INVESTIGATION ON PHYSICAL, MECHANICAL AND WETTABILITY PROPERTIES OF 3D PRINTED POLYAMIDE-12 MEMBRANE

NURUL AFIQAH BINTI ARBAIN

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

2025

Faculty of Mechanical Technology and Engineering

INVESTIGATION ON PHYSICAL, MECHANICAL AND WETTABILITY PROPERTIES OF 3D PRINTED POLYAMIDE-12 MEMBRANE

Nurul Afiqah Binti Arbain

Master of Science in Mechanical Engineering

2025

INVESTIGATION ON PHYSICAL, MECHANICAL AND WETTABILITY PROPERTIES OF 3D PRINTED POLYAMIDE-12 MEMBRANE

NURUL AFIQAH BINTI ARBAIN

A thesis submitted in fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

Faculty of Mechanical Technology and Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2025

DECLARATION

I declare that this thesis entitled "Investigation on Physical, Mechanical and Wettability Properties of 3D Printed Polyamide-12 Membrane" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....

Name : Nurul Afiqah Binti Arbain

Date : 06/02/2025

APPROVAL

I hereby declare that I have read this dissertation/report and in my opinion this dissertation/report is sufficient in terms of scope and quality as a partial fulfillment of Master of Science in Mechanical Engineering.

Signature : ....

Supervisor Name : Dr. Nurul Hilwa Binti Mohd Zini

Date : 06/02/2025

DEDICATION

To my beloved parents

ABSTRACT

Three dimensional (3D) printed polymer membrane is highly feasible for gravity-driven, oil-water separation for oil spill remediation due to its reliable selective separations, high efficiency and switchable wettability. However, its underwater switchable wettability can be a challenge due to printing parameters; any surface alteration will modify the printed membrane wettability, enhanced by the influence of water temperature which can destabilize underwater superoleophobicity of the printed membrane. This study aimed to analyse the printing parameters' effect on underwater switchable wettability in elevated water temperatures to improve the wettability of printed polymer membranes. For surface hydrophobicity improvement, printed polyamide membranes were immersed in a hydrophobic-candle soot/hexane mixture and subjected to sonication process. The parameters of 'dry' wettability, morphology, porosity, surface roughness and mechanical properties of the membranes were evaluated; the 3D printing parameters effect was also assessed. Moreover, this study uniquely examines the impact of printing parameters on underwater switchable wettability across a temperature range of 30 to 50°C. The underwater superoleophobicity of the printed polymer membranes was analysed by the oil droplet underwater contact angle measurement in the inverted sessile drop experimental setup. CM-2 B specimen (bottom surface of coated membrane specimen fabricated from 70 W of laser power and 0.12 mm of layer thickness) showed the best wettability performance with the highest water contact angle (WCA) value of 150.65°, achieving superhydrophobic behaviour. This was due to the specimen having the highest surface roughness and porosity values of 11.14 μm and 22.37 %, respectively. The increase in surface roughness increases the WCA on the membrane. For the tensile properties, the NCM-3 specimen (non-coated membrane specimen fabricated from 80 W of laser power and 0.06 mm of layer thickness) obtained the highest values (42.40 MPa) due to higher energy density (ED) transmitted during the printing process influenced by the printing parameter setting. However, the highest oil-water separation efficiency was recorded by CM-2 B specimen with 99.5%. For the underwater oil contact angle (OCA), CM-2 B specimen recorded the highest OCA values (160.56°) at 30°C. Nevertheless, as the water temperatures rose to 40°C and 50°C, OCA values for CM-2 B specimen decreased from 155.75° to 153.66 °, a similar trend for all specimens. The proposed underwater OCA model reveals that the temperature negatively affects OCA (-0.2959), while layer thickness has a strong positive influence (79.90). The ANOVA results also highlighted temperature and layer thickness as the most significant predictors for underwater OCA. From this study, it has been shown that printing parameters, surface modification and temperatures affect the performance of the membrane especially in oil-water separation process.

KAJIAN TERHADAP SIFAT FIZIKAL, MEKANIKAL DAN KEBOLEHBASAHAN MEMBRAN POLIAMIDA-12 CETAKAN 3D

ABSTRAK

Membran polimer bercetak tiga dimensi (3D) sangat sesuai untuk pemisahan minyak-air yang dipacu graviti untuk pemulihan tumpahan minyak kerana pemisahan terpilih yang boleh dipercayai, kecekapan tinggi dan kebolehbasahan boleh tukar. Walau bagaimanapun, kebolehbasahan boleh tukar dalam airnya boleh menjadi satu cabaran kerana parameter pencetakan; sebarang perubahan permukaan akan mengubah suai kebolehbasahan membran bercetak, dipertingkatkan oleh pengaruh suhu air yang boleh menjejaskan kestabilan superoleofobik dalam air membran bercetak. Kajian ini bertujuan untuk menganalisis kesan parameter percetakan terhadap kebolehbasahan boleh tukar dalam air dalam suhu air yang agak tinggi untuk meningkatkan kebolehbasahan membran polimer bercetak. Untuk penambahbaikan hidrofobik permukaan, membran poliamida bercetak direndam dalam campuran jelaga/heksana lilin hidrofobik dan tertakluk kepada proses sonikasi. Parameter kebolehbasahan 'kering', morfologi, keliangan, kekasaran permukaan, dan sifat mekanikal membran telah dinilai; kesan parameter pencetakan 3D juga dinilai. Selain itu, kajian ini secara unik mengkaji kesan parameter pencetakan pada kebolehbasahan boleh tukar dalam air merentasi julat suhu 30 hingga 50 °C. Keadaan superoleofobik bawah air membran polimer bercetak dianalisis oleh titisan minyak pengukuran sudut sentuhan bawah air dalam persediaan eksperimen titisan sesil terbalik. Spesimen CM-2 B (permukaan bawah spesimen membran bersalut yang direka daripada kuasa laser 70 W dan ketebalan lapisan 0.12 mm) menunjukkan prestasi kebolehbasahan terbaik dengan nilai sudut sentuhan air (WCA) tertinggi iaitu 150.65°, mencapai tingkah laku superhidrofobik. Ini disebabkan oleh spesimen yang mempunyai nilai kekasaran permukaan dan keliangan tertinggi masing-masing 11.14 µm dan 22.37 %. Peningkatan kekasaran permukaan meningkatkan WCA pada membran. Untuk sifat tegangan, spesimen NCM-3 (spesimen membran tidak bersalut yang direka daripada kuasa laser 80 W dan ketebalan lapisan 0.06 mm) memperoleh nilai tertinggi (42.40 MPa) disebabkan oleh ketumpatan tenaga (ED) yang lebih tinggi yang dihantar semasa proses pencetakan dipengaruhi oleh tetapan parameter percetakan. Walau bagaimanapun, kecekapan pemisahan minyak-air tertinggi dicatatkan oleh spesimen CM-2 B dengan 99.5%. Untuk sudut sentuhan minyak bawah air (OCA), spesimen CM-2 B merekodkan nilai OCA tertinggi (160.56°) pada 30°C. Namun begitu, apabila suhu air meningkat kepada 40°C dan 50°C, nilai OCA untuk spesimen CM-2 B menurun daripada 155.75° kepada 153.66°, arah aliran yang sama untuk semua spesimen. Model OCA bawah air yang dicadangkan mendedahkan bahawa suhu memberi kesan negatif kepada OCA (-0.2959), manakala ketebalan lapisan mempunyai pengaruh positif yang kuat (79.90). Keputusan ANOVA juga menyerlahkan suhu dan ketebalan lapisan sebagai peramal yang paling penting untuk OCA bawah air. Daripada kajian ini, telah menunjukkan bahawa parameter cetakan, pengubahsuaian permukaan dan suhu mempengaruhi prestasi membran terutamanya dalam proses pengasingan minyak-air.

ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious, the Most Merciful. First and foremost, I would like to take this opportunity to express my sincere acknowledgement to my supervisor Dr Nurul Hilwa Binti Mohd Zini from the Faculty of Mechanical Technology and Engineering Universiti Teknikal Malaysia Melaka (UTeM) for her essential supervision, support and encouragement towards the completion of this thesis. All the advice and great knowledge given by her helps me in completing my master's journey. I would like to express my deepest gratitude to my co-supervisor Dr Fadhilah Binti Shikh Anuar for her continuous support and motivation. A special thanks to Madam Siti Nor Habibah Binti Hassan for her goodwill in teaching me new knowledge.

I would like to thank Mrs. Hidayah, Mrs. Atiqah and Mr. Nazir technicians from Tribology laboratory, Chemistry laboratory and Oil Analysis and Calibration lab from the Faculty of Mechanical Technology and Engineering Universiti Teknikal Malaysia Melaka (UTeM) for their cooperation during the experimental works. Furthermore, I would express gratitude to Mr Idain Fahmy for his assistance and efforts in the fabrication and experimental process.

I would like to express my deepest gratitude to my parents, Arbain Bin Sabar and Zaleha Binti Mohd Saman, for their unwavering love, patience and sacrifice. Your faith in me has been my biggest source of strength. Your emotional and financial support has allowed me to pursue and accomplish my academic journey. Your encouragement means more to me than words can convey. Thank you to my friends and Sakura Girlies (Farah, Izzati, Nadia and Farhana) for always encouraging me and believing in me, even when I doubted myself. Your company has brought much-needed comfort and joy despite the difficulties of this journey.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

3D	-	3-dimensional
AM	-	Additive manufacturing
ANOVA	-	Analysis of Variance
ASTM	-	American Society for Testing and Materials
ATR-FTIR	-	Attenuated total reflection fourier transform infrared spectroscopy
CA	-	Contact angle
CAD	-	Computer-aided design
CO_2	-	Carbon dioxide
ED	-	Energy density
EHT	-	Electron high tension
FDM	-	Fused deposition modeling
ILs	-	Imidazolium-based ionic liquids
ISO	-	International Organization for Standardization
ITO	-	Indium tin oxide
MF	-	Microfiltration
MJF	-	Multi jet fusion
NF	-	Nanofiltration
OCA	-	Oil contact angle
PE	-	Polyethylene
PP	-	Polypropylene
PA-12	-	Polyamide 12

PBF	-	Powder bed fusion
PNIPAAm	-	Poly(N-isopropylacrylamide)
PLSR	-	Partial least squares regression
PSU	-	Polysulfone
RMSECV	-	Root mean square error of cross-validation
RSM	-	Response surface methodology
SEI	-	Secondary electron images
SiO_2	-	Silicone dioxide
SLA	-	Stereolithography
SLS	-	Selective laser sintering
SEM	-	Scanning electron microscope
ToF-SIMS	-	Time-of-flight secondary ion mass spectrometry
UTM	-	Universal testing machine
UF	-	Ultrafiltration
UV	-	Ultraviolet
WCA	-	Water contact angle

LIST OF SYMBOLS

$\circ$	-	Degree
θ	-	Angle
%	-	Percent
°C	-	Degree celsius
σ	-	Tensile strength
ε	-	Tensile strain
μ	-	Micro
η	-	Separation efficiency
ED_A	-	Energy density per unit area
ED_v	-	Energy density by unit volume
ED_T	-	Total energy density
R_a	-	Arithmetic average surface roughness
T_g	-	Glass transition temperature

LIST OF PUBLICATIONS

1. Arbain, N. A., Mohd Zini, N. H., Shikh Anuar, F., Abdollah, M. F.B, & Rosley, M. I. F. (2024). 'Wettability characterization of 3D printed polymer membranes with candle soot coating' *Jurnal Tribologi*, [online] 40, pp.148–163. (SCOPUS Indexed) https://jurnaltribologi.mytribos.org/v40/JT-40-148-163.pdf

2. Arbain, N. A., Mohd Zini, N. H., Shikh Anuar, F. & Abdollah, M. F.B. (2025). 'Wettability tuning of candle soot coated 3D-printed membranes via laser power control' Malaysian Journal of Microscopy. (Paper accepted)

CHAPTER 1

INTRODUCTION

1.1 Background

Oil spills pose a serious threat to the environment, as it can cause ecological damage. In the previous years, seven oil spills had taken place in Asia as reported by Oil Tanker Spill Statistics 2022 (ITOPF, 2023) which two were categorised as large oil spills, that resulted in more than 700 tonnes of oil dumped into the sea. One of the incidents involved the oil ship MT Princess Empress that sunk in February 2023 at the Philippines' Verde Island Passage, where a substantial amount of oil was discharged into the sea as shown in Figure 1.1. The spill had a catastrophic effect on fisheries, tourism and the standard of living for coastal populations, destroying coral reefs, mangroves and marine life. Fishing prohibitions and contaminated waters hampered the local economy and residents experienced health hazards such as respiratory problems and skin rashes.

Oil-water mixes comprise non-miscible and emulsified mixtures in the form of stable-state microoil-water droplets, making oil-water separation challenging. The emulsified oil in water is stable due to the low interfacial tension between the disperse (oil) and the continuous (water) phase (Barambu et al., 2021). Therefore, breaking stable oil-in-water emulsions is critical for ensuring high separation efficiency for emulsified oil-in-water mixtures.

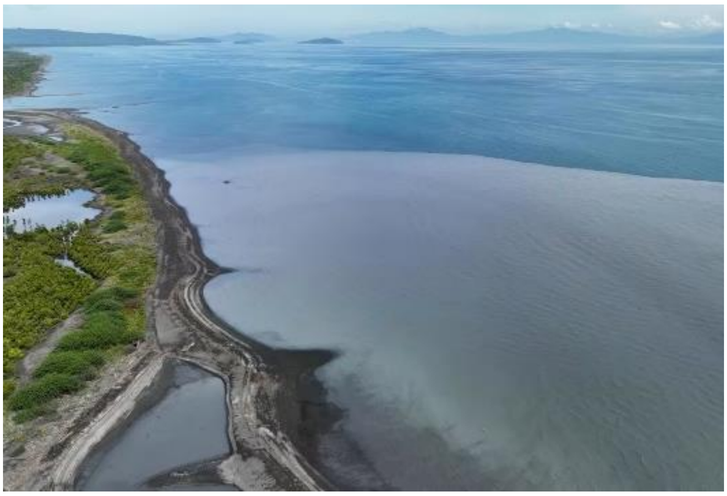

Figure 1.1: Oil spill at Philippines' Verde Island Passage (Board. J., 2023)

Membrane separation has received a lot of attention in recent years compared to other traditional approaches such as gravity separation, hydrocyclone separation and sedimentation due to its high effectiveness for oil-water separation (Thiam et al., 2022). Nowadays, porous materials have been developed for oil-water separation, including mesh-based materials (Gao et al., 2013; Zhang et al., 2019), sponge-based materials (Xia et al., 2018; Kong et al., 2021), foam-based materials (Li et al., 2016; Hailan et al., 2021) and membranes (Rana et al., 2010; Yuan et al., 2017a, Yuan et al., 2017b, 2020). For over a decade, membrane technology has been used for oil spill remediation and oily wastewater treatment due to its high selectivity, stability and economical friendly (Thiam et al., 2022). Almost all types of polymer membranes from rigid microfiltration to flexible reverse osmosis membranes have been fabricated for academic and commercial purposes.

Membrane fabrication can be categorised into conventional and three-dimensional (3D) printing methods. 3D printing is one of the methods to develop structurally viable and impermeable membranes using polymer materials such as polyamide powders to utilise their good mechanical properties. To fully benefit from membrane technology and its applications, the manufacturing process is important since it has a significant impact on both performance and cost (Thiam et al., 2022). The emerging technology of Selective Laser Sintering (SLS) 3D printing has attracted significant interest in both industry and academic researchers due to its capability of fabricating parts which implements a layer-by-layer fabrication technique without any support.

Surface wettability of a membrane is crucial to the separation efficiency of oil-water mixtures. Generally, wetting refers to a liquid's ability to retain contact with a solid surface due to intermolecular interactions. The contact angle of a liquid on a solid surface in the presence of another fluid such as oil, water and chemical liquids is widely used to characterize the condition of wetting. For effective oil removal, membranes must be hydrophobic and superoleophilic, allowing the oil to pass through the membrane while repelling water. However, Yuan et al., (2020) discovered 3D printed polymer membranes provide switchable wettability with hydrophobic and superoleophilic properties in the atmosphere but has the ability to switch into underwater superoleophobic properties when wetted with water; this behaviour allows these printed membranes to be efficiently utilised in oil spill remediation as shown in Figure 1.2.