driven membrane processes. Ahner et al. (1993) developed piezoelectric drivers as backings of UF membranes and utilised the piezoelectric effect to produce strong local turbulence that will minimise CP and fouling. The results showed that when UF is piezoelectrically-assisted, the flux was enhanced by approximately a factor of 4 to 5. However, for this method, an external piezoelectric device or driver is necessary to induce fluid instability. Recently, the construction of a novel membrane that possessed piezoelectric properties has been explored (Coster, et al., 2011; Darestani, et al., 2013; Darestani, et al., 2013a; Darestani, et al., 2013). Piezoelectric membrane itself serves as the source of agitation when it undergoes internal vibrational deformations normal to the plane (Coster, et al., 2010).

With this strategy, previous studies on piezoelectric membranes were based on commercial flat sheet PVDF membranes (Darestani, et al., 2013a; Darestani, et al., 2013; Darestani, et al., 2013; Chen & Pomalaza-Ráez, 2019), electrospun PVDF nanofiber membranes (Bae, et al., 2017; Gee, et al., 2018), and piezoceramic membranes (Krinks, et al., 2015; Mao, et al., 2018; Mao, et al., 2019). These piezoelectric membranes showed improved filtration performance under the application of AC signal or ultrasound.

2.5.1 Piezoelectric PVDF flat sheet membranes

The utilisation of electrical poling to impart piezoelectric properties and to change the crystalline structure of PVDF membranes was first proposed by Coster and co-workers (2011). Although electrical poling under intense electric field is commonly used on PVDF films, no prior study on electrical poling of PVDF membrane was performed likely due to the presence of pores and voids tend to decrease its dielectric breakdown strength and increase the chance of an electrical breakdown during poling (Venkatragavaraj, et al., 2001).

Some of the factors that could affect electrical poling of PVDF films or membranes are the applied electric field, temperature, and duration. Kawai (1969) first reported polarising temperature of PVDF films was between 50 °C and 90 °C. Coster et al. (2011) performed poling on commercial PVDF microfiltration (MF) membranes under an electric field of $16.3 \times 10^6 \text{ V.m}^{-1}$ and temperature of 90 °C. Poling duration of 2 to 4 h

was found to be sufficient for achieving maximum surface vibration (Darestani, et al., 2013a; Darestani, et al., 2014). Furthermore, poling time of up to 4 h can lead to a more packed structure, decreased hydraulic permeability, reduced molecular weight cut-off (MWCO) and increased rejection (Darestani, et al., 2014). It was found that poling for longer than 4 h resulted in structural defects that negatively impact on filtration performance of the membranes (Darestani, et al., 2014).

Coster et al. (2011) reported an average flux improvement of 136% for filtration of 1% polyethylene glycol for the poled membranes under electrical AC signals while no significant change in flux when unpoled membranes were exposed to AC signals. These results suggested that piezoelectric vibration of the poled membranes induced fluid instabilities, allowing cross-flow to be increasingly effective to remove foulants and delaying formation of cake layer. Hence, it was proposed that piezoelectric vibration increases the critical flux of the membranes (Coster, et al., 2011).

Using an LDV, it was shown that the poled membranes were vibrating when exposed to sinusoidal AC signals in air (Coster, et al., 2011; Darestani, et al., 2013a). The AC signals are typically supplied by a function generator. The parameters that could be adjusted on a function generator are the amplitude and frequency of the AC signals. Since applications for membrane separation usually occur in aqueous environments, it is important to determine if these environments damp the surface vibration of the poled membranes. Darestani et al. (2013a) performed experiments to measure the surface vibration of poled membranes when they are submerged in water and exposed to AC signals. The results demonstrated that submerging poled membranes in water did not dampen the surface but increased the amplitude of surface vibration. Also, it was shown that increasing the amplitude of AC signals leads to greater surface displacement, but vibration level was independent on frequency of the signals. Darestani, Coster, & Chilcott (2013) further studied on the most suitable frequency range to operate piezoelectric membranes and their results showed that operating between 500 and 1 000 Hz was most suitable, considering from the aspect of energy consumption. It was also found that the energy requirement for operating piezoelectric flat sheet PVDF membrane was 110 W.m^{-2} , which was only 20% of that of VSEP.

Darestani et al. (2013a) further confirmed the increase in β phase content and the change in microstructure of the commercial PVDF MF membrane from porous isotropic to

multi-layered anisotropic after electrical poling as shown in Figure 2.9. In the absence of AC signals

Figure 2.9: The SEM images of the cross-section of commercial PVDF MF membrane (a) before poling and (b) after poling (Darestani, et al., 2013a).

The results from the study performed by Chen & Pomalaza-Ráez (2019) indicated that velocity of vibration has greater importance over the amplitude of vibration for fouling control of piezoelectric PVDF membranes. Their filtration tests revealed that continuous vibration of piezoelectric (poled) membranes, at frequency that yielded maximum vibration velocity, had 87% higher permeate flux than non-piezoelectric (unpoled) membranes. They also found that intermittent vibration does not provide anti-fouling effect that was shown in continuous vibration.

Zhang et al. (2019) and Cao et al. (2020) fabricated flat sheet PVDF membranes via TIPS. During the fabrication process, ionic liquid was added to the polymer solution to promote the formation of β phase. The resulted membranes were electrically poled to maintain β phase crystal formation. The filtration experiments performed by Zhang et al. (2019) demonstrated improvement in stable flux by approximately 54 % and 91 % for calcium carbonate suspension and BSA solution respectively. Cao et al. (2020) used the poled membranes in the operation of anaerobic membrane bioreactor filtering synthetic wastewater (Cao, et al., 2020). It was shown that the steady-state water flux of poled PVDF membranes under electrical signal was enhanced by 72.6% as compared to unpoled membranes.

2.5.2 Electrospun piezoelectric membranes

Bae et al. (2017) prepared piezoelectric electrospun PVDF nanofiber membranes via electrospinning. A key benefit of preparing piezoelectric membrane by electrospinning is the simultaneous fabrication and polarisation of the membrane. After electrospinning, the membranes were subjected to heat treatment to improve their mechanical properties. The optimal preparation conditions of the electrospun membranes were a solvent ratio of 5:5 for acetone and N-methyl-2-pyrrolidone (NMP), a tip-to-collector distance (TCD) of 20 cm and a heat treatment duration of 30 min. As compared to commercial MF membrane, the optimised electrospun membrane showed three times higher for pure water permeability. It also had rejection performance of 99.87 % for particulates. Moreover, when AC signal was applied to the electrospun membrane during filtration of 10 ppm alginate solution, the flux decline was reduced by 15% as compared to membrane without application of AC signal.

Gee, Johnson, & Smith (2018) studied the effect of three solvents (dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and NMP) on fiber formation and piezoelectric properties. It was found that PVDF fibers prepared using solvent had the smallest fiber diameter and highest piezoelectric properties. Furthermore, the optimised parameters for piezoelectric properties were a solvent DMF ratio of 6:4 for DMF and acetone, a TCD of 16 cm, a flow rate of 0.8 mL.h^{-1} , and a voltage setting of 14 kV. Minimal decline in flux or increase in TMP was observed for membranes under the influence of AC signal for the filtration of synthetic biofouling solution. The results from this study demonstrated the potential of piezoelectric membranes in water treatment applications, in particular systems with high level of biofouling.

2.5.3 Piezoceramic membranes

Krinks et al. (2015) fabricated porous lead zirconate titanate (PZT) ceramic disks and these disks were electrically poled in air between two aluminium electrodes under an electric field of $2.5 \times 10^6 \text{ V.m}^{-1}$. Although piezoceramics are usually poled while immersed in oil, membrane wetting problems occurred when they were immersed in oil during poling (Krinks, et al., 2015). However, the maximum electric field that could be applied during poling is limited if poling is performed in air as dielectric breakdown of air happened at about $3 \times 10^6 \text{ V.m}^{-1}$ (Pedersen, 1989). Ultrasound was generated by the PZT membranes when an alternating voltage was applied across the membrane and no

water flux was observed over 3 h filtration of 10 mg.L⁻¹ of 500 nm latex particles. On the other hand, in the absence of alternating voltage, the flux reduced by more than 20 % within 3 h filtration.

Mao et al. (2018) synthesised PZT ceramic membranes and poled the membranes sandwiched between two copper electrodes submerged in mineral oil under an electric field of 4×10^6 V.m⁻¹. The above-mentioned membrane wetting issues were prevented by immersing the poled membranes in ethanol at elevated temperature for 3 h to dissolve the mineral oil that filled the membrane pores and then subsequently cleaned using deionised (DI) water. The normalised membrane permeance of poled PZT membranes with the application of ultrasound was raised by 15 to 20 % for filtration of 500 ppm oil-in-water emulsion. Mao et al. (2019) further fabricated a composite membrane comprised of piezoelectric PZT separation layer and macroporous titanium (Ti) support. The Ti support strengthened the mechanical properties of the membrane and served as one of the electrodes for the application of alternating voltage during filtration. The stationary normalised permeance of the poled membranes was approximately 64 % greater than that of membranes without in-situ ultrasound generation during filtration of 500 ppm oil-in-water emulsion.

2.6 Concluding remarks

The preceding literature review reveals the research gaps, issues of relevance to piezoelectric membranes, and potential of piezoelectric membranes as a fouling control in water treatment processes. Previous studies on piezoelectric PVDF membranes mainly focused on enhancing the piezoelectricity of commercial PVDF membranes through electrical poling and determining the optimal operating conditions for piezoelectric membranes for improved filtration performance. Further studies on this topic are necessary to extend the research work on piezoelectric membrane to cover areas such as the fundamental relationship between membrane properties and piezoelectricity. The following are the key issues that would be addressed in this thesis:

- The fundamental understanding between membrane properties (e.g., morphology, pore structure etc.) and piezoelectricity of PVDF membrane and its impact on fouling;

- The incorporation of BaTiO₃ nanoparticles in PVDF membranes for piezoelectricity enhancement and its impact on filtration performance;
- The implementation of piezoelectric membranes in real wastewater filtration to evaluate suitability and long-term performance;
- The assessment of energy consumption of piezoelectric membrane in comparison with conventional method of VSEP.

CHAPTER 3

Effect of morphology on performance of piezoelectric PVDF membrane

3.1 Introduction

Although the improved filtration performance of poled PVDF membranes has been confirmed by many studies (Coster, et al., 2011; Chen & Pomalaza-Ráez, 2019), membrane properties such as morphology and polymorphism that would affect the piezoelectric properties of PVDF membranes have yet to be explored. The different membrane morphologies could be obtained by adjusting the solvent types for phase inversion of polymer solution (Yeow, et al., 2004). The degree of miscibility between solvent and nonsolvent during phase inversion affects the solvent-nonsolvent exchange rate which in turn results in different morphologies (Guillen, et al., 2011). A poor miscibility between solvent and nonsolvent leads to slow solvent-nonsolvent exchange which results in sponge-like morphology whilst a good miscibility between solvent and nonsolvent leads to fast solvent-nonsolvent exchange which results in finger-like structure. Tao et al. (2013) investigated the effect of different solvents on membrane polymorphism and found that the polymorphism of PVDF membranes was primarily determined by the extent of dissolution of PVDF in each solvent. Phase inversion of polymer solutions in which the PVDF was well dissolved, formed membranes with α phase, while poorly dissolved PVDF solutions formed membranes with β phase. Darestani et al. (2014) studied the electric breakdown behaviour of a wide range of commercial membranes and concluded that membrane morphology was a key factor that determined the dielectric strength or electric breakdown behaviour of the membranes. Moreover, the presence of pores and defects in PVDF membranes may cause electrical breakdown during poling.

In this chapter, the effects of morphology on the dielectric and piezoelectric behaviours of the membranes were explored. Flat sheet PVDF membranes with different morphologies were fabricated via non-solvent induced phase separation (NIPS) using different solvents. Electrical poling was then performed on the PVDF membranes to further improve its piezoelectric properties. The filtration performances of the unpoled and poled membranes were also discussed.

3.2 Experimental

3.2.1 Materials

PVDF powder (Solef® 6020) was supplied by Solvay Specialty Polymers and it was dried in a vacuum oven at 60 °C prior to use. N,N-dimethylformamide (DMF, anhydrous, 99.8%, Sigma-Aldrich), 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%, Sigma-Aldrich) and triethyl phosphate (TEP, ReagentPlus®, ≥ 99.8%, Sigma-Aldrich) were used as solvents to prepare the PVDF membranes. The chemical reagents were utilised without further purification. Commercial PVDF membranes (250 kDa UF BX PVDF), that were used for comparison, were supplied by Synder Filtration. These membranes are referred to as UF-Synder in this chapter.

For membrane fouling tests, 200 mg.L⁻¹ colloidal silica solution was selected as the model foulant. The silica solution was prepared from LUDOX® TMA colloidal silica (Sigma-Aldrich) supplied in the form of 34 wt.% in deionised (DI) water at pH 7.0. No significant change in the pH was detected upon the addition of silica to the test solution, which remained at pH 6.5 ± 0.5 throughout the experiment. The nominal size of silica particles was 22 nm based on the datasheet provided by the manufacturer.

3.2.2 Preparation of PVDF membranes

Flat sheet PVDF membranes were fabricated via the NIPS process. The solvents used to separately prepare the polymer solutions were DMF, NMP and TEP. 15 wt.% PVDF powder was dissolved in each solvent at 80 ± 5 °C under constant stirring rate to form a homogeneous polymer solution. The polymer solution was then left undisturbed at room temperature for 12 h for degassing. The degassed solution was uniformly spread onto a glass plate by casting knife (Elcometer) set with gap thickness of 250 µm to form an

incipient membrane. Subsequently, the glass plate was immersed in water coagulation bath at room temperature. Once peeled off from the glass plate, the solidified membrane was transferred into a fresh DI water bath and stored for 24 h to remove residual solvent. The membranes were then freeze-dried. The three types of fabricated membranes were termed as PVDF-DMF, PVDF-NMP and PVDF-TEP, i.e. PVDF-TEP refers to PVDF membrane prepared using TEP as the solvent.

3.2.3 Membrane characterisation

3.2.3.1 Scanning electron microscopy

The morphology and thickness of the membrane samples were examined using a field emission scanning electron microscope (FESEM, JOEL, JSM-7200F Schottky). Prior to FESEM analysis, the samples were coated with 2-nm of platinum layer through the sputtering technique. The average thickness of the membranes was reported based on five separate measurements.

3.2.3.2 Dielectric strength analysis

Dielectric strength is defined as the electrical breakdown voltage divided by the thickness of the sample. The electrical breakdown voltage was determined by sandwiching a 30 mm $\times$ 30 mm rectangular membrane sample between two stainless steel electrodes at room temperature. The potential difference applied across the sample was then gradually increased at a rate of 50 V.min⁻¹ until the membrane was charred at a particular spot which caused overload in the high voltage power supply to trip. Electrical arcing around the edge of the membrane was prevented by using a smaller top electrode (20 mm $\times$ 20 mm) as compared to bottom electrode (200 mm $\times$ 200 mm). An average dielectric strength was calculated for each sample based on five different measurements.

3.2.3.3 Piezo-response force microscopy

Piezo-response force microscopy (PFM) is a variant of atomic force microscopy (AFM) that allows imaging of domains of piezoelectric materials. The PFM technique is based on the detection of converse piezoelectric effect. In addition to an AFM system, a functional generator and a lock-in amplifier are required in PFM analysis. The functional generator generates an oscillating voltage that is applied to the tip of

cantilever whilst the lock-in amplifier amplifies the PFM signals to improve signal-to-noise ratio. During PFM scanning, the cantilever tip deflects according to the local piezoelectric displacement of the samples. The cantilever tip displacement (z) is:

$$z = z_{AC} \cdot \sin(\omega t + \phi) \quad (3.1)$$

where ω is the angular frequency, t is the time, ϕ is the phase difference, and z_{AC} is the amplitude which is proportional to the piezoelectric coefficient of the sample (Uršič & Prah, 2019). In this study, PFM was operated in contact mode using the PFM scanning mode on an atomic force microscope (Park Systems, Park NX 10). Besides PFM amplitude and PFM phase images, topography images were also generated to characterise the average surface roughness of the samples. In PFM imaging, an electrically conductive cantilever with tip coated with Chromium/Platinum (force constant of 3 N.m^{-1} , resonance frequency of 75 kHz) was brought into contact with the surface of the sample.

An alternating current (AC) bias of 8 V riding on a direct current (DC) bias of -8 V was applied between the cantilever tip and the bottom electrode. A total of 256×256 pixels was measured for a scan area of $2 \text{ } \mu\text{m} \times 2 \text{ } \mu\text{m}$. The piezoelectric coefficient, d_{33} , was derived by performing piezoelectric response spectroscopy and applying equation (3.2):

$$d_{33} = \frac{3 \times \text{PFM Amplitude}}{(A - B)\text{Sensitivity} \times (A + B)\text{DC} \times \text{Tip Bias}} \quad (3.2)$$

where PFM Amplitude (mV) is the maximum amplitude obtained on the amplitude-voltage hysteresis loop as shown in Figure 3.1, $(A - B)\text{Sensitivity}$ is the sensitivity of the cantilever with value of $33.333 \text{ V.}\mu\text{m}^{-1}$, $(A + B)\text{DC}$ is the intensity of the laser beam which was aligned prior to scanning with values that ranged between 3 and 4, and Tip Bias is the applied AC tip bias which was set at 10 V . It should be pointed out that PFM imaging and piezoelectric response spectroscopy are two different techniques, and their settings were dissimilar. During piezoelectric response spectroscopy, tip deflection was detected while applying DC bias sweep (-10 V to $+10 \text{ V}$) and fixed AC bias on the sample and tip respectively. Tip deflection was expressed in terms of PFM amplitude as shown in Figure 3.1. Note that equation (3.2) was given by Park Systems and it is only applicable to NX systems provided by Park Systems.

Figure 3.1: An example of amplitude-voltage hysteresis loop of a PVDF membrane sample. PFM Amplitude in equation (3.2) refers to the maximum amplitude on the amplitude-voltage hysteresis loop as depicted by the arrow.

3.2.3.4 Infrared spectroscopy and X-ray diffraction analysis

The crystalline phase in the membrane sample was investigated by infrared (IR) spectroscopy. The IR spectrum of a sample was obtained using a Shimadzu IRPrestige-21 fourier-transform infrared spectroscopy (FTIR) spectrometer in an attenuated total reflectance mode. IR spectra were measured in the range of 400 to 1,500 cm^{-1} at room temperature of 25 $^{\circ}\text{C}$. The relative fraction of β phase ($F(\beta)$) was calculated using equation (3.3) (Rinaldo Gregorio & Cestari, 1994):

$$F(\beta) = \frac{A_{\beta}}{\frac{K_{\beta}}{K_{\alpha}} A_{\alpha} + A_{\beta}} \quad (3.3)$$

where A_{α} and A_{β} are the absorbance values at 763 cm^{-1} and 840 cm^{-1} respectively while K_{α} and K_{β} are absorption coefficients with values of 6.1×10^4 and $7.7 \times 10^4 \text{ cm}^2 \cdot \text{mol}^{-1}$ respectively. IR absorption peaks, at 763 cm^{-1} and 840 cm^{-1} , are characteristic peaks of α and β phases respectively (Rinaldo Gregorio & Cestari, 1994). The average $F(\beta)$ was calculated based on five different measurements for each membrane.

The phases present in crystalline PVDF could also be identified by X-ray diffraction (XRD). The XRD results of the membrane samples were characterised using Bruker Advance D8 X-ray diffractometer with Cu- K_{α} radiation of wavelength 0.154 nm operated at 40 kV and 40 mA.

3.2.3.5 Mechanical strength analysis

The mechanical properties of the membranes were characterised by a universal testing machine (Instron 5567 electromechanical tester). The membrane sample was clamped using the tensile grips and pulled longitudinally at a rate of 20 mm.min⁻¹ at room temperature. The test was repeated three times to get average values for each sample.

3.2.3.6 Evapo-porometry

Mass-based pore diameter and porosity of a membrane sample were determined using evapo-porometry (EP) (Krantz, et al., 2013). This technique is based on the Kelvin equation that relates the evaporation rate of volatile liquid to the pore diameter. The membrane sample was wetted using ethanol (ethanol absolute EMSURE® ACS, Merck) after placing it into the EP cell. The cell was then stationed in an incubator (LE-150D, Yihder Technology) maintained at 28.0 ± 0.1 °C. Evaporation of free-standing ethanol layer occurred first, followed by evaporation of ethanol from the membrane pores. The gravimetric data were measured semi-micro balance (ME235S, Sartorius) and logged on a computer. The evaporation rate was then calculated based on the gravimetric data. The onset of pore draining was indicated by deviation of evaporation rate from initial constant evaporation rate. Membrane porosity was determined using equation (3.4) (Wang, et al., 2010):

$$\text{Porosity(\%)} = \frac{\frac{m_{wet} - m_{dry}}{\rho_w}}{\frac{m_{wet} - m_{dry}}{\rho_w} + \frac{m_{dry}}{\rho_m}} \times 100\% \quad (3.4)$$

where m_{wet} is the mass of the wetted membrane before pore draining, m_{dry} is the mass of the dry membrane, ρ_w is the density of the wetting liquid (for ethanol, 0.789 g.cm⁻³), and ρ_m is the density of the membrane. The average pore diameter and porosity were determined by three separate measurements.

3.2.4 Electrical poling setup

Electrical poling was employed to enhance the piezoelectric properties of PVDF membranes. During poling, a 90 mm × 90 mm membrane sample was sandwiched between two stainless steel electrodes as depicted in Figure 3.2.

Figure 3.2: Electrical poling setup enclosed within an oven.

The membrane sample was heated in the oven from ambient temperature to 50 ± 5 °C. By poling the sample in the oven, it would ensure uniform heating. Once the temperature of 50 °C was attained, the potential difference across the two electrodes was slowly increased from 0 V to the desired value at a rate of $50 \text{ V} \cdot \text{min}^{-1}$. The potential difference was achieved by utilising a high voltage DC power supply (Stanford Research Systems, model PS375). The membrane sample was maintained at the elevated temperature and potential difference conditions for a duration of 2 h. The sample was allowed to cool to ambient temperature by switching off the oven while still applying the potential difference. Once the sample was cooled, the potential difference was gradually decreased to 0 V at a rate of $50 \text{ V} \cdot \text{min}^{-1}$. To reduce the possibility of electrical breakdown from occurring during poling, the top electrode (80 mm × 80 mm) was smaller than the bottom electrode (200 mm × 200 mm). Hence, only the portion of the sample exposed to intense electric field between the electrodes was characterised and subjected to filtration analysis.

The poling temperature was fixed at 50 °C while the poling potential difference varied among the different type of membranes due to the disparity of thicknesses. For effective poling, the desired electric field to be applied across the membrane is 10 MV.m⁻¹ (megavolts per meter). Darestani et al. (2014) reported that an electric field of approximately 10 MV.m⁻¹ was needed to change the microstructure of membranes. However, electrical breakdown occurred for PVDF-NMP and UF-Synder before 10 MV.m⁻¹ of electric field was reached. In these cases, the electric field was lowered to prevent the occurrence of electrical breakdown. Electrical breakdown was undesirable because the high voltage power supply would be tripped resulting in termination of poling. The poling conditions applied to the different type of membranes were shown in Table 3.1.

Table 3.1: Poling conditions applied for different type of membranes.

	Temperature (°C)	Potential difference applied (V)	Electric field across membrane (MV.m ⁻¹)
UF-Synder	50	500	2
PVDF-DMF	50	500	10
PVDF-NMP	50	650	7
PVDF-TEP	50	800	10

3.2.5 Filtration performance analysis

A stainless steel cross-flow filtration cell was used to analyse the filtration performance of the membranes. The cell has an effective membrane area of $16.25 \times 10^{-4} \text{ m}^2$. The schematic diagram of the cross-flow cell is presented in Figure 3.3.

Figure 3.3: Schematic diagram of the cross-flow filtration cell used for filtration tests.

Figure 3.4: Process flow diagram of the filtration system used for filtration tests.

Referring to Figure 3.4, the filtration system consisted of a feed tank (10 L), a temperature control system (9106AA2P, PolyScience), a peristaltic pump (Masterflex® L/S® Standard Digital Drives, Cole-Parmer), three pressure gauges (302174SD02L100, Ashcroft), a signal generator (AFG1022, Tektronix) connected to the cross-flow filtration cell, a mass flow controller (L30C5I, Bronkhorst) located on the permeate stream and a data acquisition system (LabVIEW, National Instruments). The pure water permeability (PWP) of the membranes was determined by varying the permeate flux to obtain five distinct transmembrane pressure (TMP) data. The PWP was computed as the gradient of the plot of permeate flux against TMP. During fouling tests, the filtration setup was operated as a closed system in which both permeate and retentate were recycled back into the feed tank. The temperature of the feed (200 mg.L^{-1} silica solution) was kept constant at $25 \pm 1 \text{ }^{\circ}\text{C}$ via chiller and the cross-flow velocity was fixed at 0.1 m.s^{-1} . To investigate the effect of electrical AC signal on the filtration performance of the unpoled and poled membranes, AC signal of 10 V peak-to-peak (V_{pp}) and 500 Hz was applied to the filtration cell via the signal injecting points as shown in Figure 3.3 (Darestani, et al., 2013).

3.3 Results and discussion

3.3.1 Effect of morphology on dielectric strength

By using different solvents, PVDF membranes with different morphologies were fabricated. The solvents used were DMF, NMP and TEP. These solvents have different solubility for PVDF which led to membranes with different morphology and polymorphism (Yeow, et al., 2004; Tao, et al., 2013; Bottino, et al., 1991; Chang, et al., 2017). During casting of the membranes, the gap between casting knife and glass plate, and the speed of the casting knife were consistent for all the membranes. The resulting film thickness depends on the viscosity of the polymer solution as shown in elastohydrodynamic film thickness regression equation, equation (3.5) (Smeeth, et al., 1996):

$$h = kU^{0.67}\mu^{0.67} \quad (3.5)$$

where h is the film thickness, U is the rolling speed and μ is the dynamic viscosity of the solution at atmospheric pressure. Hence, the varied thicknesses of the resulting membranes were due to the viscosity of the polymer solution. Figure 3.5 compares the FESEM images of the top surface and entire cross-section of commercial and fabricated PVDF membranes before and after poling. The explanation of the morphology change after poling could be found in section 3.3.3.

Figure 3.5: FESEM images of the top surface and cross-section of unpoled and poled UF-Synder (a, b, c and d), PVDF-DMF (e, f, g and h), PVDF-NMP (i, j, k and l) and PVDF-TEP (m, n, o and p). FESEM images of the top surface are at 20 000 times magnification. FESEM images of the cross-section are at 250, 1 500, 800 and 1 000 times magnification respectively for UF-Synder, PVDF-DMF, PVDF-NMP and PVDF-TEP.

For commercial UF-Synder membranes, Figure 3.5a and Figure 3.5b reveal that it consisted of spherulites on its top surface and macrovoids, with a support layer in its cross-section. The porous top skin layer of commercial UF-Synder resulted in high permeability of UF-Synder as shown in Table 3.2. The fabricated PVDF-DMF exhibited a dense skin layer with minimally visible pores on its top surface (Figure 3.5e) and short finger-like cavities with sponge-like sublayer in its cross-section structure (Figure 3.5f).

In the case of fabricated PVDF-NMP, large and irregular voids can be observed in Figure 3.5j. Conversely, membranes casted with TEP solvent exhibited asymmetrical sponge-like structure that was denser nearer to the top surface as depicted in Figure 3.5n. The results of the dielectric strength analysis are listed in Figure 3.6. The influence of membrane morphology on dielectric strength can be deduced by comparing different morphologies with their respective dielectric strengths.

Figure 3.6: Dielectric strength (MV.m⁻¹) of commercial and fabricated PVDF membranes.

Figure 3.7: Plot of dielectric strength (MV.m⁻¹) against tensile strain at maximum load (%) for unpoled fabricated PVDF membranes.

Table 3.2: The properties of unpoled and poled UF-Synder, PVDF-DMF, PVDF-NMP and PVDF-TEP.

	Unpoled				Poled			
	UF-Synder	PVDF-DMF	PVDF-NMP	PVDF-TEP	UF-Synder	PVDF-DMF	PVDF-NMP	PVDF-TEP
<i>Membrane properties</i>								
Pore diameter (nm)	57 ± 1	51 ± 7	72 ± 2	81 ± 14	64 ± 7	49 ± 2	69 ± 10	60 ± 10
Porosity (%)	34.8 ± 0.4	71.8 ± 4.1	75.9 ± 2.8	69.2 ± 0.2	47.8 ± 1.0	68.7 ± 0.7	61.0 ± 3.9	57.4 ± 0.9
Thickness (μm)	278 ± 6 (112 ± 9 ^a)	49 ± 1	94 ± 4	78 ± 2	234 ± 5 (108 ± 6 ^a)	48 ± 1	91 ± 2	78 ± 1
Permeability (L.m ⁻² .h ⁻¹ .bar ⁻¹)	1287 ± 170	61 ± 6	277 ± 32	362 ± 7	2117 ± 77	60 ± 2	259 ± 43	308 ± 49
Average surface roughness (nm)	32	40	36	66	21	33	21	20
<i>Mechanical properties</i>								
Young's modulus (MPa)	227.8 ± 12.5	119.1 ± 4.8	41.5 ± 1.8	60.0 ± 10.7	459.5 ± 28.9	136.5 ± 4.8	43.1 ± 1.6	40.1 ± 3.4
Tensile strength at break (MPa)	16.6 ± 0.8	13.0 ± 0.5	3.0 ± 0.4	4.3 ± 0.3	32.1 ± 1.4	13.0 ± 2.0	3.2 ± 0.1	2.9 ± 0.1
Tensile strain at break (%)	32 ± 2	697 ± 76	186 ± 62	478 ± 109	29 ± 2	677 ± 111	182 ± 20	273 ± 97
<i>Piezoelectric properties</i>								
Number of points where hysteresis loops were observed	94	87	53	47	62	93	76	62
Average d33 (pm.V ⁻¹)	5.15 ± 3.36	3.25 ± 0.41	3.29 ± 0.70	2.18 ± 0.58	5.13 ± 2.35	3.38 ± 0.45	3.71 ± 1.35	2.73 ± 0.20
<i>F</i> (β)	0.884 ± 0.005	0.493 ± 0.020	0.509 ± 0.007	0.259 ± 0.019	0.886 ± 0.004	0.504 ± 0.004	0.549 ± 0.012	0.266 ± 0.009

^a This refer to the thickness of PVDF layer in UF-Synder.

Among the four different membranes referred to in Figure 3.6, commercial UF-Synder showed the lowest dielectric strength. This is likely due to the presence of two layers of PVDF and a non-woven support which coincides with findings from another study where they reported discontinuities within membranes led to early electrical breakdown (Darestani, et al., 2014). Similarly, fabricated PVDF-NMP exhibited discontinuities as it has large macrovoids which plausibly gave rise to a relatively low dielectric strength. Although finger-like cavities were observed in the morphology of PVDF-DMF (Figure 3.5f), its dielectric strength was found to be the highest. This could possibly be due to the fact that the bulk of its structure consisting of a uniform sponge-like sublayer. Since morphology is the key factor in determining the dielectric strength of a membrane (Darestani, et al., 2014), it would be expected that PVDF-TEP would have the highest dielectric strength. However, the dielectric strength of PVDF-TEP is lower than that of PVDF-DMF. It was suggested previously that membranes that had high electric breakdown field were also able to withstand greater elongation before mechanical failure (Darestani, et al., 2014). PVDF-TEP displayed a lower tensile strain at break as compared to PVDF-DMF as shown in Table 3.2 which is consistent with the lower dielectric strength of PVDF-TEP. It is known that dielectric strength and mechanical properties of materials follow the weakest-link theory (Blok & LeGrand, 1969; Zweben & Rosen, 1970). From the results, the membranes that endured greater extension before mechanical fracture were also able to withstand greater force by electric fields. Figure 3.7 shows a linear relationship between the dielectric strength and the tensile strain at break which is in agreement with the previous study (Darestani, et al., 2014). Since the intrinsic properties of polymers are the key factors in affecting their mechanical properties (Hong & Kertesz, 1990), comparison between mechanical and electric breakdown behaviours could only be made for membranes with same material (Darestani, et al., 2014). Thus, commercial UF-Synder was not included in Figure 3.7 as it was made up of two different materials.

From the analysis above, it can be concluded that short finger-like cavities with sponge-like sublayer resulted in high dielectric strength and outstanding mechanical properties. This was followed by sponge-like structure with moderate dielectric strength, whilst large macrovoids or non-woven substrate layers led to low dielectric strength. Moreover, the results suggest that dielectric strength of the membranes could be inferred from their

tensile tests as there was a linear correlation between dielectric strength and tensile strain at break.

3.3.2 Piezoelectric properties and crystalline phase of PVDF membranes

PFM was employed to characterise the piezoelectric membranes at nanoscales. PFM is capable of imaging both out-of-plane (OP) and in-plane (IP) piezo-responses. OP and IP piezo-responses reflect the deflections that are perpendicular and parallel to the surface plane respectively. Since the anti-fouling behaviour of piezoelectric membrane is mainly dependent on the OP piezoelectric response (Coster, et al., 2010), only OP PFM was performed. Topography, PFM amplitude and PFM phase images of unpoled UF-Synder, PVDF-DMF, PVDF-NMP and PVDF-TEP can be found in Figure 3.13. The PFM amplitude profiles (Figure 3.8a2, b2, c2 and d2) illustrate that the amplitude ranges of PVDF-DMF, PVDF-NMP and PVDF-TEP were similar while the amplitude range of UF-Synder was wider. The PFM phase profiles (Figure 3.8a4, b4, c4 and d4) show that the phase varied between -90° and 90° horizontally across the scan area for all the membranes. This indicates that the domains in these membranes were randomly orientated.

Piezoelectric response spectroscopy was performed with 10×10 points on the scan area of $2 \mu\text{m} \times 2 \mu\text{m}$. Since the range of DC bias sweep performed was limited by the capability of the instrument, not all the points generated a hysteresis loop (e.g. Figure 3.1). These points corresponded to areas of weak piezoelectric response and larger DC bias sweep might be required to produce the hysteresis loops. The number of points where hysteresis loops were observed is listed in Table 3.2. The piezoelectric coefficient d_{33} was calculated for points that generated hysteresis loop using equation (3.2). Average d_{33} value and surface roughness for each membrane sample are also indicated in Table 3.2. Among the membranes, commercial UF-Synder had the greatest error bar which implies that there was a wide variance in d_{33} value within the membrane.

Figure 3.8: PFM amplitude and PFM phase images of UF-Synder (a1 and a3), PVDF-DMF (b1 and b3), PVDF-NMP (c1 and c3) and PVDF-TEP (d1 and d3). Amplitude and phase profiles along the red line in PFM amplitude and PFM phase images of UF-Synder (a2 and a4), PVDF-DMF (b2 and b4), PVDF-NMP (c2 and c4) and PVDF-TEP (d2 and d4).

Figure 3.9 shows the FTIR spectra of the unpoled commercial and fabricated PVDF membranes from 1500 to 400 cm^{-1} . The presence of absorption peaks, at 1275, 840, 510 and 447 cm^{-1} , indicate the presence of β and γ phases in UF-Synder while no distinct peak, representing α phase, could be observed (Cai, et al., 2017). Prominent absorption peaks at 1209, 1148, 975, 763 and 613 cm^{-1} denote the existence of α phase in PVDF-TEP with weaker peaks of β and γ phases (Cai, et al., 2017). PVDF-DMF and PVDF-NMP show similar trend in their FTIR spectra where absorption peaks of α , β and γ phases could be seen. The different crystalline phases among the membranes were also supported by the XRD spectra as shown in Figure 3.10. The key difference between FTIR and XRD techniques is the penetration depth of IR radiation in FTIR is a few micrometres whilst that of X-rays in XRD is only a few nanometres. This implies that the FTIR analysis would provide information on the bulk material. On the other hand, XRD analysis would give information on material closer to the surface.

Figure 3.9: FTIR spectra of unpoled commercial and fabricated PVDF membranes.

Figure 3.10: patterns of unpoled and poled (a) UF-Synder, (b) PVDF-DMF, (c) PVDF-NMP and (d) PVDF-TEP.

To quantify the proportion of β phase in each membrane, $F(\beta)$ was calculated using equation (3.3). The average $F(\beta)$ for each membrane is specified in Table 3.2. The results for $F(\beta)$ are in agreement with the FTIR spectra shown in Figure 3.9. UF-Synder, with prominent β phase peaks, has the greatest $F(\beta)$ while PVDF-TEP has the lowest $F(\beta)$. The FESEM image of top surface of UF-Synder (Figure 3.5a) reveals the presence of uniform spherulites which possibly contributed to UF-Synder having the highest $F(\beta)$. The diffraction peaks at 20.0° , 20.6° , and 20.3° in the XRD spectra correspond to α , β , and γ phases in semi-crystalline PVDF. The XRD results are consistent with that of the FTIR in which UF-Synder and PVDF-TEP displayed prominent and subtle β -phase peaks respectively. By comparing the results obtained for d_{33} values and $F(\beta)$ for the membranes, a correlation could be identified. Figure 3.11 shows that the higher the $F(\beta)$, the greater the d_{33} value. This finding is consistent with the notion that the β phase in PVDF contributes to its electroactive properties (Kochervinskii, 2003).

Intuitively, piezoelectric properties of PVDF membranes can be enhanced by increasing its $F(\beta)$. In ascending order of d_{33} and $F(\beta)$ values, the degree of piezoelectric attributes for the membranes examined were PVDF-TEP, PVDF-DMF, PVDF-NMP and UF-Synder.

Figure 3.11: Piezoelectric coefficient, d_{33} , against fraction of β phase, $F(\beta)$, for unpoled commercial and fabricated PVDF membranes.

Based on the results above, UF-Synder has the greatest number of points where hysteresis loops were observed, highest d_{33} and largest $F(\beta)$. However, UF-Synder has the lowest dielectric strength. Out of the three fabricated PVDF membranes, PVDF-DMF had the greatest number of points where hysteresis loops were observed. PVDF-DMF and PVDF-NMP displayed similar d_{33} and $F(\beta)$ values.

3.3.3 Effect of electrical poling on PVDF membranes

Electrical poling was performed on the commercial and fabricated PVDF membranes to explore the possibility of enhancing the piezoelectric properties of the membranes. However, as discussed in section 3.2.4, commercial UF-Synder and fabricated PVDF-

NMP membranes could not withstand high electric fields. For these membranes, the electric field was lowered such that electrical breakdown did not occur. The poling conditions of the membranes are listed in Table 3.1. The poling voltage used was much lower than the electrical breakdown voltage at room temperature because the electrical breakdown voltage reduces as temperature increases (Darestani, et al., 2014). Hence, the poling voltage was set such that electrical breakdown did not occur at the increased temperatures used during poling.

Contrary to previous studies (Darestani, et al., 2013a; Darestani, et al., 2014), electrical poling did not significantly change the microstructure of UF-Synder and PVDF-NMP membranes. This could be possibly due to the lower electric field applied to these membranes during poling. The presence of macrovoids in UF-Synder and PVDF-NMP limited the electric field that could be applied. On the other hand, visible differences could be observed between unpoled and poled PVDF-DMF or PVDF-TEP membranes. Instead of the finger-like cavities in the unpoled PVDF-DMF as shown in Figure 3.5f, the cavities were drop-like after poling. Although the cavities were shorter, the thickness of the PVDF-DMF was similar before and after poling. One possible explanation for the drastic change in morphology of the cross-section is the alignment of electric dipoles in the direction of electric field. Figure 3.12 illustrates a schematic diagram for the proposed explanation of the change in morphology during poling.

Figure 3.12: Schematic diagram of the proposed explanation of the change in morphology in cross-section before and after poling. The red oval-shaped symbol represents the PVDF dipole domains and the light gray arrow represents the force exerted by the PVDF dipole domains.

Prior to poling, the electric dipole domains were randomly orientated in the membrane structure. During poling, the electric dipoles gradually aligned themselves in the direction of the electric field. It is proposed that as the dipoles rotated, they exerted a force on the other dipoles above them. The dipoles, that were closer to the finger-like cavities, were more "free" than those in the sublayer. As the dipoles beneath them were aligned, these dipoles exerted a force on the boundaries of the cavities. Due to the alignment, the membrane was stretched and the cavities shrank in depth. It can be seen from Figure 3.5h that the membrane near the cavities appeared to be stretched in the direction that is parallel to the direction of electric field. This is similar to the finding from previous study that there was possibly stretching force exerted on the membrane during poling (Darestani, et al., 2013a). The cavities did not disappear completely, probably because of the intensity of electric field was insufficient to achieve that. After poling, two distinct layers could be observed in cross-section FESEM image of poled PVDF-TEP in Figure 3.5p. Even though unpoled PVDF-TEP exhibited asymmetrical structure that was denser nearer to the top surface, it was a gradual change in the void density across its cross-section. Similar to PVDF-DMF, the change in morphology of poled PVDF-TEP could be attributed to the alignment of electric dipoles during poling. The electric field applied to PVDF-DMF and PVDF-TEP membranes during poling was identical at 10 MV.m^{-1} .

Figure 3.13 shows the topography, PFM amplitude and PFM phase images of unpoled and poled UF-Synder, PVDF-DMF, PVDF-NMP and PVDF-TEP. It is important to note that similar scan settings were used – for all the scans and that the scales of PFM images were consistent among the unpoled and poled membranes. The 3D topography images could be found in Figure 3.14. The regions that are vibrant in PFM amplitude images signify greater tip deflection which in turn means higher amplitude of vibration, and vice versa. From the comparison between the topography and PFM amplitude images, bright PFM amplitude regions exist in both the dull and vibrant parts of the topography image. Hence, it could be substantiated that the topography had negligible effect on the PFM amplitude signals obtained. The PFM amplitude and phase images of the UF-Synder and PVDF-NMP membranes were similar before and after poling. This means that poling did not alter the piezoelectric behaviours of these membranes at nanoscales. This could be possibly due to the fact that electric field applied to these membranes during poling was insufficient. In contrast, the PFM amplitude images of poled PVDF-

DMF and PVDF-TEP were more vibrant as compared to that of the unpoled which implies that poled PVDF-DMF and PVDF-TEP presented more areas with higher amplitudes of vibration in response to the applied biases. Figure 3.13l also suggests that the dipole domains were mainly aligned in a single direction for poled PVDF-DMF as there is less contrast in its PFM phase image.

Besides the changes observed from FESEM and PFM images on poling, there were also changes in the other properties, which are summarised in Table 3.2. Similar trends were observed for the fabricated PVDF membranes before and after poling. Firstly, the pore diameter and porosity became smaller which would impact on their permeability (see also next section). This agrees with previous studies where it was found that electrical poling decreased pore size and hydraulic permeability of commercial PVDF membranes (Darestani, et al., 2013; Darestani, et al., 2014). Since EP characterisation is based on Kelvin equation which is increasingly accurate for determining pore sizes ranging from 4 nm to 150 nm, EP may not be able to accurately detect pores larger than 150 nm. The significant porosity reduction for PVDF-NMP membranes was likely attributed by the smaller pores whilst the size of the larger pores remained relatively unchanged. Hence, there is negligible difference between the FESEM images of PVDF-NMP membrane before and after poling as shown in Figure 3.5.

Figure 3.13: Topography, PFM amplitude and PFM phase images of unpoled UF-Synder (a, b and c), poled UF-Synder (d, e and f), unpoled PVDF-DMF (g, h and i), poled PVDF-DMF (j, k and l), unpoled PVDF-NMP (m, n and o), poled PVDF-NMP (p, q and r), unpoled PVDF-TEP (s, t and u) and poled PVDF-TEP (v, w and x).

Figure 3.14: 3D AFM images of unpoled and poled UF-Synder (a and b), PVDF-DMF (c and d), PVDF-NMP (e and f) and PVDF-TEP (g and h).

Figure 3.15: Pore-size distribution of unpoled and poled PVDF-DMF membranes plotted as the percent of total mass against pore diameter (nm).

Figure 3.15 compares the mass-based pore size distribution of unpoled and poled PVDF-DMF membranes. It can be seen that the largest pore diameter reduced from 255 nm to 235 nm and the mass percentages of smaller pore sizes generally increased. This further confirms that electrical poling aligned the dipoles and reduced the size of large cavities or pores. Secondly, the thickness of the membrane was slightly reduced, possibly because of the compression force exerted by the weight of the top electrode whilst the membrane was at an elevated temperature. Thirdly, the piezoelectric properties and $F(\beta)$ were improved which is in agreement with Darestani et al. (2013a) who reported more prominent β phase absorption peaks and increased d_{33} value after poling. Lastly, consistent with a previous study (Darestani, et al., 2013), the surface became smoother. This was perhaps due to heat and compression during poling that smoothens the surface. A smoother surface is more favourable for membrane separation purposes as foulants tend to adhere to a greater extent to rough surface (Hoek, et al., 2003; Chen, et al., 2012). Hence, electrical poling could have an additional function in smoothing the surface of membranes. Although commercial UF-Synder indicated outstanding d_{33} and $F(\beta)$ values, it had the lowest dielectric strength and this limited the field strength that could be applied during poling. Contrary to the fabricated membranes, the pore diameter and

porosity of UF-Synder became larger after poling which enhanced its permeability. Moreover, the average d_{33} and $F(\beta)$ of UF-Synder remained fairly similar after poling. The mechanical properties of unpoled and poled membranes are listed in Table 3.2. Generally, the Young's modulus and tensile strength at break increased after poling except that for PVDF-TEP, and the tensile strain at break decreased slightly after poling. After poling, the morphology of the PVDF-TEP membranes consists of two distinct layers as shown in the FESEM images (Figure 3.5p). The worse mechanical properties of poled PVDF-TEP could possibly be explained by its layered morphology.

3.3.4 Filtration performance of unpoled and poled PVDF membranes

The effect of AC electrical signal (10 Vpp, 500 Hz) on the critical flux of silica particle for unpoled and poled PVDF membranes was explored. Flux stepping experiments were performed where the flux was increased at an interval of $20 \text{ L.m}^{-2}.\text{h}^{-1}$ and each flux step lasted for 20 min. The rate of TMP increase ($d\text{TMP}/dt$) at each flux was determined. According to the definition of critical flux, its flux value corresponds to the highest flux for $d\text{TMP}/dt = 0$; this the x-intercept of the $d\text{TMP}/dt$ vs. flux plot (Figure 3.16) gives the value of critical flux. The critical flux of silica particles determined at different conditions are tabulated in Table 3.3. For all the fabricated membranes, the critical flux values increased for poled membranes with AC applied during filtration compared to controls, i.e., poled membrane without AC applied during filtration and unpoled membrane with or without AC applied during filtration. For example, the critical flux value for PVDF-DMF showed the greatest increase of 46%, while the increases were 34% and 25% for PVDF-NMP and PVDF-TEP, respectively. Meanwhile, for commercial UF-Synder, a slight difference in the critical values were observed for unpoled and poled membranes (<15%), but no change in the critical flux values regardless of AC application. First, the change in microstructure after poling was likely the reason to impact the critical flux value between unpoled and poled UF-Synder. This could be substantiated by the permeability of UF-Synder was greatly increased from an average of $1287 \text{ L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$ to $2117 \text{ L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$ (Table 3.3). Second, the application of AC signal showed negligible effect on critical flux value as the non-woven support of UF-Synder does not possess piezoelectric properties, which might result in the ineffective electrical poling or limited the overall micro-vibration effect of poled UF-Synder under AC signal.

Figure 3.16: Plot of $dTMP/dt$ ($kPa.s^{-1}$) vs. flux ($L.m^{-2}.h^{-1}$) for flux stepping experiments of unpoled and poled commercial and fabricated membranes (a) UF-Synder, (b) PVDF-DMF, (c) PVDF-NMP and (d) PVDF-TEP with and without AC signal (10 Vpp, 500 Hz) applied during filtration. Experimental conditions: 200 mg.L^{-1} silica feed solution, cross-flow velocity of 0.1 m.s^{-1} .

Table 3.3: The critical flux values for unpoled and poled commercial and fabricated membranes without and with an AC signal (10 Vpp, 500 Hz) applied during filtration.

Membrane	Application of AC	Critical flux ($L.m^{-2}.h^{-1}$)	Membrane	Application of AC	Critical flux ($L.m^{-2}.h^{-1}$)
Unpoled UF-Synder	No	141.1 ± 5.3	Unpoled PVDF-DMF	No	52.5 ± 2.7
Unpoled UF-Synder	Yes	139.8 ± 3.5	Unpoled PVDF-DMF	Yes	48.3 ± 3.3
Poled UF-Synder	No	160.4 ± 0.6	Poled PVDF-DMF	No	51.5 ± 3.4
Poled UF-Synder	Yes	159.6 ± 1.6 (+ 0%) ^b	Poled PVDF-DMF	Yes	76.4 ± 3.9 (+ 46%) ^b
Unpoled PVDF-NMP	No	87.7 ± 1.5	Unpoled PVDF-TEP	No	96.7 ± 3.5
Unpoled PVDF-NMP	Yes	86.6 ± 1.8	Unpoled PVDF-TEP	Yes	92.9 ± 2.8

Poled PVDF-NMP	No	86.6 ± 3.7	Poled PVDF-TEP	No	99.8 ± 3.8
Poled PVDF-NMP	Yes	117.6 ± 5.5 (+ 34%) ^b	Poled PVDF-TEP	Yes	121.0 ± 2.9 (+ 25%) ^b

^b These values refer to the percentage increase in critical flux of poled membranes.

Based on the improvement in critical flux values, the PVDF-DMF was selected for longer fouling test to confirm the improvement in filtration performance. The operating flux was set at $150 \text{ L.m}^{-2}.\text{h}^{-1}$ (~2 times higher than the critical flux value for poled membrane) and crossflow of 0.1 m.s^{-1} and 200 mg.L^{-1} silica solution was used as model foulant. The normalised TMP profiles are illustrated in Figure 3.17.

Figure 3.17: Effect of AC signal (10 Vpp, 500 Hz) on normalised TMP (P/P_0) of unpoled and poled PVDF-DMF membranes during filtration of 200 mg.L^{-1} silica solution at fixed permeate flux of $150 \text{ L.m}^{-2}.\text{h}^{-1}$ and cross-flow velocity of 0.1 m.s^{-1} .

Our results validated that the application of electrical signal improved the filtration performance of poled fabricated membranes but not that of unpoled membranes as shown in Figure 3.17, similar to previous findings (Coster, et al., 2011; Chen & Pomalaza-Ráez, 2019). The poled PVDF-DMF under AC signal (10 Vpp, 500 Hz) took ~175 min (or $d\text{TMP}/dt = 0.8 \text{ kPa.min}^{-1}$) to reach the TMP of 600 kPa, i.e., maximum

pressure attained by the pump, vs. ~55 min for the controls, which corresponded to a remarkable improvement in the filtration duration by a factor of approximately three. The piezoelectric vibrations of poled PVDF-DMF disturbed the silica fouling layer with less prominent foulant layer enclosing areas of non-fouled spaces (Figure 3.18d), while large chunks of foulant layers are observed for controls (Figure 3.18a, b and c); thus resulted in lower cake resistance.

Figure 3.18: SEM images of fouled unpoled and poled PVDF-DMF membranes with or without application of AC signal (10 Vpp, 500 Hz) at 1 000 times magnification.

3.4 Chapter conclusion

The effect of morphology on the performance of piezoelectric PVDF membranes was discussed in this chapter. PVDF membranes with different morphology were fabricated using three different solvents: N,N-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP) and triethyl phosphate (TEP). The different compatibility of these solvents for PVDF resulted in distinctive morphologies. Dielectric strength analysis and PFM characterisation showed that PVDF membranes, with finger-like cross-section morphology, had better dielectric and piezoelectric behaviour among all the fabricated membranes. Although commercial UF-Synder membrane displayed outstanding intrinsic piezoelectric properties, it had a low dielectric strength, and its filtration performance did not improve after electrical poling at mild conditions. Thus, besides possessing outstanding piezoelectric properties, it was also crucial for an ideal piezoelectric PVDF membrane to have the appropriate morphology that was suitable for electrical poling. Morphologies, such as macrovoids and distinct layers, resulted in low dielectric strength which was undesirable for electrical poling. The results from piezoelectric response spectroscopy indicated that electrical poling aligned the dipoles and enhanced the piezoelectric properties of the fabricated PVDF membranes. Moreover, electrical poling reduced the finger-like cavities to drop-like cavities in PVDF-DMF membranes as illustrated in FESEM while minimal change was observed for PVDF-NMP membrane. Flux stepping experiments showed piezoelectric vibrations of poled membranes under the application of electrical signal dramatically enhanced critical flux by 25 to 46%. Filtration fouling test on PVDF-DMF membranes further demonstrated piezoelectric vibrations of poled PVDF membranes under electrical signal dramatically delayed fouling progression (66% reduction in $dTMP/dt$), and thus extending filtration duration by a factor of approximately three.

CHAPTER 4

Incorporation of barium titanate nanoparticles in piezoelectric PVDF membrane

4.1 Introduction

Piezopolymers can be classified into three main categories based on their properties and operating principles: bulk piezopolymers, piezocomposites and voided charged polymers (Ramadan, et al., 2014; Xu, et al., 2017). Piezopolymers are preferable for making membranes than inorganic piezoelectric materials due to low cost, less toxicity and simpler processing (Ramadan, et al., 2014). Examples of bulk piezopolymers include PVDF and its copolymer such as poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE). Piezocomposites consist of a polymeric material embedded with inorganic piezoelectric material, generally ceramic. The use of piezocomposites is increasingly popular as it combines high piezoelectric activity of ceramics and mechanical flexibility of polymers (Eltouby, et al., 2021). Piezoceramics such as barium titanate (BaTiO_3) and lead zirconate titanate (PZT) offer advantages such as high stiffness and good piezoelectric coefficients. Inorganic BaTiO_3 and PZT have piezoelectric d_{33} coefficients of 191 pm.V^{-1} and $225\text{-}590 \text{ pm.V}^{-1}$ respectively while that of PVDF is only approximately $24 \text{ to } 34 \text{ pm.V}^{-1}$ (Narita & Fox, 2017). Although PZT possess exceptional d_{33} coefficient, lead oxide, one of the constituents of PZT, is highly toxic and poses environmental threats during its production and operation (Panda, 2009). In contrast to PZT, lead-free BaTiO_3 has low toxicity due to its insolubility. Baji & Mai (2018) incorporated BaTiO_3 during the preparation of PVDF fibers to study the potential of these fibers for future nanoscale electronic devices. They found that the incorporation of BaTiO_3 encouraged the formation of piezoelectric β phase and improved the mechanical properties of the fibers. It was reported that d_{33} of PVDF fibers reinforced

with BaTiO₃ was up to 50 pm.V⁻¹ (Baji, et al., 2011), whilst d_{33} of electrospun PVDF fibers was approximately 17 pm.V⁻¹ (Wu, et al., 2018).

PVDF, a semi-crystalline polymer, is commonly used in membrane applications due to its outstanding chemical and mechanical resistance (Mulder, 1996). However, membrane fouling is one of the significant challenges faced by PVDF membranes. This is due to the hydrophobic nature of PVDF which is susceptible to fouling as natural organic materials are readily adsorbed onto the membrane surface and can block the surface pores (Liu, et al., 2011). It is widely acknowledged that resistance to membrane fouling could be achieved with an increase in hydrophilicity (Rana & Matsuura, 2010). A hydrophilic surface promotes the formation of a pure water layer which hinders the adsorption and deposition of hydrophobic foulants on the membrane surface (Kang & Cao, 2012). One of the methods to enhance hydrophilicity of PVDF membranes is the incorporation of inorganic particles or nanoparticles (NPs) such as aluminum oxide (Al₂O₃) (Yan, et al., 2009), titanium dioxide (TiO₂) (Oh, et al., 2009), silica dioxide (SiO₂) (Hashim, et al., 2011) and zinc oxide (ZnO) (Liang, et al., 2012). In recent years, NPs have risen to prominence in various technological areas because of their tuneable properties when compared to their bulk material properties. (Jeevanandam, et al., 2018). In general, the NPs could be introduced into the PVDF membranes by two approaches: blending them in polymer solution or in coagulation bath (Purkait, et al., 2018). The main drawback on incorporating inorganic NPs a in polymer matrix is the issue of aggregation (Ng, et al., 2013; Kang & Cao, 2014). The aggregation phenomenon is caused by the intrinsic characteristics of NPs and the poor compatibility between the NPs and bulk polymer (Kang & Cao, 2014; Yang, et al., 2016). The agglomeration of NPs leads to uneven dispersion of particles in the membranes which possibly change the topography, microstructure, and performance of the membranes (Razmjou, et al., 2011; Liu, et al., 2011). The other issue of modification of membranes with NPs is leaching (Ng, et al., 2013). Due to the strong interactions of the nanoparticles, conventional mixing or stirring is insufficient to disperse the NPs (Yang, et al., 2016; Razmjou, et al., 2012). There are generally two techniques used to minimise the tendency of agglomeration. One is the dispersion of NPs via sonication method, and other is surface pre-treatment of NPs using surface modification agents such as silane coupling agents (Subasi & Cicek, 2017).

Table 4.1: Summary of past studies on the incorporation of BaTiO₃ in PVDF or P(VDF-TrFE).

	Concentration of BaTiO ₃	Other properties of BaTiO ₃	Surface modification agent of BaTiO ₃	Application	Performance	Reference(s)
PVDF fiber	0, 10, 20 and 40 wt. %	BaTiO ₃ fibers prepared by sol-gel based electrospinning	-	Nanoscale electronic devices	d_{33} (no barium titanate): 17 pm.V ⁻¹ d_{33} (with barium titanate): 50 pm.V ⁻¹	(Baji, et al., 2011), (Wu, et al., 2018)
PVDF film	40.0 vol. %	Fine BaTiO ₃ powders, about 700 nm in diameter	KH550/APTES	Capacitors	Dielectric constant of PVDF/BaTiO ₃ composite modified by 1.0 wt % KH550 is 20% higher than unmodified composite	(Dang, et al., 2006)
P(VDF-TrFE) film	30, 45 and 60 vol. %	Sub-micron sized and micron sized BaTiO ₃ powders	APTES	Energy storage	Dielectric losses were lower when modified BaTiO ₃ particles were used	(Vacche, et al., 2014)
P(VDF-TrFE) membrane	0, 1, 3, and 5 vol. %	BaTiO ₃ NPs, average particle size of 100 nm	Polydopamine	Bone regenerative therapies	Surface potential of polarized nanocomposite membranes with 5 vol. % BaTiO ₃ NPs reached to -76.8 mV	(Zhang, et al., 2016)
PVDF membrane	20 wt. %	BaTiO ₃ NPs, 400 nm in diameter	Low temperature plasma treatment	Piezoelectric and dielectric devices	Enhanced formation of β -phase in PVDF/modified BaTiO ₃ membrane	(Lin, et al., 2018)
PVDF film	0, 10, 20, 30, 40, 50, 55 and 60 vol. %	BaTiO ₃ NPs, average size of 100 nm	Polyvinylpyrrolidone (PVP)	Energy storage and power capacitor	Dielectric permittivity and electric breakdown strength of nanocomposites were optimal at 55 vol. % and 10 vol. % respectively	(Yu, et al., 2013)
PVDF film	0, 1, 2, 3 and 5 vol. %	BaTiO ₃ NPs, average diameter of 100 nm	Dopamine hydrochloride	Capacitors	For 1 vol. % BaTiO ₃ loading, 150% increase in dielectric breakdown strength and tripled energy density compared to pure PVDF	(Hou, et al., 2015)

Table 4.1 summarises some of the past studies on the incorporation of BaTiO₃ in PVDF or P(VDF-TrFE), including the respective methods used to modify the surfaces of BaTiO₃ such as silane coupling agents. Silane coupling agents could reduce agglomerations and increase polymer-particle interactions by reducing hydrophilic nature and surface energy of the NPs (Rong, et al., 2006; Kango, et al., 2013). BaTiO₃ particles are known to have high surface energy, hence they have a greater tendency to agglomerate (Cohen, 2000). Dang et al. (2006) reported an improvement in compatibility, i.e., dispersion, between BaTiO₃ and PVDF when BaTiO₃ was pre-treated with silane coupling agent as illustrated in Figure 4.1. Silane coupling agents acted as linkage between BaTiO₃ and PVDF which could also prevent leaching of BaTiO₃ when it is incorporated in a PVDF matrix. The dielectric properties of PVDF and pre-treated BaTiO₃ composite were improved by approximately 20% (Dang, et al., 2006). Vacche et al. (2014) also mentioned that the surface modification of BaTiO₃ by (3-Aminopropyl)triethoxysilane (APTES) lowers the surface energy of BaTiO₃. This minimises the occurrence of large aggregates of BaTiO₃ and promotes better dispersion of BaTiO₃ in composite.

Figure 4.1: Schematic diagram of (a) hydrolysis of silane coupling agent, (3-Aminopropyl)triethoxysilane (APTES) followed by (b) hydrolysed APTES acting as a linkage between PVDF and BaTiO₃.

Zhang et al. (2016) modified the surfaces of BaTiO₃ NPs with polydopamine to minimise aggregation, leading to a homogeneous dispersion of NPs in P(VDF-TrFE) in membranes. These nanocomposite membranes mimicked endogenous electric potential

to support bone regeneration *in vivo*. Shen et al. (2018) used low temperature plasma to modify the surface of BaTiO₃ NPs which improved interfacial compatibility between PVDF and BaTiO₃ and promoted the formation of β phase in modified PVDF/BaTiO₃ membrane that could be applied in piezoelectric and dielectric devices.

Although the incorporation of BaTiO₃ in PVDF has been investigated in the previous studies, their PVDF/BaTiO₃ or P(VDF-TrFE)/BaTiO₃ composites were mostly used in applications of energy storage and capacitors. Also, the fundamental relationship between nanoparticle properties and pore structure of PVDF membranes which in turn affects its piezoelectric properties has yet to be explored. Moreover, besides the electrospun PVDF/BaTiO₃ fibers and P(VDF-TrFE)/BaTiO₃ nanocomposites that were cited (Baji, et al., 2011; Zhang, et al., 2016; Baji & Mai, 2018), the other PVDF/BaTiO₃ composites were not electrically poled in their studies. In this chapter, we incorporate piezoelectric BaTiO₃ NPs in polymeric PVDF membranes for fouling control purposes in water treatment applications. To the best of our knowledge, this is the first work that incorporated BaTiO₃ NPs in PVDF membranes for water filtration. To this end, different quantities of piezoelectric BaTiO₃ NPs were incorporated into PVDF membranes which were fabricated through a non-solvent induced phase separation (NIPS) method. Ethanol and silane coupling agent were used to treat some of the BaTiO₃ NPs prior to incorporating to PVDF membranes. The functions of modified BaTiO₃ NPs are dispersant and linking agent between BaTiO₃ and PVDF. The effects of incorporating unmodified and modified BaTiO₃ NPs on the morphology and piezoelectric properties of PVDF membranes were investigated. Electrical poling was also performed on the composite membranes, enhancing their piezoelectricity. Flux-stepping and multiple filtration cycles were performed to study the improvements in filtration performance of the poled BaTiO₃-PVDF membranes.

4.2 Experimental

4.2.1 Materials

The previous chapter reveals that PVDF membranes fabricated using N,N-dimethylformamide (DMF) solvent had satisfactory piezoelectric properties and filtration performance. Thus, the solvent used to fabricate the PVDF membranes was N,N-dimethylformamide (DMF, anhydrous, 99.8%, Sigma-Aldrich). To study the effect of incorporating piezoelectric NPs in PVDF membranes, barium titanate (IV) (BaTiO_3 , <100 nm particle size, Sigma-Aldrich) was added to the polymer solution. According to the specification sheet from the supplier, the BaTiO_3 NPs incorporated were in the form of a cubic crystalline phase. Since NPs have a strong tendency to agglomerate, (3-Aminopropyl)triethoxysilane (APTES, 99%, Sigma-Aldrich), a silane coupling agent, was used as a dispersant to improve the dispersion of NPs in polymer solution.

For the filtration performance of the membranes, test solutions containing 200 mg.L^{-1} of silica was prepared from fumed silica powder (0.2-0.3 μm avg. part. size (aggregate), Sigma-Aldrich). No significant change in the pH was detected, which remained at $\text{pH } 6.5 \pm 0.5$ throughout the filtration experiment.

4.2.2 Fabrication of BaTiO_3 -PVDF membranes

4.2.2.1 Modification of BaTiO_3

Dang, Wang, & Xu (2006) investigated the effect of different concentration of APTES (3-Aminopropyl)triethoxysilane (0.5, 1.0, 1.5, 2.0, 3.0 and 5.0 wt.%) during the modification of BaTiO_3 powders. They found that 1.0 wt.% APTES resulted in good distribution of BaTiO_3 in PVDF polymer with minimal aggregation. However, when the concentration of APTES was less or more than 1.0 wt.%, the dispersion and compatibility between BaTiO_3 and PVDF was poor. Vacche et al. (2014) also modified BaTiO_3 powder by 0.5, 1.0 and 2.0 wt.% APTES. They discovered increasing the ratio of APTES/ BaTiO_3 during modification did not significantly increase the amount of APTES on the surface of BaTiO_3 powders.

In this study, 1 wt.% of APTES was used to modify the BaTiO_3 NPs and the technique used to modify BaTiO_3 was adopted from Vacche et al. (2014). First, 99 wt.% of BaTiO_3 NPs and 1 wt.% of APTES were added to a mixture of 95 vol.% of ethanol (ethanol

absolute EMSURE® ACS, Merck) and 5 vol.% of DI water in the ratio of 1:10 for APTES-BaTiO₃ to ethanol mixture. Second, the mixture was sonicated for 5 min and magnetically stirred at 70 °C for 1 h. Third, the stirred mixture underwent centrifugation at 5000 rpm for 10 min and dried at 110 °C for 1 h to allow silanol condensation to take place. Lastly, the resulting mixture was vacuum-dried at 80 °C overnight.

4.2.2.2 Preparation of PVDF membranes with BaTiO₃

The steps involved in the fabrication of neat PVDF membranes (no BaTiO₃ NP) are described in section 3.2.2 under chapter 3. During the preparation of BaTiO₃ and PVDF polymer solutions, 0.05, 0.1, 0.2, 0.4 and 0.5 wt.% of unmodified or modified BaTiO₃ was added to 85 wt.% of DMF solvent. The mixture of BaTiO₃ and DMF solvent was subjected to probe sonication (Sonics & Materials, VCX 750) for 5 min. PVDF powder at 15 wt.% was then added and mixed under constant stirring rate to form a homogeneous polymer solution. The resulting solution was sonicated for 15 min. The polymer solution was left to degas overnight before casting. The schematic diagram on the preparation of polymer solution containing BaTiO₃ NPs is shown in Figure 4.2. After the preparation of polymer solution, membrane casting was performed. The steps for membrane casting are described in section 3.2.3.

Figure 4.2: Schematic diagram on the preparation of polymer solution containing BaTiO₃ NPs prior to casting.

4.2.3 Membrane characterisation

The information of the following characterisation techniques could be found in section 3.2.3 under chapter 3: infrared (IR) spectroscopy, piezo-response force microscopy (PFM), dielectric strength analysis, mechanical strength analysis, and evapo-porometry (EP).

4.2.3.1 Particle size determination

The particle size of 0.1 wt.% BaTiO₃ NPs in DMF solvent suspension before and after modification by silane coupling agent was measured at 25 °C by Zetasizer Nano ZS (Malvern, ZEN3600). Particle size was measured using dynamic light scattering method in which the scattered light was collected at an angle of 173°. The number-based particle size distribution and polydispersity index were acquired using the Zetasizer software after the measurement. The calculations used by software analysis are defined in ISO standard documents: ISO 13321 and ISO 22412.

4.2.3.2 Transmission electron microscopy

BaTiO₃ NPs before and after modification by APTES were imaged by transmission electron microscopy (TEM, JEOL JEM-1400 Plus) at an accelerating voltage of 120 kV. The samples for TEM were prepared by drop casting method on a standard 200-mesh carbon-coated copper grid.

4.2.3.3 Contact angle measurement

The contact angle of the membrane samples was measured using a goniometer (DataPhysics OCA 15) via the sessile drop method. The membrane sample was stuck onto a glass slide and its contact angle was immediately determined using SCA20 software after 3 µl of DI water was dispensed on its surface. An average contact angle was estimated based on five separate measurements.

4.2.3.4 Backscattered electron imaging

The surface and cross-section of the membranes were examined using a field emission scanning electron microscope (FESEM, JOEL, JSM-7200F Schottky). Backscattered electron (BSE) imaging was carried out via backscattered electron detector. The surface of the membrane samples was sputter-coated with a 2-nm thick platinum layer before FESEM analysis. The BSE image contrast is due to the difference in atomic number of different elements. Since the elements present in BaTiO₃ are higher in atomic weight as compared to PVDF, BaTiO₃ would appear to be brighter on BSE images. The thickness of the membranes was determined via FESEM by measuring the thickness at five different spots.

4.2.3.5 Viscosity measurement

Since membrane casting was performed at approximately room temperature, the viscosity of the polymer solutions at 25 °C was determined by modular compact rheometer (MCR 102, Anton Paar). An average viscosity value for each solution was computed from three separate measurements.

4.2.4 Electrical poling setup and filtration performance analysis

The methodology of membrane poling has been detailed in section 3.2.4. The potential difference applied across the membrane sample was set such that it is equivalent to an electric field strength of 10 MV.m⁻¹.

The critical flux and filtration performance of the membranes were examined using cross-flow filtration set-up as shown in Figure 3.4. The colloidal silica used as model foulant was prepared from fumed silica powder (0.2-0.3 µm average particle size, Sigma-Aldrich) dispersed in DI water via sonication. The description of the set up and experimental procedure could be found in section 3.2.5.

4.3 Results and discussion

4.3.1. FTIR spectra and particle size distribution of barium titanate

Figure 4.3a shows the FTIR spectra of BaTiO₃ NPs before and after modification by silane coupling agent, APTES. The spectrum peaks at 1080, 2854 and 2923 cm⁻¹ represent the stretching vibration of Si–O–Si, symmetric vibration of –CH₂– and asymmetric vibration of –CH₂– respectively (Palma, et al., 2007; Iijima, et al., 2009). These peaks indicate the presence of APTES on the surfaces of modified BaTiO₃ NPs which confirms that APTES had reacted with BaTiO₃ using the technique described in section 4.2.2.1 to modify the BaTiO₃. Referring to Figure 4.3b, the particle size distribution of BaTiO₃ NPs was shifted to the left after it was modified by APTES. There was a higher number % of particles with sizes of 90 nm after modification compared to 160 nm prior to modification. This agrees with the TEM images of BaTiO₃ NPs before and after modification are shown in Figure 4.4. The polydispersity index (PDI) was also slightly reduced after the modification by APTES. The shift of particle size distribution and PDI of BaTiO₃ NPs after modification could be caused by electrostatic repulsion

and steric hinderance. Ethanol induces a positive surface charge on NPs by proton exchange and adsorption of coupling agent on surface of NPs led to steric hinderance (Liauw, et al., 2003). Thus, the modification of BaTiO₃ NPs by ethanol and APTES led to repulsion among NPs, counteracting the van der Waals attractive forces and leading to improved particle dispersion. The above results reveal an improved dispersion and reduced agglomeration of BaTiO₃ NPs when the NPs were modified by APTES.

Figure 4.3 : (a) FTIR spectra and (b) Number-based particle size distribution of BaTiO₃ NPs before and after modification by silane coupling agent, APTES.

Figure 4.4: TEM images of BaTiO₃ nanoparticles (a) before and (b) after modification by silane coupling agent, APTES.

4.3.2. PVDF membranes containing barium titanate

4.3.2.1 Piezoelectric properties of BaTiO₃-PVDF membranes

Different amounts of BaTiO₃ NPs (0.05, 0.1, 0.2, 0.4 and 0.5 wt.%) were incorporated into PVDF membranes. It was found that the average piezoelectric d_{33} coefficient of the membranes was enhanced with the addition of BaTiO₃ NPs as shown in Figure 4.5a. The d_{33} value of PVDF membranes peaked at a concentration of 0.1 wt.% BaTiO₃ both with unmodified and modified BaTiO₃ NPs. In the previous chapter, it was observed that poled membranes with a greater value of d_{33} have higher critical fluxes for filtration (of colloidal silica solutions) when an electrical signal was applied during filtration.

Figure 4.5: (a) Average piezoelectric coefficient, d_{33} (pm.V⁻¹) for various weight % of BaTiO₃ for unpoled PVDF membranes containing unmodified or modified BaTiO₃ and (b) dielectric strength (MV.m⁻¹) and electrical breakdown voltage (V) of PVDF membranes with or without BaTiO₃.

In the subsequent sections, only results for 0.1 and 0.5 wt.% BaTiO₃ are presented in this article as significant contrast in results could be observed between these two BaTiO₃ loadings. The membranes are termed as BT-0.1, BT-0.5 for unmodified BaTiO₃ NPs and BT-m-0.1, BT-m-0.5 for modified BaTiO₃ NPs. The neat PVDF membrane is termed as BT-0 as it does not contain BaTiO₃. Table 4.3 shows the membrane, mechanical and piezoelectric properties of BT-0, BT-0.1, BT-m-0.1, BT-0.5 and BT-m-0.5 membranes.

The incorporation of BaTiO₃ NPs in PVDF membranes increased the dielectric strength of the membranes as shown in Figure 4.5b which agrees with a previous study (Yu, et al., 2013). It could be seen that unmodified BaTiO₃-PVDF membranes, i.e. BT-0.1 and BT-0.5, had greater increments in their dielectric strength than modified BaTiO₃-PVDF membranes, i.e. BT-m-0.1 and BT-m-0.5. This could be explained by their intrinsic mechanical properties; a linear relationship between the dielectric strength and tensile strain at break can be discerned as evident in Figure 4.6, which agrees also with previous studies (Darestani, et al., 2014). In agreement with previous studies (Baji, et al., 2011; Baji & Mai, 2018), the piezoelectric properties of the membranes improved significantly with the addition of BaTiO₃ NPs. The 2D/3D topography, PFM amplitude and PFM phase images of unpoled and poled membranes can be found in Figure 4.7 and Figure 4.8. With the addition of BaTiO₃ NPs, a greater standard deviation in d_{33} was observed, as shown in Table 4.3. This was likely due to the limited presence of BaTiO₃ NPs within the PVDF membranes because only 0.1 or 0.5 wt.% of BaTiO₃ NPs were added. Hence, a larger d_{33} value was computed for regions containing BaTiO₃ whilst a smaller d_{33} value was computed for regions without BaTiO₃. The PVDF membranes with modified BaTiO₃ NPs had larger d_{33} value as compared to those that contained unmodified BaTiO₃ NPs. This was probably due to the better dispersion of the modified BaTiO₃ NPs in the PVDF matrix. This would result in an increase in the number of regions within the membrane that contained at least some BaTiO₃ NPs (with increased d_{33}). As pointed out above, it was found that 0.1 wt.% BaTiO₃-PVDF membranes had greater d_{33} values compared to those with 0.5 wt.% BaTiO₃-PVDF membranes. This could possibly be because of the aggregation of BaTiO₃ in BT-0.5 and BT-m-0.5 simply as a result of the larger wt.% of BaTiO₃ present; the greater the amount of NPs added to the membranes, the greater the likelihood of agglomeration (Zare, 2016). For the BT-0.5 and BT-m-0.5 membranes, the main contribution to d_{33} is that arising from the PVDF rather than BaTiO₃.

Figure 4.6: Plot of dielectric strength (MV.m⁻¹) against tensile strain at break (%) for unpoled BaTiO₃-PVDF membranes.

Figure 4.7: Topography, PFM amplitude and PFM phase images of unpoled BT-0.1 (a, b and c), poled BT-0.1 (d, e and f), unpoled BT-m-0.1 (g, h and i), poled BT-m-0.1 (j, k and l), unpoled BT-0.5 (m, n and o), poled BT-0.5 (p, q and r), unpoled BT-m-0.5 (s, t and u) and poled BT-m-0.5 (v, w and x).

Figure 4.8: 3D AFM images of unpoled and poled BT-0.1 (a and b), BT-m-0.1 (c and d), BT-0.5 (e and f) and BT-m-0.5 (g and h).

Compared to the other d_{33} values reported in the literature for BaTiO₃/PVDF fibers (Baji, et al., 2011), the d_{33} values reported in this study were lower, probably due to two primary reasons. Firstly, only small amounts of BaTiO₃ NPs were added in this study as compared to 30 wt.% BaTiO₃ in the other literature. Secondly, the PVDF fibers reinforced with BaTiO₃ fibers were prepared by electrospinning at 18 kV which electrically poled the fibers as it was fabricated due to the high voltage. On the other hand, the incorporation of BaTiO₃ NPs did not change the $F(\beta)$ values as shown in Table 4.3. This is justifiable because $F(\beta)$ values were based on the relative amount of β phase in PVDF and not the addition of BaTiO₃ NPs. Hence, the addition of BaTiO₃ in PVDF membranes did not significantly alter their $F(\beta)$ values. No distinctive relationship could be observed between the values of $F(\beta)$ and d_{33} . After electrical poling, the piezoelectric properties of the membranes were improved. Similarly, $F(\beta)$ values increased after electrical poling which signifies that there was an increase in β phase in PVDF. This was likely due to the alignment of electric dipoles of PVDF during the poling process which is in agreement with the previous chapter.

4.3.2.2 Morphology of BaTiO₃-PVDF membranes

The BSE images of the top surface and cross-section of the membranes are shown in Figure 4.9. As mentioned earlier in section 4.2.3.4, the bright spots on BSE image were due to the high atomic weights of elements in BaTiO₃. Since no BaTiO₃ was present in BT-0, as expected, no bright spots are observed in Figure 4.9a and Figure 4.9b. The addition of BaTiO₃ NPs in PVDF membranes changed the pore structure of the membranes. Large aggregates of BaTiO₃, which can be observed in the BSE images of BT-0.1 (Figure 4.9c and Figure 4.9d) and BT-0.5 (Figure 4.9g and Figure 4.9h), generally resulted in the disappearance of finger-like pores and had cross-section morphologies closer to sponge-like structures. This could be because no dispersant APTES was used to modify the BaTiO₃ NPs that were added during membrane preparation. Nano-sized particles have high surface energy due to their high surface area to volume ratio. To minimise the overall energy, agglomeration of NPs occurs resulting from attractive Van der Waals forces that exist between particles. With BT-0.1 and BT-0.5, that had sponge-like structures, the value of d_{33} was also lower which agrees with the previous chapter where it was found that sponge-like morphology resulted in poor piezoelectric behaviour. On the other hand, modified BaTiO₃ NPs were better dispersed in the PVDF membranes as shown in Figure 4.9e, f, i and j. It can be seen that there

were more finger-like or drop-like pores, when BaTiO₃ NPs were better dispersed. The area of the agglomerated BaTiO₃ was estimated by image analysis program, ImageJ. The results for the estimation can be found in the Figure 4.10 and Table 4.2. The area of largest agglomerated particles varied significantly between BT-m-0.1 (0.5 μm^2) and BT-0.5 (17.1 μm^2). From Table 4.2, it can be inferred that modification and lower quantities (wt.%) of BaTiO₃ NPs would contribute to the better dispersion of BaTiO₃ NPs in PVDF membranes and that achieves morphology closer to that of the neat membrane, i.e., BT-0.

Figure 4.9: BSE images of top surface and cross-section of unpoled BT-0 (a and b), BT-0.1 (c and d), BT-m-0.1 (e and f), BT-0.5 (g and h) and BT-m-0.5 (i and j).

Figure 4.10: 2D distribution of BaTiO₃ agglomerates in cross-section of BT-0.1, BT-m-0.1, BT-0.5 and BT-m-0.5. The areas highlighted in red (by ImageJ) indicates the BaTiO₃ agglomerates present in the cross-section of membranes.

Table 4.2: Quantification of the agglomerated BaTiO₃ particles depicted in Figure 4.10.

	BT-0.1	BT-m-0.1	BT-0.5	BT-m-0.5
Total area of agglomerated particles (μm^2)	13.957	4.353	47.609	19.316
Percentage of area of agglomerated particles (%)	0.36	0.12	1.27	0.52
Area of largest agglomerated particle (μm^2)	2.134	0.540	17.101	1.292
Mean area of agglomerated particle (μm^2)	0.202 ± 0.359	0.106 ± 0.136	0.233 ± 1.263	0.115 ± 0.189

Since the addition of BaTiO₃ NPs did not significantly change the viscosity of the solution as shown in Figure 4.11, the incorporation of BaTiO₃ NPs in PVDF membranes would not be expected to significantly change the thickness of the membranes as seen in the results tabulated in Table 4.3. Referring to Figure 4.12, after poling, the cavities that were observed in unpoled BaTiO₃-PVDF membranes (Figure 4.9) were further diminished. This coincides with the previous chapter where electrical poling causes the alignment of electric dipoles in the direction of the electric field. It is proposed that the alignment of the dipoles exerted a force on the boundaries of the cavities which led to shrinking in depth of these cavities. Moreover, the poled BaTiO₃-PVDF membranes shrunk slightly as compared to their respective unpoled membranes, see Table 4.3.

Figure 4.11: Viscosity (mPa.s) at 25 °C of the polymer solutions used for the preparation of PVDF membranes.

Figure 4.12: BSE images of top surface and cross-section of poled BT-0.1 (a and b), BT-m-0.1 (c and d), BT-0.5 (e and f) and BT-m-0.5 (g and h).

The incorporation of BaTiO₃ NPs reduced the pore size and porosity of the membranes as shown in Table 4.3 which explains the decreased (pure) water permeability from 61 to approximately 29-37 L.m⁻².h⁻¹. It is suggested that the inclusion of BaTiO₃ NPs possibly obstructed some of the continuous, transmembrane, pores, leading to effectively smaller pore sizes and reduced permeability. The pore size of modified BaTiO₃-PVDF membranes was marginally smaller than those that contained unmodified BaTiO₃ NPs, presumably due to better dispersion of modified BaTiO₃ NPs which resulted in an increased number of pores affected by obstruction of NPs in PVDF membranes. Electrical poling slightly decreased the pore size and porosity of the membranes as shown in Table 4.3. This was likely due to the alignment of electric dipoles which reduced the size of pores. This finding is consistent to that observed in BSE images (Figure 4.12) in which the pores appeared to be slightly smaller after poling.

Since the surfaces of BaTiO₃ are hydrophilic (Xiang & Zhang, 2018), the addition of BaTiO₃ NPs into the PVDF membranes, some of which may be close to the surface, reduced the hydrophobic nature of PVDF which was evidenced by the decreased contact angle in Table 4.3. The modified BaTiO₃-PVDF membranes had water contact angles like neat PVDF membranes possibly because the NPs are well dispersed and do not affect the surface of the membrane to the same extent. The effect of hydrophilicity of the membranes on their filtration performance are to be discussed in section 4.3.2.4 and 4.3.2.5 below.

Table 4.3: The properties of unpoled and poled BT-0, BT-0.1, BT-m-0.1, BT-0.5 and BT-m-0.5.

	Unpoled					Poled				
	BT-0	BT-0.1	BT-m-0.1	BT-0.5	BT-m-0.5	BT-0	BT-0.1	BT-m-0.1	BT-0.5	BT-m-0.5
<i>Membrane properties</i>										
Pore diameter (nm)	49 ± 5	34 ± 2	31 ± 2	32 ± 1	30 ± 2	49 ± 2	29 ± 2	28 ± 2	30 ± 2	26 ± 1
Porosity (%)	70 ± 3	35 ± 2	32 ± 2	29 ± 1	30 ± 2	69 ± 1	28 ± 3	22 ± 1	26 ± 1	28 ± 1
Thickness (µm)	49 ± 1	48 ± 1	47 ± 2	51 ± 1	49 ± 1	48 ± 1	45 ± 1	44 ± 1	41 ± 1	44 ± 1
Permeability (L.m ⁻² .h ⁻¹ .bar ⁻¹)	56 ± 4	37 ± 2	34 ± 2	32 ± 4	29 ± 4	60 ± 2	25 ± 1	28 ± 3	25 ± 2	25 ± 5
Contact angle (°)	86 ± 3	70 ± 4	76 ± 1	77 ± 2	76 ± 3	88 ± 1	80 ± 2	82 ± 3	82 ± 3	83 ± 3
<i>Mechanical properties</i>										
Young's modulus (MPa)	119.1 ± 4.8	120.1 ± 15.5	122.0 ± 7.3	127.7 ± 5.1	137.5 ± 9.2	136.5 ± 4.8	206.7 ± 4.7	191.2 ± 0.5	162.6 ± 2.4	176.6 ± 5.4
Tensile strength at break (MPa)	13.0 ± 0.5	17.2 ± 1.2	15.6 ± 1.5	19.4 ± 0.7	14.4 ± 0.6	13.0 ± 2.0	15.9 ± 1.6	13.7 ± 2.2	15.4 ± 2.5	13.1 ± 2.0
Tensile strain at break (%)	697 ± 76	901 ± 55	830 ± 86	1000 ± 36	859 ± 11	677 ± 111	782 ± 35	660 ± 25	854 ± 11	772 ± 57
<i>Piezoelectric properties</i>										
Average d_{33} (pm.V ⁻¹)	3.27 ± 0.38	4.45 ± 2.06	4.67 ± 2.14	3.81 ± 2.21	3.90 ± 2.42	3.47 ± 0.43	5.02 ± 2.10	5.62 ± 2.22	3.95 ± 2.37	4.05 ± 2.39
$F(\beta)$	0.493 ± 0.020	0.495 ± 0.011	0.514 ± 0.020	0.492 ± 0.002	0.512 ± 0.007	0.504 ± 0.004	0.525 ± 0.003	0.542 ± 0.010	0.497 ± 0.006	0.522 ± 0.034

4.3.2.3 Mechanical properties of BaTiO₃-PVDF membranes

Figure 4.13: Young's modulus (MPa) as a function of weight % of BaTiO₃, for unpoled PVDF membranes containing unmodified or modified BaTiO₃.

Referring to Table 4.3, the addition of BaTiO₃ NPs in PVDF membranes resulted in improvement of the mechanical properties, notably the Young's modulus. The improvement in mechanical properties after incorporation of BaTiO₃ was also reported by a previous study (Baji & Mai, 2018). In the present study it was found that the Young's modulus increased with increasing weight ratios of both unmodified and modified BaTiO₃. However, with modified BaTiO₃ NPs in PVDF membranes, the Young's modulus increased more rapidly with increasing weight % of the BaTiO₃ NPs, as can be seen in Figure 4.13. The other mechanical properties, tensile strength at break and tensile strain at break, also improved after BaTiO₃ NPs were incorporated in the PVDF membranes. More significant improvements were observed for unmodified BaTiO₃ PVDF membranes in comparison to modified BaTiO₃ PVDF membranes. This could be due to better mechanical properties of large BaTiO₃ aggregates in contrast to well-dispersed BaTiO₃. After poling, the Young's modulus of the membranes increased

whilst their tensile strength and tensile strain at break decreased. The shifts in mechanical properties of the membranes maybe linked to the heating and compression effects during poling.

4.3.2.4 Effect of piezoelectric properties on critical flux

For a given cross-flow velocity, no or negligible membrane fouling occurs below the critical flux; while operating at fluxes beyond the critical flux will lead to the onset of membrane fouling, i.e., particle deposition in colloidal fouling (Field, et al., 1995). The critical flux of the unpoled and poled membranes, with or without the application of an electrical AC signal (10 Vpp, 500 Hz), was determined via flux stepping experiments (Chong, et al., 2008; Ho, et al., 2016) at a cross-flow velocity of 0.1 m.s^{-1} using water with a model foulant of colloidal silica (particle size of 0.2 to $0.3 \mu\text{m}$) at concentration of 200 mg.L^{-1} . Cake filtration was the main fouling mechanism for fouling as mean pore size of the membranes was much smaller than the size of silica particles. In these experiments, the flux, at each step of an increasing interval of $20 \text{ L.m}^{-2}.\text{h}^{-1}$, is held constant for 20 mins by adjusting the transmembrane pressure (TMP). At each flux step, the rate of transmembrane pressure increase ($d\text{TMP}/dt$) was determined. Critical flux is defined as the greatest flux value for $d\text{TMP}/dt = 0$. Hence, the x -intercept of the plot of $d\text{TMP}/dt$ vs. flux (Figure 4.14) corresponds to the value of critical flux. The values of the critical flux determined at different conditions are tabulated in Table 4.4.

Figure 4.14: Plot of $dTMP/dt$ ($kPa \cdot s^{-1}$) vs. flux ($L \cdot m^{-2} \cdot h^{-1}$) for flux stepping experiments of unpoled and poled membranes (a) BT-0, (b) BT-0.1, (c) BT-m-0.1, (d) BT-0.5 and (e) BT-m-0.5 with and without application of electrical AC signal (10 V_{pp}, 500 Hz). Experimental conditions: 200 mg.L⁻¹ silica (200 to 300 nm) feed solution, cross-flow velocity of 0.1 m.s⁻¹.

Table 4.4: The critical flux values for unpoled and poled membranes with or without an electrical AC signal (10 Vpp, 500 Hz) applied during flux stepping experiments.

Membrane	Critical flux ($\text{L.m}^{-2}.\text{h}^{-1}$)				
	BT-0	BT-0.1	BT-m-0.1	BT-0.5	BT-m-0.5
Unpoled (no AC)	48.9 ± 2.2	56.1 ± 2.9 (+ 14.7%) ¹	54.5 ± 2.1 (+ 11.5%) ¹	54.7 ± 2.4 (+ 11.9%) ¹	54.9 ± 1.4 (+ 12.3%) ¹
Unpoled (AC)	46.0 ± 3.4	60.4 ± 2.9	55.9 ± 1.2	52.1 ± 3.0	56.1 ± 1.3
Poled (no AC)	47.6 ± 1.5	57.9 ± 2.7	54.2 ± 1.0	53.7 ± 2.6	50.2 ± 3.6
Poled (AC)	60.9 ± 1.9	72.6 ± 2.5 (+ 19.2%) ²	74.1 ± 1.7 (+ 21.7%) ²	62.4 ± 1.4 (+ 2.5%) ²	60.9 ± 2.7 (+ 0.0%) ²

¹ These values refer to the percentage increase in critical flux of unpoled membranes incorporated with BaTiO₃ as compared to BT-0.

² These values refer to the percentage increase in critical flux of poled membranes incorporated with BaTiO₃ as compared to poled BT-0 under AC signal.

As shown in Figure 4.15 and Figure 4.16, a decreasing linear trend could be seen between the critical flux with and without the application of AC and contact angle for unpoled membranes. Similar trend of critical flux without AC could also be observed for poled membranes (Figure 4.17). The inclusion of BaTiO₃ NPs in PVDF membranes enhanced the hydrophilicity of membranes, reducing their water contact angle, which consequently resulted in a greater value of critical flux. These findings agreed with previous studies (Madaeni, et al., 1999). On the other hand, for poled membranes with the application of AC signal, no linear relationship (Figure 4.18) was observed between the critical flux and contact angle, which suggests that the hydrophilicity of membrane was not the key contributing factor. The critical flux of poled membranes with AC applied increased with increasing d_{33} coefficient, showing a linear relationship with $R^2 = 0.9391$, as can be seen in the results plotted in Figure 4.19. However, for poled (no AC applied) membranes, a weak linear relationship with $R^2 = 0.4995$ was observed between critical flux and d_{33} coefficient as shown in Figure 4.20.

Figure 4.15: The critical flux ($\text{L.m}^{-2}.\text{h}^{-1}$) obtained in experiments without the application of AC signals as a function of contact angle ($^{\circ}$) for unpoled PVDF and BaTiO_3 -PVDF membranes.

Figure 4.16: The critical flux ($\text{L.m}^{-2}.\text{h}^{-1}$) obtained in experiments with the application of AC signals as a function of contact angle ($^{\circ}$) for unpoled PVDF and BaTiO_3 -PVDF membranes.

Figure 4.17: The critical flux (L.m⁻².h⁻¹) obtained in experiments without the application of AC signals as a function of contact angle (°) for poled PVDF and BaTiO₃-PVDF membranes.

Figure 4.18: The critical flux (L.m⁻².h⁻¹) obtained in experiments with the application of AC signals as a function of contact angle (°) for poled PVDF and BaTiO₃-PVDF membranes.

Figure 4.19: The critical flux (L.m⁻².h⁻¹) determined in experiments with the application of AC signals as a function of average piezoelectric coefficient, d_{33} (pm.V⁻¹) for poled PVDF and BaTiO₃-PVDF membranes.

Figure 4.20: The critical flux (L.m⁻².h⁻¹) determined in experiments without the application of AC signal as a function of average piezoelectric coefficient, d_{33} (pm.V⁻¹) for poled PVDF and BaTiO₃-PVDF membranes.

4.3.2.5 Comparison of multiple filtration cycles

Based on the flux stepping experiments, poled BT-m-0.1 under AC signal appeared to be the most promising BaTiO₃-PVDF membrane for filtration. Since it has been demonstrated that the application of electrical signal only improved the filtration performance of piezoelectric (poled) membrane (Coster, et al., 2011; Chen & Pomalaza-Ráez, 2019), poled BT-m-0.1 (with AC) was subjected to multiple filtration cycles to study its long term performance and the unpoled BT-0 (i.e., neat PVDF) without AC signal was chosen as the control. The colloidal silica fouling experiment was conducted at fixed flux of 100 L.m⁻².h⁻¹ and cross-flow velocity of 0.1 m.s⁻¹. Each filtration cycle was stopped when the normalised TMP reached a value of 2 (~ 600 kPa). The fouled membrane then underwent a pressure relaxation mode by reducing the TMP (i.e., to atmospheric pressure) and increasing cross-flow rate at 0.2 m.s⁻¹ for approximately 10 min. After the relaxation, the subsequent cycle was commenced, and the above process was repeated until five cycles were completed. The results of the multiple filtration cycles are shown in Figure 4.21. It can be observed that unpoled BT-0 (no AC applied) had filtration cycles of shorter duration compared to poled BT-m-0.1 (AC applied). Overall, the filtration duration of poled BT-m-0.1 (AC applied) was increased by roughly a factor of 2 to 4 compared to unpoled BT-0 (no AC applied). The impact was increasingly prominent as the number of filtration cycles increased. *Irreversible* fouling ($R_{irreversible}$) could be estimated by $R_{irreversible} = R_{i,n} - R_m$ where $R_{i,n}$ is the initial resistance at the start of n^{th} cycle and R_m is the intrinsic membrane resistance. Each resistance is defined as $R = TMP/(\mu \cdot J)$ where μ is the permeate viscosity and J is the permeate flux. The normalised TMP (TMP/TMP₀) of poled BT-m-0.1 (AC applied) was almost restored to the value of 1 after physical cleaning involving pressure relaxation and increased cross-flow velocity. Since the only differed parameter between unpoled BT-0 (no AC applied) and poled BT-m-0.1 (AC applied) was TMP, $R_{i,n}$ after every cycle was lower for poled BT-m-0.1 (AC applied), which suggested minimal irreversible fouling. On the other hand, for neat PVDF membranes, the initial normalised TMP was not fully restored in each cycle and indeed an increasing trend was observed for subsequent cycles (i.e., +25 to +44% in cycle 2 to 5), which suggests that severe irreversible fouling had built up. As compared to another study on axial vibration membrane, the irreversible fouling rate after 2-h filtration of 0.4 g.L⁻¹ algae solution was reported to be ~35 to 40% at different vibration frequency from 0 to 10 Hz (Zhao, et al.,

2017). In this study, after multiple cycles, the irreversible fouling rates were about 40% and 10% for unpoled BT-0 (no AC applied) and poled BT-m-0.1 (AC applied) respectively. This suggests that self-agitation by piezoelectric membrane is likely to be as effective or even more effective than mechanically vibrating the membrane cell or module. The FESEM images of the fouled membranes can be found in Figure 4.22 in which a distinctive foulant layer can be seen across the large area of the unpoled BT-0 (no AC applied). The stability of the BaTiO₃ NPs in piezoelectric membrane was evaluated based on the cross-section BSE image of fouled piezoelectric BT-m-0.1 (Figure 4.23), which shows that hydrophilic BaTiO₃ NPs remained intact in the membrane after multiple filtration cycles. Moreover, no barium element was detected in feedwater and permeate water that were collected during filtration experiments for inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis. More information on ICP-OES can be found in Section 5.2.4.

Figure 4.21: Plots of normalised TMP (P/P_0) against filtration time (min) for unpoled BT-0 (no AC applied) and poled BT-m-0.1 (AC applied) during filtration of 200 mg.L^{-1} colloidal silica solution at permeate flux of $100 \text{ L.m}^{-2}.\text{h}^{-1}$ and cross-flow velocity of 0.1 m.s^{-1} .

Figure 4.22: FESEM images of fouled (a) unpoled BT-0 (without application of AC) and (b) poled BT-m-0.1 (AC, 10 Vpp and 500 Hz) at 1 000 times magnification.

Figure 4.23: FESEM image of cross-section of poled BT-m-0.1 (AC, 10 Vpp and 500 Hz) at 1 000 times magnification after multiple filtration cycles experiment.

4.4 Chapter conclusion

The effects of incorporating BaTiO₃ nanoparticles (NPs) in PVDF membranes were investigated in this chapter. The silane coupling agent, APTES ((3-Aminopropyl)triethoxysilane), was used to modify some of the BaTiO₃ NPs to improve its compatibility and dispersion in the PVDF membranes. Different amounts of unmodified and modified BaTiO₃ NPs, 0.05, 0.1, 0.2, 0.4 and 0.5 wt.%, were added into the polymer solution during BaTiO₃-PVDF membrane preparation. Dimethylformamide (DMF) was used as the solvent for the fabrication of PVDF membranes via a non-solvent induced phase separation (NIPS). The modified BaTiO₃ NPs, particularly 0.1 wt.%, were more dispersed in the PVDF membranes than unmodified BaTiO₃ NPs, which had finger-like structures similar to neat PVDF membranes. The addition of BaTiO₃ NPs to PVDF membranes improved its dielectric strength, piezoelectric d_{33} coefficient, $F(\beta)$, as well as mechanical properties. Electrical poling of the membranes enhanced their piezoelectric d_{33} coefficient and $F(\beta)$. A linear correlation ($R^2 = 0.9391$) between piezoelectric d_{33} coefficient and critical flux was observed for poled piezoelectric membranes under the influence of an applied electrical signal (10 Vpp, 500 Hz) when colloidal silica was used as model foulant. The application of an electrical AC signal on poled BaTiO₃-PVDF (0.1 wt% BaTiO₃) membrane further improved the critical flux value by up to 51% and prolonged the duration of multiple filtration cycles by up to a factor of 2 to 4 compared to neat PVDF membrane.

CHAPTER 5

Application of piezoelectric membrane for wastewater treatment

5.1 Background

In the previous chapters, piezoelectric polyvinylidene fluoride (PVDF) membranes, with finger-like morphology and incorporation of barium titanate (BaTiO_3) nanoparticles that were modified by (3-Aminopropyl)triethoxysilane (APTES), demonstrated satisfactory piezoelectric properties and filtration performance using colloidal silica as model foulant.

This chapter extends the application of piezoelectric membrane for wastewater treatment. Wastewater contains various foulants which increases complexity due to the occurrence of different fouling mechanisms during filtration process. To the extent of our knowledge, the application of piezoelectric membrane for wastewater treatment has not been explored.

In this chapter, the performances of non-piezoelectric and piezoelectric PVDF membranes for wastewater filtration were evaluated. The fouled membranes were periodically cleaned using chemicals to assess the effect of piezoelectric properties on fouling. Also, the effects of different AC voltages and crossflow velocities, which successively affect the energy consumption and on the intensity of fouling were investigated. Moreover, the feedwater and permeate water quality were analysed to illustrate wastewater treatment efficiency of the filtration processes for non-piezoelectric and piezoelectric membranes. Membrane autopsies for these membranes were also performed to quantify the foulant load on the membrane surfaces.

5.2 Experimental

The piezoelectric membranes studied in this chapter for filtration of wastewater were poled BT-0 and BT-m-0.1. The control membrane used for comparison was unpoled BT-0. The description of the electrical poling process employed to enhance piezoelectric properties could be found in Chapter 3 while the steps on membrane fabrication are in Chapter 3 for BT-0 and in Chapter 4 for BT-m-0.1. More information on the set-up and experiment for filtration can be found in Chapter 3.

In brief, prior wastewater filtration, clean water permeability using deionised (DI) water was performed for each membrane to obtain the membrane resistance. For all the tests, the cross-flow velocity was fixed at 0.1 m.s^{-1} and permeate flux was fixed at $30 \text{ L.m}^{-2}.\text{h}^{-1}$, i.e., the transmembrane pressure (TMP) increased during membrane fouling in constant flux experiment. In each cycle of wastewater filtration, when the normalised TMP ($\text{TMP}/\text{TMP}_0 = 2$) had been reached, physical cleaning was implemented where pressure relaxation (no permeation) was performed by reducing the TMP to atmospheric pressure and increasing the cross-flow velocity to 0.2 m.s^{-1} (twice of operating cross-flow velocity) for approximately 10 min. After extended period of wastewater filtration, i.e., five filtration cycles, chemical cleaning was implemented where the fouled membrane was first cleaned with 2 wt. % citric acid for 30 min, followed by 0.1 M sodium hydroxide for 30 min. A total of three sets of five filtration cycles were performed to study a longer-term filtration performance of piezoelectric membrane. For filtration experiments with AC signals, a 10 V peak-to-peak sinusoidal voltage was applied.

5.2.1 Feed wastewater

The feed wastewater used in filtration experiments was collected from the outlet line of the primary settling tank at Ulu Pandan Water Reclamation Plant in Singapore and stored in cold room maintained at 4°C . Before performing filtration experiment, the wastewater was warmed to room temperature and diluted with tap water to have a total organic carbon (TOC) of $\sim 20 \text{ mg.L}^{-1}$ to simulate low organic concentration present in wastewater after pre-treatment processes.

5.2.2 Specific energy consumption analysis

The total specific energy consumption, E (kWh.m⁻³), of operating piezoelectric membrane could be estimated by considering the specific energy consumption, $E_{\Delta P}$ (kWh.m⁻³), associated with the pump for sustaining the transmembrane pressure across the membrane and the specific energy consumption, E_{AC} (kWh.m⁻³), associated with supplying electrical AC signals to the filtration cell, i.e., $E = E_{\Delta P} + E_{AC}$.

$E_{\Delta P}$ (kWh.m⁻³) is the power supplied to pump the feed per unit of permeate produced:

$$E_{\Delta P} = \frac{\Delta P \cdot Q_f}{\eta_p \cdot Q_p} = \frac{\Delta P}{\eta_p \cdot Y} \quad (5.1)$$

where ΔP (kPa) is the transmembrane pressure, η_p is the pump efficiency (assumed to be 80% in this study), Q_f (m³.s⁻¹) is the volumetric flow rate of feed, Q_p (m³.s⁻¹) is the volumetric flow rate of permeate, and Y is the recovery.

The power, P_{AC} (W), for supplying the electrical AC signals to the system could be determined by measuring the current I_{Peak} and voltage V_{Peak} during filtration:

$$\begin{aligned} P_{AC} &= I_{RMS} V_{RMS} \cos \phi \\ &= \left(\frac{I_{Peak}}{\sqrt{2}} \right) \left(\frac{V_{Peak}}{\sqrt{2}} \right) \cos \phi \\ &= \frac{I_{Peak} V_{Peak} \cos \phi}{2} \end{aligned} \quad (5.2)$$

where I_{Peak} (A) is the peak current and V_{Peak} (V) is the peak voltage. I_{Peak} and V_{Peak} are measured using an oscilloscope (Tektronix, MDO3034). The phase angle, ϕ , between current and voltage waveforms could be known by direct observation of time delay, Δt , between the current and voltage waveforms as shown in Figure 5.1 and applying the following equation:

$$\phi = 360^\circ \times f \times \Delta t \quad (5.3)$$

where f (Hz) is the frequency of system.

Figure 5.1: Current and voltage waveforms illustrating the peak current, peak voltage, and time delay between the waveforms.

E_{AC} (kWh.m⁻³) could be computed from P_{AC} (W), filtration time, t (h), and volume of permeate, V_p (m³):

$$E_{AC} = \frac{P_{AC} \cdot t}{V_p \times 1000} \quad (5.4)$$

5.2.3 Estimation of fouling resistance

The fouling resistance can be evaluated using resistance-in-series model based on Darcy's law (Broeckmann, et al., 2006). The intrinsic membrane resistance (R_{mem} in m⁻¹) was determined from water permeability test of clean membrane using DI water at a flux of 30 L.m⁻².h⁻¹. After a long-term wastewater filtration, the total fouling resistance, R_{total} (m⁻¹), was estimated using:

$$R_{total} = \frac{\Delta P}{J \cdot \mu} - R_{mem} \quad (5.5)$$

where ΔP (Pa) is the transmembrane pressure, J (m³.m⁻².s⁻¹) is the permeate flux, and μ (Pa.s) is the permeate viscosity. The total fouling resistance consists of various components as shown below:

$$R_{\text{total}} = R_{\text{reversible}} + R_{\text{irreversible}} + R_{\text{irremovable}} \quad (5.6)$$

where $R_{\text{reversible}}$ (m^{-1}) is the reversible fouling resistance, represents foulants that can be easily removed by physical cleaning (e.g., membrane relaxation, strong shear force, bubbling, backwashing etc.). $R_{\text{irreversible}}$ (m^{-1}) is the irreversible fouling resistance, represents foulants that could only be removed via chemical cleaning as these foulants are strongly attached to the membrane. $R_{\text{irremovable}}$ (m^{-1}) is the irremovable fouling resistance, represents the residual foulants left after chemical cleaning. Figure 5.2 illustrates reversible, irreversible, and irremovable fouling of a porous membrane. Table 5.1 summarises the methods applied in this work to determine each resistance.

Figure 5.2: Schematic diagram on the formation of fouling and removal of fouling via physical cleaning and chemical cleaning (Meng, *et al.*, 2009).

Table 5.1: Summary of the different resistances determined experimentally and calculated based on formulae shown.

Symbol	Resistance	Method	Formula	Remark(s)
R_m	Membrane	Based on water permeability test	$R_m = \frac{\Delta P_0}{J \cdot \mu_w}$	ΔP_0 is the TMP in water permeability test μ_w is the viscosity of DI water
R_{total}	Total fouling	Based on TMP at the end of filtration cycle	$R_{total} = \frac{\Delta P}{J \cdot \mu} - R_m$	ΔP is the TMP at the end of filtration cycle
$R_{irremovable}$	Irremovable fouling	Based on TMP after chemical cleaning	$R_{irremovable} = \frac{\Delta P_i}{J \cdot \mu} - R_m$	ΔP_i is the TMP after i^{th} cycle of chemical cleaning
$R_{irreversible}$	Irreversible fouling	Based on TMP after physical cleaning	$R_{irreversible} = \frac{\Delta P_n}{J \cdot \mu} - R_{irremovable} - R_m$	ΔP_n is the TMP after n^{th} cycle of physical cleaning
$R_{reversible}$	Reversible fouling	The difference between total fouling and irremovable and irreversible fouling resistances	$R_{reversible} = R_{total} - R_{irremovable} - R_{irreversible}$	

5.2.4 Evaluation of water quality

The wastewater feed and permeate samples (~50 mL) were collected from the filtration system at the beginning of each set of filtration cycles. The measurements of conductivity, total dissolved solids (TDS), and pH value were taken using a water quality meter (UltraMeter II Series, Myron L Company). A total organic carbon/total nitrogen (TOC/TN) analyser (Shimadzu, TOC-V_{CSH}, TNM-1, ASI-V) was employed to measure TOC level in the samples. A liquid chromatography-organic carbon detection (LC-OCD, DOC-Labor GmbH) analyser, a size-exclusion chromatography system coupled with organic carbon detection and organic nitrogen detection, was used to quantify the soluble organic fractions in terms of molecular weights (MWs), e.g. biopolymers (MW > 20 kDa), humic substances (MW of ~1000 Da), building blocks (MW of ~300 to 500 Da), low MW organic acids and neutrals (MW < 300 Da) (Huber, et al., 2011). An inductively coupled plasma-optical emission spectroscopy (Avio™ 550 Max ICP-OES, Perkin Elmer) was used to analyse the inorganic elements (Na, Mg, and Ca) after filtration (0.45 µm) and acidification (with 1% HNO₃ solution) of the samples. The live and dead cells in the foulant samples were measured using a flow cytometer (BD Bioscience) after staining with LIVE/DEAD® BacLight™ bacterial viability kit

(Invitrogen). The adenosine triphosphate (ATP) levels in the foulant samples were measured using luminometer (Kikkoman) along with CheckLite 250 Plus reagent kit (Kikkoman).

5.2.5 Autopsy of fouled membrane

At the end of the filtration cycles, the fouled membranes were removed for autopsy analysis. The middle section of the fouled membranes (2 cm × 2 cm) was cut and soaked in 30 mL of DI water. The foulants were dislodged from the membrane via ultrasonication of 10 min. First portion (10 mL) of the foulant solution was analysed for live and dead cells counts and ATP levels. The next 10 mL of the foulant solution was filtered through a 0.45 µm filter and the subsequent filtered solution was analysed using TOC/TN analyser and LC-OCD. The last 10 mL of foulant solution was examined for inorganic element analysis by ICP-OES after filtering the solution by 0.45 µm filter. Another section of the fouled membranes was cut out where the morphology of the foulant layers were observed using a field emission scanning electron microscope (FESEM, JOEL, JSM-7200F Schottky) coupled with energy dispersive X-ray spectroscopy (EDS). The membrane samples were first freeze-dried and then sputter-coated with platinum before FESEM analysis.

5.3 Results and discussion

5.3.1 Effect of piezoelectricity on filtration performance

The filtration experiments were performed under constant flux of $30 \text{ L.m}^{-2}.\text{h}^{-1}$, which is within the normal range in municipal wastewater treatment (Sadr & Saroj, 2015). The normalised TMP (TMP/TMP_0) development as a function of time was recorded. Figure 5.3, Figure 5.4 and Figure 5.5 show the three sets of five filtration cycles before 1-h chemical cleaning with solutions of citric acid and sodium hydroxide. The control used in this experiment is unpoled BT-0 without AC signals being applied. Since no poling was performed and no AC signals was applied during filtration, unpoled BT-0 displayed performance without any interference of piezoelectric properties. Referring to Figure 5.3, the approximate total filtration duration for first set of five cycles are 400, 600 and 700 min for unpoled BT-0 without AC, poled BT-0 with AC and poled BT-m-0.1 with AC, respectively. The first cycle in Figure 5.3 demonstrated slower rate of increase in normalised TMP for the poled membranes.

During the initial ~ 40 min of wastewater filtration, the normalised TMP rapidly increased by about 70%, 50% and 30% for unpoled BT-0 without AC, poled BT-0 with AC and poled BT-m-0.1 with AC, respectively. This initial rapid increase in TMP followed the intermediate pore blocking model. The time dependence of ΔP for intermediate pore blocking is shown in the following equation (5.7) (Kirschner, et al., 2019):

$$\Delta P_t = \frac{\Delta P_0}{\left(\frac{1}{K_i} + \left(1 - \frac{1}{K_i}\right) \exp(-K_i B t)\right)} \quad (5.7)$$

where ΔP_0 is the initial TMP (Pa), K_i is the intermediate pore blocking constant, and B is the particle resuspension rate at which foulants are displaced from membrane surface by shear force of crossflow (s^{-1}). This suggests that deposition of foulants onto the open pores occurred during the initial phase of filtration and resulted in rapid loss in effective membrane area. Since foulants of different sizes are present in wastewater, the threshold flux of individual foulant differs among them. If the actual flux is above the threshold flux of small-sized foulants, these particles would likely to block the membrane pores prior to large-sized foulants approach the membrane surface (Zhang, et al., 2006).

After the initial rapid increase in normalised TMP, a slower rate of linear rise in normalised TMP with filtration time was noticed for the remaining filtration time. This period corresponded to fouling mechanism of cake filtration. The time dependence of ΔP for cake filtration could be written as the following equation (5.8) (Kirschner, et al., 2019):

$$\Delta P_t = \Delta P_0(1 + K_c J t) \quad (5.8)$$

where K_c is the cake filtration constant for cross-flow filtration (m^{-1}) and J is the permeate flux (m.s^{-1}). For prolonged filtration, cake filtration is presumed to be the main fouling mechanism when the membrane surface has been covered during the initial stage of filtration. By applying equation (5.8), the values of K_c are 5.76 ($R^2 = 0.921$), 5.57 ($R^2 = 0.806$) and 4.81 ($R^2 = 0.941$) m^{-1} for unpoled BT-0 without AC, poled BT-0 with AC and poled BT-m-0.1 with AC, respectively. These values of K_c indicate that the rates of cake formation in ascending order are poled BT-m-0.1 with AC, poled BT-0 with AC, and unpoled BT-0 without AC. When the filtration occurs for an extended period of time (i.e., t approaches infinity), the exponent term in the equation (5.7) becomes negligible (i.e. $\exp(-K_i B t) \approx 0$). The overall membrane fouling mechanism, combining intermediate pore blocking and cake filtration, could then be written as equation (5.9) (Kirschner, et al., 2019):

$$\Delta P_t = \Delta P_0 K_i (1 + K_c J t) \quad (5.9)$$

$\Delta P_0 K_i$ in equation (5.9) denotes intermediate pore blocking which could be estimated based as the value of y -intercept extended from the cake filtration model as shown in Figure 5.3. The estimated values of K_i are 1.57, 1.46 and 1.24 for unpoled BT-0 without AC, poled BT-0 with AC and poled BT-m-0.1 with AC, respectively. A lower value of K_i implies lesser increase in normalised TMP or lesser decrease in effective membrane area due to intermediate pore blocking. Similar trends in K_c and K_i could be observed for the first cycle in the subsequent sets.

Figure 5.6 shows the plot of K_c against filtration cycle number for the three sets of filtration cycles. Referring to Figure 5.6, within first set of filtration cycles, an increasing trend could be observed for K_c values for all types of membranes. The only difference between the different membranes is the slope of K_c against filtration cycle number. The steepest is unpoled BT-0 without AC and the most gradual is poled BT-m-0.1 with AC.

For the subsequent second and third sets of filtration cycles for unpoled BT-0 without AC, the starting value of K_c was larger than initial value but lower than end value in first/second set, followed by a logarithmic increase. This suggests that 1-h chemical cleaning was effective in removal of cake layer on the membrane surface. However, chemical cleaning could not completely remove the cake layer that was formed. Better removal of cake foulants may be possible through longer cleaning duration or the use of chemicals with higher cleaning efficiency. The logarithmic increase in K_c for unpoled BT-0 without AC could be explained by the maximum achievable K_c that could be obtained was in the range of 20 to 22 m^{-1} . At this point (i.e., $K_c = 20 - 22 \text{ m}^{-1}$), the deposition rate and back-diffusion rate of the foulants were balanced, hence K_c remained fairly constant. For poled membranes, K_c was greatly recovered after chemical cleaning followed by linearly increased against filtration cycle number for second and third sets. This indicates that piezoelectricity enhanced the effectiveness of chemical cleaning as the poled membranes experienced internal vibration deformations normal to the plane (Coster, et al., 2010), dislodging the foulants from membrane pores and surface.

Beyond the first filtration cycle, intermediate pore blocking was not the dominant fouling mechanism. In pore blocking fouling, most of the foulants are immobilised in the membrane which cannot be removed easily by physical cleaning. Intermediate pore blocking mainly happened in the first cycle and pressure relaxation was inadequate in eradicating foulants deposited in membrane pores. This is supported by the much shorter periods of subsequent filtration cycles in comparison to first cycle. Smaller extent of intermediate pore blocking occurred as lesser pores were available for deposition. Cake filtration fouling was the main fouling mechanism for the remaining cycles as supported by the increasing K_c values as more cycles were being performed.

In comparison to BT-0 with AC, the duration of the first filtration cycle of BT-m-0.1 with AC was prolonged as shown in Figures 5.3, 5.4, and 5.5. This indicated the improvement in piezoelectric properties of BT-m-0.1 led to the delaying increase in $R_{irreversible}$ and $R_{irremovable}$. Pressure relaxations, which were performed between cycles, would likely decrease $R_{reversible}$ only. The duration for the subsequent cycles (i.e., second cycle to last cycle) was similar between BT-0 with AC and BT-m-0.1 with AC as shown in Figures 5.3 and 5.4 likely due to the similarity in the value of $R_{reversible}$.

However, in the last set of filtration cycles (Figure 5.5), the duration of the second to last cycles for BT-m-0.1 with AC was slightly longer than that of BT-0 with AC. This implies that the improved piezoelectric properties of BT-m-0.1 could delay the increase in R_{total} better in the longer term.

To summarise, piezoelectricity of the poled membranes led to slower fouling rate for both intermediate pore blocking, and cake filtration as reflected by the lower values of K_i and K_c . Pressure relaxations could help with lessening cake filtration but less likely with lessening intermediate pore blocking whereby foulants were being trapped in membrane pores. Self-agitation of piezoelectric poled membranes complemented the higher cross-flow during pressure relaxation and the efficiency of chemicals during chemical cleaning, synergising as an effective anti-fouling method during wastewater filtration.

Figure 5.3: Plot of normalised TMP (TMP/TMP_0) against time (min) for the first set of filtration cycles for different types of membranes.

Figure 5.4: Plot of normalised TMP (TMP/TMP_0) against time (min) for the second set of filtration cycles for different types of membranes.

Figure 5.5: Plot of normalised TMP (TMP/TMP_0) against time (min) for the third set of filtration cycles for different types of membranes.

Figure 5.6: Plot of cake filtration constant, K_c (m⁻¹) against filtration cycle number for three sets of filtration cycles.

5.3.2 Effect of piezoelectricity on fouling resistance

All three membranes had similar R_m , about $6 - 7 \times 10^9 \text{ m}^{-1}$, computed based on clean water permeability test. Figure 5.7 shows the fouling resistance profiles for unpoled BT-0 without AC, poled BT-0 with AC and poled BT-m-0.1 with AC that were computed after the last cycle of three sets of filtration cycles. The total fouling resistances for all membranes were similar, approximately equivalent to $\sim 15 \times 10^9 \text{ m}^{-1}$ (i.e., $R_{total} = \frac{\Delta P}{J \cdot \mu} - R_m$), since each constant flux filtration cycle was stopped when TMP reached $\sim 600 \text{ kPa}$.

The values of $R_{irremovable}$ of different membranes were derived from the difference in resistance after chemical cleaning and intrinsic membrane resistance. For all the membranes, $R_{irremovable}$ increased from the first set to the last set of filtration cycles despite chemical cleaning was performed. Though, poled BT-m-0.1 with the application of AC signals displayed prominent anti-fouling effect as the values of $R_{irremovable}$ were approximately one order of magnitude lower than that of unpoled BT-0 without AC signals supplied, i.e., $1 - 2 \times 10^9 \text{ m}^{-1}$ vs. $6 - 12 \times 10^9 \text{ m}^{-1}$ from set 1 to set 3, while the anti-fouling effect of poled BT-0 with AC was in-between unpoled BT-0 and poled BT-

m-0.1. Moreover, as compared to the control membrane, the incorporation of BaTiO₃ nanoparticles shifted the fouling pattern from irremovable dominance (i.e., 39 – 78 % from set 1 to set 3 for unpoled BT-0 without AC) to reversible dominance (i.e., 58 – 61 % from set 1 to set 3 for poled BT-m-0.1 with AC); as well as significantly lowered the rate of build-up of irremovable fouling, which suggested that the modified piezoelectric membrane could be easily recovered by physical cleaning and required less chemical cleaning, thus could last longer before the need for membrane replacement.

Figure 5.7: Fouling resistance profiles of unpoled BT-0 without AC, poled BT-0 with AC and poled BT-m-0.1 with AC that were computed after the last cycle of the three sets of filtrations.

5.3.3 Effect of piezoelectricity on energy consumption

The power required per unit membrane area for supplying electrical AC signals of 10 V at 500 Hz to the piezoelectric membrane during filtration was computed to be ~ 0.036 kW.m⁻². In comparison, the reported value for commercially available vibratory shear-enhanced process (VSEP) technology is 0.5 kW.m⁻² (Zamani, et al., 2015). The

significant difference in power required per unit membrane area between the two methods is expected since the former consumes less energy as piezoelectric membrane itself serves as a source of agitation whereas the latter requires more energy to mechanically vibrate the entire membrane module. It should be highlighted that the specific power of supplying electrical signals was computed based on a small membrane area ($16.25 \times 10^{-4} \text{ m}^2$). Thus, more analysis on specific power would be needed when scaling-up piezoelectric membrane. If similar power is consumed even after scaling-up, then specific energy consumption of piezoelectric membrane would be much lower. Otherwise, if higher specific power is required, it would translate into higher specific energy consumption.

Figure 5.8 depicts the total specific energy consumption (kWh.m^{-3}) of different types of membranes. In general, the total specific energy consumption of the poled piezoelectric membranes with AC were higher than that of the unpoled membrane without AC (control). Although the anti-fouling effect of poled piezoelectric membranes slowed the rate of TMP increase which led to a decrease in energy consumption of the pump, additional energy was required to supply AC signals to piezoelectric membranes. Despite of higher total specific energy consumption, the use of piezoelectric membrane for fouling control is still desirable as it delays the fouling rate and extends the filtration duration. Moreover, other factors such as less downtime, less chemicals usage and longer membrane lifespan shall be considered when assessing the advantages of piezoelectric membrane as an anti-fouling strategy. This section also highlights the potential of piezoelectric membrane as an anti-fouling strategy in water treatment processes after necessary optimisation in membrane fabrication.

Figure 5.8: Total specific energy consumption (kWh.m⁻³) for unpoled BT-0 without AC signals, poled BT-0 with AC signals and poled BT-m-0.1 with AC signals. The total specific energy consumption includes energy consumed by the pump and supplying AC signals.

5.3.4 Effects of AC voltage and cross-flow velocity on fouling reduction

Based on the results above, poled BT-m-0.1 with AC signals exhibited the most outstanding filtration performance and anti-fouling effect among all the membranes studied. In this section, the comparison between AC voltage and cross-flow velocity on the reduction in total fouling resistance (R_{total}) will be discussed.

Figure 5.9: Plot of % decrease in total resistance, R_{total} (primary vertical axis) and total specific energy consumption, E_{AC} (kWh.m^{-3}) (secondary vertical axis) against different AC voltages for poled BT-m-0.1 at cross-flow velocity of 0.1 m.s^{-1} .

Figure 5.9 shows the % decrease in R_{total} after filtration of wastewater for poled BT-m-0.1 when electrical AC signals of different voltages were applied. The % decrease in R_{total} was determined by the difference between R_{total} at default condition (i.e., no AC signal or no increased cross-flow) and R_{total} at respective condition (either applied AC signals or increased cross-flow) divided by R_{total} at default condition. Electrical AC signals of 0, 5, 10, 15 and 20 V were experimented. The greater the value of alternating voltage, the larger the value of E_{AC} in Figure 5.9. As demonstrated in Figure 5.9, there was an initial linear increase of % reduction in R_{total} when the applied voltage was

increased from 0 to 10 V. After which, % decrease in R_{total} flattened out for applied voltage between 10 V and 20 V which suggested that 10 V seemed like the optimal alternating voltage for the operation of piezoelectric membrane from the perspectives of anti-fouling performance and energy consumption. Alternating voltage of less than 10 V had lower energy consumption but minimal anti-fouling effects. On the other hand, any value of voltage greater than 10 V showed minor improvement in fouling reduction at the expense of a much greater energy consumption.

Figure 5.10: Plot of % decrease in total resistance, R_{total} (primary vertical axis) and total specific energy consumption, E_{AC} (kWh.m⁻³) (secondary vertical axis) against cross-flow velocity (m.s⁻¹) for unpoled BT-0 without AC signals.

A similar trend to AC voltage was observed for cross-flow velocity as shown in Figure 5.10. The reduction in R_{total} was predictable as higher cross-flow provided a greater shear force to sweep away foulants from the membrane surface and to prevent foulants from depositing in the pores or on the surface of membrane. Although it is optimal to operate at high cross-flow velocity due to its anti-fouling effect, its unfavourable energy consumption impedes its application in real-life filtration processes (Vatai, et al., 2009).

Beyond 0.3 m.s^{-1} , % decrease in R_{total} began to plateau out which means little enhancement in anti-fouling effect even with the further increase in cross-flow velocity. Increasing both alternating voltage and cross-flow velocity displayed an initial linear increase in % decrease in R_{total} before reaching a plateau, showing minimal improvement for further increment in alternating voltage or cross-flow velocity.

Figure 5.11: Plot of % decrease in total resistance, R_{total} against energy consumption increase, ΔE (kWh.m⁻³) of cross-flow velocity or AC voltage.

Figure 5.11 summarises the % reduction in R_{total} against energy consumption increase, ΔE (kWh.m⁻³), for cross-flow and AC voltage based results from Figure 5.9 and Figure 5.10. If 10 V is supplied to piezoelectric membrane, ~13% reduction in R_{total} would be observed for an additional energy consumption of 1.2 kWh.m⁻³. For an equivalent energy consumption increase by increasing the cross-flow velocity, only ~5% decrease in R_{total} would be observed. From the analysis above, it could be concluded that piezoelectric membrane under the influence of electrical signals seemed to be more effective in fouling control over increasing cross-flow velocity in terms of reduction in R_{total} and energy consumption.

5.3.5 Water quality

Table 5.2 summarises the characteristics of the feedwater and permeate that were collected at the start of the filtration experiments from different membranes. These characteristics were examined by various analytical methods as described in section 5.2.4 and were presented as average data based on several measurements. Referring to Table 5.2, unpoled and poled membranes showed similar rejection performances of the foulants that were present in identical wastewater feed. Thus, it implies that the use of piezoelectric membrane does not compromise permeate quality even as the occurrence of fouling was reduced.

The following observation are made from each category of the foulants listed in Table 5.2. First, significant removal of live cells and dead cells was observed among all the foulants analysed, approximately 85 to 87% removal of live cells and 93 to 94% removal of dead cells. Second, the negligible removal of monovalent (Na^+) and divalent (Mg^{2+} and Ca^{2+}) cations by the membranes was demonstrated. The removals of Na^+ , Mg^{2+} , and Ca^{2+} were 17 to 20%, 22 to 28%, and 19 to 22% respectively. The removals of these ions could be attributed to deposition of ions in the cake layer, or the micro-vibration of piezoelectric membrane hinders the movement of the ions across the membrane. However, the tested inorganic ions were not significantly removed, which could be attributed to the relatively large pore size of ultrafiltration (UF) membrane. Third, the TOC of feedwater was ~ 18 to 20 mg.L^{-1} whilst that of permeate was ~ 16 to 17 mg.L^{-1} , demonstrating 10 to 16% decrease in removal of TOC. Lastly, negligible removals of soluble organics were noticed.

Biopolymers were the main soluble organics removed with a removal rate of 51 to 59% and almost insignificant removal of other soluble components was detected. Low molecular weight (LMW) neutrals and LMW acids were analysed to be of higher concentrations in permeate than in feed. These results are in agreement with previous studies in which similar observations were made (Chomiak, et al., 2015; Lee, et al., 2019; Hube, et al., 2021). This could conceivably be due to the breakdown of substances that were larger in size (e.g., biopolymers and building blocks) to substances that were smaller in size (e.g. LMW neutrals and LMW acids) by the action of biofilm that was formed on the membrane surface. Since these LMW matters were relatively small compared to the membrane pores, the membranes were not able to effectively retain

these LMW matters and hence, they were detected in the permeate. The other reason for the higher concentrations of LMW matters is the influence of cross-flow velocity. The action of cross-flow may encourage the breaking down of large-sized matters to small-sized matters. In comparison to membrane bioreactor (MBR) which is widely used in wastewater treatment, the removal of organics in one-step ultrafiltration may not be as effective due to the absence of biodegradation.

Table 5.2: Characteristics of feedwater and permeate collected for different membranes.

	Feed			Permeate		
	Unpoled BT-0 with no AC	Poled BT-0 with AC	Poled BT-m-0.1 with AC	Unpoled BT-0 with no AC	Poled BT-0 with AC	Poled BT-m-0.1 with AC
Conductivity(μ S)	291.4 ± 2.3	287.7 ± 2.9	288.6 ± 2.9	249.7 ± 2.8	247.0 ± 2.6	246.9 ± 2.0
TDS (mg. L ⁻¹)	189.3 ± 1.7	186.6 ± 2.1	187.3 ± 2.6	161.2 ± 1.3	159.5 ± 1.5	159.2 ± 1.4
pH	7.53 ± 0.35	7.55 ± 0.10	7.65 ± 0.11	7.29 ± 0.10	7.31 ± 0.17	7.25 ± 0.12
TOC (mg. L ⁻¹)	18.24 ± 2.99	18.86 ± 1.68	19.81 ± 1.16	16.37 ± 1.35	16.41 ± 1.53	16.63 ± 1.31
Biopolymers (mg. L ⁻¹)	2.07 ± 0.55	1.93 ± 0.61	2.34 ± 0.44	1.02 ± 0.36	0.85 ± 0.24	0.96 ± 0.31
Building blocks (mg. L ⁻¹)	4.54 ± 0.73	4.66 ± 0.52	4.27 ± 0.65	4.65 ± 1.53	6.08 ± 2.12	5.83 ± 1.86
LMW neutrals (mg. L ⁻¹)	2.86 ± 0.38	2.72 ± 0.45	2.52 ± 0.47	3.03 ± 1.11	3.64 ± 1.66	2.94 ± 0.92
LMW acids (mg. L ⁻¹)	0.81 ± 0.20	0.96 ± 0.13	0.77 ± 0.14	0.83 ± 0.31	0.79 ± 0.22	0.78 ± 0.27
Na ⁺ (mg. L ⁻¹)	18.04 ± 0.92	17.90 ± 0.81	17.67 ± 0.69	14.96 ± 0.73	14.48 ± 0.86	14.13 ± 0.66
Mg ²⁺ (mg. L ⁻¹)	1.47 ± 0.11	1.44 ± 0.09	1.40 ± 0.07	1.14 ± 0.07	1.06 ± 0.05	1.01 ± 0.04
Ca ²⁺ (mg. L ⁻¹)	25.30 ± 0.66	24.86 ± 0.83	24.38 ± 0.78	20.57 ± 0.54	19.72 ± 0.70	19.12 ± 0.41
Live cells (10 ⁵ count mL ⁻¹)	2.56 ± 0.41	2.27 ± 0.11	2.49 ± 0.02	0.38 ± 0.05	0.30 ± 0.03	0.35 ± 0.03
Dead cells (10 ⁵ count mL ⁻¹)	10.07 ± 0.49	10.49 ± 0.34	11.38 ± 0.31	0.68 ± 0.02	0.70 ± 0.04	0.66 ± 0.04
ATP (pg.mL ⁻¹)	249 ± 18	194 ± 16	252 ± 24	91 ± 2	100 ± 6	81 ± 1

5.3.6 Membrane foulants

At the end of the experiment, the fouled membrane was collected and a section of the membrane coupon was cut for autopsy analysis. The foulants were dislodged from the membrane coupon into DI water via sonication. The sample (i.e., DI water and irremovable foulants) was then characterised as mentioned in section 5.2.4. Table 5.3 summarises characteristics of foulants extracted from different membranes. As shown in Table 5.3, the main constituents detected in the samples were inorganic foulants (e.g., Mg and Ca), organic foulants (e.g., building blocks and LMW neutrals), and biological foulants (e.g., live cells, dead cells and ATP). In general, the membranes, in decreasing order of the amount of foulants (i.e., inorganic, organic and biological), are unpoled BT-0 without AC, poled BT-0 with AC and poled BT-m-0.1 with AC.

Table 5.3: Characteristics of cake layer foulants for different membranes.

	Unpoled BT-0 without AC	Poled BT-0 with AC	Poled BT-m-0.1 with AC
TOC ($\mu\text{g. cm}^{-2}$)	2542 ± 230	2391 ± 244	1945 ± 208
Biopolymers ($\mu\text{g. cm}^{-2}$)	560 ± 66	412 ± 32	387 ± 36
Building blocks ($\mu\text{g. cm}^{-2}$)	1018 ± 82	856 ± 93	693 ± 57
LMW neutrals ($\mu\text{g. cm}^{-2}$)	1134 ± 101	787 ± 85	722 ± 61
LMW acids ($\mu\text{g. cm}^{-2}$)	327 ± 60	288 ± 25	214 ± 32
Mg ($\mu\text{g. cm}^{-2}$)	182 ± 6	101 ± 9	76 ± 7
Ca ($\mu\text{g. cm}^{-2}$)	456 ± 11	379 ± 13	324 ± 9
Live cells (10^7 count cm^{-2})	8.3 ± 1.9	3.4 ± 0.6	2.7 ± 0.8
Dead cells (10^7 count cm^{-2})	42.6 ± 2.2	41.8 ± 3.0	37.9 ± 2.6
ATP (pg.cm^{-2})	1248 ± 90	537 ± 48	391 ± 43

Figure 5.12: FESEM images of top surface of fouled (a) unpoled BT-0 (without application of AC), (b) poled BT-0 (with application of AC), and (c) poled BT-m-0.1 (with application of AC) at $\times 1000$ times magnification.

Figure 5.13: (a) FESEM image of top surface of fouled unpoled BT-0 (without application of AC), (b) EDS mapping image of (a).

It is known that the presence of divalent ions (e.g., Ca^{2+} or Mg^{2+}) during filtration may accelerate fouling by forming molecular bridges with colloidal or organic foulants that are also present in complex wastewater feed (She, et al., 2012). This could then explain the higher levels of inorganics and organics present on unpoled membrane without AC

signals. Moreover, biofilm growth was more evident in unpoled BT-0 without AC than the poled membranes, as supported by greater level of ATP ($1248 \pm 90 \text{ pg.cm}^{-2}$). Foulants such as inorganic Mg (up to 58% reduction) and live cells (up to 69% reduction) showed the most reduction between unpoled membrane without AC signals and poled membranes with AC signals. Hence, the cake layer foulants obtained from the poled membranes were generally fewer than those present in the unpoled membrane. This agrees with the FESEM images in Figure 5.12 where the foulants covered a smaller area on membrane surface of poled membranes. The FESEM images of the top surface of the fouled membranes (at the end of filtration experiments) at $\times 1000$ times magnification are shown in Figure 5.12. It could be noted that the foulants covered a large area on the unpoled BT-0 membrane without AC signals. On the other hand, the foulants were scattered and covered lesser area on poled BT-0 and BT-m-0.1 membranes with AC signals. This agrees with the reduced irremovable fouling as shown in Figure 5.7. EDS analysis was performed on the fouled BT-0 membrane after filtration of wastewater to understand the inorganic foulant structure. The EDS mapping, as shown in Figure 5.13, reveals the presence of calcium, oxygen, fluorine, and carbon on the membrane surface. Since PVDF membrane consists of carbon and fluorine atoms, the remaining elements (i.e., calcium and oxygen) detected were likely to be the foulants. Hence, it can be deduced that the majority of the inorganic foulant is likely to be insoluble calcium carbonate consisting of calcium, carbon, and oxygen. The piezoelectric vibrations reduced the occurrence of irremovable fouling and synergised with chemical cleaning, leading to fewer foulants being deposited on the membrane surface. This implies that piezoelectrically vibrating poled membranes could retard the deposition of fouling material regardless of the nature of fouling materials.

5.4 Chapter conclusion

The filtrations of real wastewater by non-piezoelectric and piezoelectric membranes were examined in this chapter. The presence of different types of foulants (i.e., inorganic, organic and biological) was detected in the wastewater and on the membrane. The developments of reversible, irreversible, and irremovable fouling were significantly lowered for piezoelectric membrane, especially the poled BT-m-0.1 with AC signals applied that shifted the fouling pattern from irremovable dominance to reversible dominance. These could be attributed to the micro-agitation caused by the inverse piezoelectric effect (i.e., mechanical strain resulting from applied electrical field) of the poled membranes which disturbed the foulant layer and substantially reduced the rate of fouling. The fouling reduction resulted in a longer filtration duration and lesser chemical usage because of lower frequency of cleaning. The effects of different AC voltages and cross-flow velocities on the alleviation in fouling were also investigated. The use of piezoelectric membrane as anti-fouling strategy is more favourable than increasing cross-flow due to greater fouling reduction for equivalent energy consumption. Less foulants were also detected on the poled membranes at the end of the filtration experiments, indicating a synergy between piezoelectric effects and chemical cleaning.

CHAPTER 6

Conclusions and future work

6.1 Overall conclusions

This thesis presents the development of piezoelectric PVDF flat-sheet membranes via NIPS method. Flat-sheet PVDF membranes that are commercially available have been previously shown to demonstrate inverse piezoelectric effect after high voltage electrical poling was performed on these membranes. Nevertheless, little insights could be established on commercial flat-sheet membranes due to the lack of information on the fabrication process for these membranes and limited modifications could be carried out on these membranes to enhance their piezoelectricity. Consequently, it is desirable to fabricate piezoelectric membranes from scratch to understanding the effects of different membrane properties on piezoelectricity and to perform modification during membrane fabrication. In this thesis, PVDF flat-sheet membranes with various morphologies were fabricated using different solvents (**Chapter 3**), followed by the further incorporation of piezoelectric inorganic nanoparticles (NPs) (**Chapter 4**) and application of piezoelectric membrane in real wastewater filtration (**Chapter 5**).

The fundamental understanding of membrane properties on its piezoelectricity was established by characterising PVDF membranes fabricated using different solvents by NIPS. Subsequently, the PVDF membranes were electrically poled to enhance piezoelectric properties. Flux-stepping and fouling experiments were performed to investigate the filtration performance of non-piezoelectric and piezoelectric membranes. Highly piezoelectric inorganic barium titanate (BaTiO_3) NPs were then incorporated in PVDF membranes. Prior to incorporation of NPs, BaTiO_3 NPs were modified by silane coupling agent to explore if more uniform dispersion of NPs in PVDF dope solution could be achieved. The above-mentioned fabricated piezoelectric membranes were finally applied in the filtration of wastewater to examine its potential as an anti-fouling control method.

The major findings and conclusions are summarised as follows:

- The dielectric and piezoelectric properties of PVDF membranes were affected by the morphology of the membranes. Membranes with finger-like cross-section morphology, prepared using N,N-dimethylformamide (DMF) solvent, had better dielectric and piezoelectric behaviour among all the fabricated membranes. Morphological features, such as macrovoids and distinctive separate layers, resulted in weak dielectric strength which is undesirable for electrical poling due to the increased possibility of an electrical breakdown during poling.
- Piezoelectric properties of the membranes were improved after electrical poling was performed attributable to the alignment of electric dipoles during poling. Besides alignment of dipoles, electrical poling transformed membranes with finger-like cavities to drop-like cavities while minimal change was observed for more symmetric membranes.
- The values of critical flux were increased by 25 to 46% for poled membranes under the application of electrical AC signals as compared to unpoled membranes without electrical signal resulting from the anti-fouling effect of piezoelectric vibrations.
- The anti-fouling effect of piezoelectric vibrations increased the values of critical flux were increased by 25 to 46% and exhibited up to 66% reduction in the rate of transmembrane pressure (TMP) rise, delaying fouling progression and extending filtration duration by a factor of approximately three for equal increase in TMP.
- BaTiO₃ NPs that were modified by (3-Aminopropyl)triethoxysilane (APTES), a type of silane coupling agents, demonstrated improved compatibility and dispersion in PVDF membranes, particularly for membranes incorporated with 0.1 wt.% of modified BaTiO₃ NPs.
- The addition of BaTiO₃ NPs into PVDF membranes also showed improvements in piezoelectric d_{33} coefficient, dielectric strength and mechanical properties because of the intrinsically better piezoelectric and mechanical properties of BaTiO₃ than PVDF.
- A decline in critical flux could be noticed for non-piezoelectric membranes as contact angle of the membranes was increased whilst no obvious correlation between critical flux and contact angle was spotted for piezoelectric membranes.

BaTiO₃ NPs are hydrophilic in nature and the inclusion of BaTiO₃ NPs in PVDF membranes decreased the membrane contact angle (i.e., reduced hydrophobicity), increasing critical flux of the non-piezoelectric membranes.

- An increasing linear correlation between piezoelectric d_{33} coefficient and critical flux of colloidal silica was observed for poled piezoelectric membranes under the influence of AC signals, demonstrating critical flux of piezoelectric membranes could be improved by increasing their piezoelectric properties.
- As compared to non-piezoelectric membranes, piezoelectric membranes incorporated with BaTiO₃ NPs had greater critical flux value by up to 51% and displayed longer filtration cycle duration by up to a factor of 2 to 4 during multiple filtration cycles. The normalised TMP of piezoelectric membranes incorporated with BaTiO₃ NPs was almost restored to the original value after pressure relaxation (i.e., reduced to atmospheric pressure and increased cross-flow), suggesting minimal irreversible fouling.
- Lower values of intermediate pore blocking constant (K_I) and cake filtration constant (K_C) were computed for piezoelectric membranes, suggesting slower fouling rates for both intermediate pore blocking and cake filtration.
- The value of $R_{irremovable}$ for piezoelectric membrane incorporated with BaTiO₃ NPs ($\sim 1 \times 10^9$ to $2 \times 10^9 \text{ m}^{-1}$) is approximately one order of magnitude lower than non-piezoelectric membrane ($\sim 6 \times 10^9$ to $12 \times 10^9 \text{ m}^{-1}$), implying inverse piezoelectric effect works synergistically with other cleaning methods during fouling removal.
- An initial increase followed by dampening in % reduction in total fouling was observed when alternating voltage or cross-flow velocity was raised during wastewater filtration. In comparison to increasing cross-flow, piezoelectric membrane as anti-fouling method in filtration is a better option when considering from the perspective of energy consumption.

6.2 Recommendations for future work

It was demonstrated that piezoelectric membranes have the potential to offer cost-effective and energy efficient anti-fouling strategy for water treatment processes. However, many challenges, that are hindering the realisation of piezoelectric membrane in industrial use, need be overcome such as industrial-scale manufacturing of piezoelectric membrane. More studies must be performed on piezoelectric membrane to realise its potential in real-life applications. The areas of potential and future research are proposed as follows:

i. Fabrication of piezoelectric membranes in other pore sizes

In the work presented earlier, the piezoelectric membranes prepared via NIPS had pore sizes within the range of ultrafiltration (UF) membrane. Microfiltration membranes can be fabricated using thermally induced phase separation (TIPS) while nanofiltration (NF) membranes can be fabricated by NIPS with the addition of additives or under controlled conditions. However, non-woven layer should not be used as support for the fabricated membrane which is commonly used for UF and NF membranes. This is because subsequent electrical poling could not be performed on membranes that exhibit discontinuities due to their low dielectric strength. Piezoelectric membranes can also be used as substrate layer for NF or reverse osmosis (RO) membranes in which layer-by-layer (LbL) electrostatic assembly or interfacial polymerisation (IP) can be performed to prepare the selective layer on the piezoelectric substrate layer.

ii. Fabrication of dual-layer piezoelectric membranes

During the incorporation of BaTiO₃ NPs, the NPs were dispersed in PVDF dope solutions to prepare a single-layer BaTiO₃-PVDF membranes. The optimal placement of BaTiO₃ NPs within the PVDF membranes could be investigated by fabricating dual-layer membranes. BaTiO₃ NPs could either be added to the top or bottom layer to confirm if surface micro-vibrations (i.e., anti-fouling effects) would be as effective as compared to BaTiO₃ NPs that are within the entire membrane. As mentioned above, non-woven layer cannot be used as support for piezoelectric membrane. So, an alternative to

a support is to fabricate membranes with a greater thickness which could be achieved by dual-layer membrane preparation.

iii. *Comparison of piezoelectric membrane with other commercial membrane*

In chapter 3, comparison among the fabricated PVDF membranes and a commercial UF PVDF membrane was performed. Instead of commercial PVDF membrane, the next part of the research could focus on comparing the performance of other polymeric commercial membranes with that of the piezoelectric membranes to evaluate the practicality of piezoelectric membranes in commercial applications.

iv. *Scale up for flat-sheet piezoelectric membrane*

As mentioned earlier on, the industrial use of piezoelectric membrane would only be possible if industrial-scale manufacturing of piezoelectric membrane is achieved. The main issue that must be solved is to perform electrical poling as part of the fabrication process instead of as a post-treatment. This may be overcome if high voltage electrical poling can be simultaneously performed during membrane fabrication, comparable to tip voltage applied during electrospinning. This would also shorten the electrical poling process, achieving greater efficiency.

v. *Fabrication of piezoelectric hollow fibre membranes*

Previous studies performed on piezoelectric membranes were limited to polymeric flat-sheet membranes, tubular ceramic membranes and electrospun fibres. Hollow fiber membranes (HFMs) are often preferred over flat or tubular membranes for several reasons such as high surface-to-volume ratio, conceptual simplicity, simple incorporation in flow streams, and broad availability (Bruijnsvoort & Schoenmakers, 2000). Moreover, there is a possibility of greater enhancement of vibrations for HFMs due to secondary flow effects (i.e., flow around a bend) (Zamani, et al., 2015). Hence, it would be ideal to have piezoelectric HFMs to harness benefits of vibrations and secondary flow effects. Though many studies were performed on fabrication

of PVDF HFMs, the challenge of poling HFMs need to be addressed first to realise the concept of piezoelectric HFMs.

vi. *Modelling of surface vibration and hydrodynamics for piezoelectric membrane*

After sufficient experimental work is performed on piezoelectric membranes, next part of the research is to perform modelling of the surface vibration and hydrodynamics for piezoelectric membranes. Modelling could help to explain or predict filtration performance of piezoelectric membranes. The model could be verified by experimental data and the validated model could then provide a systematic guide to future work.

vii. *Application of piezoelectric membrane in water treatment processes and compare with other conventional fouling control methods*

To further test out the applicability of piezoelectric membrane in water treatment processes, piezoelectric membrane can be implemented in processes such as membrane bioreactor (MBR). The assessment of the cost and long-term impact of vibration on piezoelectric membrane in such processes could be studied. Piezoelectric membrane can also be compared to common anti-fouling strategies (e.g., gas sparging, bubbling etc) to evaluate its effectiveness.

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