PREPARATION AND CHARACTERIZATION OF POLYLACTIC ACID MODIFIED POLYVINYLIDENE FLUORIDE HOLLOW FIBER MEMBRANES WITH ENHANCED WATER FLUX AND ANTIFOULING RESISTANCE

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DEDICATION

This thesis is dedicated to my father, who taught me that the best kind of knowledge is to learn by yourself. It is also dedicated to my mother, who taught me that even the most difficult task can be accomplished if it is done one step at a time.

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ABSTRACT

Although ultrafiltration (UF) membranes have gained considerable attention in water separation and purification process, most of the materials used for commercial UF membranes fabrication are not able to degrade/decompose easily and tend to cause severe environmental problem when they are discarded. In view of this, an environmentally friendly hydrophilic polymeric material - polylactic acid (PLA) has been considered in this work, aiming to reduce not only the environmental impacts caused by the existing membranes but also to improve membrane water flux and antifouling resistance. In this study, the effects of PLA quantity and air gap (during spinning process) on the morphology and liquid separation performance of polyvinylidene fluoride (PVDF) hollow fiber membranes were investigated. The membrane properties were characterised using scanning electron microscope, atomic force microscope, Fourier transform infrared spectrometer, tensile tester and contact angle goniometer before filtration experiment was conducted. Results showed that the incorporation of low quantity of PLA (with PLA/PVDF weight ratio of ≤1.0) could significantly improve the membrane water flux from ~30 to 376.7 $L/m^2.h.bar$ without compromising rejection (95–97%). More importantly, the PLA-modified PVDF membranes required a much lower temperature to decompose which minimizes environmental impacts. Owing to the improved surface hydrophilicity (lower water contact angle), the PLA-modified PVDF membranes also exhibited a higher flux recovery rate than that of pure PVDF membrane, revealing the improved antifouling resistance against bovine serum albumin. The findings of this work demonstrated that biodegradable PLA has the potential to modify the characteristics of UF membranes, leading to an enhanced water treatment process.

ABSTRAK

Walaupun membran ultrafiltrasi (UF) telah banyak mendapat perhatian dalam proses pemisahan dan penulenan air, kebanyakan bahan yang digunakan untuk fabrikasi membran UF komersial tidak dapat diuraikan dengan mudah dan cenderung menyebabkan masalah alam sekitar yang teruk apabila dibuang. Berdasarkan pandangan ini, bahan polimer hidrofilik yang mesra alam - asid polilaktik (PLA) telah dipertimbangkan dalam kerja ini, bertujuan untuk mengurangkan bukan sahaja kesan alam sekitar yang disebabkan oleh membran yang sedia ada tetapi juga untuk memperbaiki fluks air membran dan rintangan antikotoran. Dalam kajian ini, kesan kuantiti PLA dan sela udara (semasa proses berputar) pada morfologi dan prestasi pemisahan cecair membran gentian berongga polivinilidena fluorida (PVDF) telah disiasat. Sifat-sifat membran dicirikan dengan menggunakan mikroskop elektron imbasan, mikroskop daya atomik, spektrometer infra-merah jelmaan fourier, penguji tegangan dan goniometer sudut sentuhan sebelum filtrasi dijalankan. Keputusan menunjukkan bahawa penggabungan kuantiti kecil PLA (dengan nisbah berat PLA / PVDF $\leq$1.0) dapat meningkatkan fluks air membran dari ~ 30 hingga 376.7 $L/m^2.h.bar$ tanpa menjejaskan penolakan (95-97%). Lebih penting lagi, membran PLA-terubahsuai PVDF memerlukan suhu yang lebih rendah untuk mengurai yang mana meminimumkan kesan alam sekitar. Oleh kerana peningkatan hidrofilik permukaan yang lebih baik (sudut sentuhan air yang lebih rendah), membran PLA-terubahsuai PVDF juga mempamerkan kadar perolehan fluks yang lebih tinggi daripada membran PVDF tulen, mendedahkan rintangan antikotoran yang lebih baik terhadap albumin serum lembu. Penemuan kerja ini menunjukkan bahawa PLA boleh biodegradasi berpotensi untuk digunakan untuk mengubah ciri-ciri membran UF, yang membawa kepada peningkatan proses rawatan air.

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LIST OF ABBREVIATIONS

AFM	-	Atomic Force Microscopy
BSA	-	Bovine Serum Albumin
COD	-	Chemical Oxygen Demand
DBPs	-	Disinfection by Products
DER	-	Dope Extrusion Rate
DOM	-	Dissolved Organic Matter
DON	-	Dissolved Organic Nitrogen
EG	-	Ethylene Glycol
FRR	-	Flux Recovery Rate
FTIR	-	Fourier Transform Infrared
GC-MS	-	Gas Chromatography–Mass Spectrometry
HA	-	Humic Acid
HAAs	-	Haloacetic Acids
HANs	-	Halocetonitriles
HPLC	-	High Performance Liquid Chromatography
ID	-	Inner Diameter
MF	-	Microfiltration
MW	-	Molecular Weight
MWCO	-	Molecular Weight Cut Off
NCI	-	National Cancer Institute
NF	-	Nanofiltration
NIPS	-	Nonsolvent Induce Phase Separation
NMP	-	N-Methyl-Pyrrolidone
NOM	-	Natural Organic Matter
OD	-	Outer Diameter
PAN	-	Polyacrylonitrile
PD	-	Polydopamine
PE	-	Polyethylene
PEG	-	Polyethylene Glycol
PEI	-	Polyetherimide

PES	-	Polyethersulfone
PHEMA	-	Poly(2-hydro xyethyl methacrylate)
PI	-	Polyimide
PLA	-	Polylactic Acid
PP	-	Polypropylene
PPO	-	Polypropylene Oxide
PSF	-	Polysulfone
PTFE	-	Polyetrafluoroethylene
PU	-	Poly(urethane)
PVDF	-	Polyvinylidene Fluoride
PVP	-	Polyvinylpyrolidone
PWF	-	Pure Water Flux
PWP	-	Pure Water Permeation
RO	-	Reverse Osmosis
SEM	-	Scanning Electron Microscopy
TGA	-	Thermogravimetric Analysis
THMs	-	Trihalomethanes
TIPS	-	Thermal Induced Phase Separation
TOC	-	Total Organic Carbon
UF	-	Ultrafiltration
US	-	United States
USEPA	-	United State Environmental Protection Agency
UV-Vis	-	Ultraviolet Visible
WTP	-	Water Treatment Plant
XA	-	Xantham Gum

LIST OF SYMBOLS

β	-	Beta
℃	-	Celcius
℃/min	-	Celcius Per Minute
ρ	-	Density
l	-	Thickness
$<$	-	Less Than
$>$	-	More Than
μm	-	Micrometer
μL	-	Microlitre
ΔP	-	Operating Pressure
%	-	Percent
ε	-	Porosity
A	-	Effective area
$(C_3H_4O_2)n$	-	Polylactic acid
CO_2	-	Carbon Dioxide
C_P	-	Concentration of permeate
C_f	-	Concentration of feed
cm	-	centimetre
cP	-	Centipoises
Da	-	Dalton
g	-	Gram
g/mol	-	Gram Per Mole
H_2O	-	Water
h	-	Hour
J_W	-	Flux Pure Water
K	-	Kelvin
L	-	Litre
L/min	-	Litre Per Minute
m	-	Mass of Hollow Fiber Membrane
ml	-	Millilitre

ml/min	-	Millilitre Per Minute
mm	-	Millimetre
mm/min	-	Millimetre Per Minute
mg	-	Milligram
mg/L	-	Milligram Per Litre
min	-	Minute
MPa	-	Mega Pascal
m^2	-	Meter Square
m^3/s	-	Meter Cube Per Second
n	-	Number of Unit
nm	-	Nanometre
n	-	Water Viscosity
ppm	-	Part Per Millions
psig	-	Pound Per Square in Gauge
R	-	Rejection
r	-	Mean Pore Radius
t	-	Filtration Time
v	-	Volume
wt.%	-	Percent Weight

CHAPTER 1

INTRODUCTION

1.1 Research Background

Drinking water is essential to human life. Drinking water resources are mainly from rivers or water bodies that enter water treatment plant (WTP) before distribution. WTPs are designed to treat contaminants that exist in water bodies such as natural organic matter (NOM) and ammonia. These compounds are found in the water body or soil in the upstream of water bodies. Mostly they are from plantation or aquatic plants that flow in water bodies by precipitation, underground flow and flood.

However, there are some problems in existing WTP where the presence of free chlorine content that is used as a disinfectant is found to react with residual NOMs. This reaction process has been found to have a tendency to form disinfection by-products (DBPs) such as trihalomethanes, haloacetic acids and other halogenatic organics. DBPs are carcinogens and direct exposure may lead to cancers, miscarriages and nervous system complications [1–4].

The increasing soil erosion and flood from unplanned construction and rapid economic development on the other hand had also increased the amount of NOMs, causing problems to the existing WTP [5]. Certainly, up to date, some of the existing WTPs are not able to eliminate these DBPs to a satisfactory level, thus an advanced treatment process is needed [6].

At present, the development of membrane technologies has attracted attention in the field of water treatment process. Ultrafiltration (UF) membranes in particular are used for removal of large particles. Although UF membranes have gained considerable attention in water separation and purification process, most of the materials used for commercial UF membranes fabrication are not able to degrade/ decompose easily and tend to cause severe environmental problems when they are discarded. In view of this, an environmentally friendly hydrophilic polymeric material - polylactic acid (PLA) has been considered in this work, aiming to reduce not only the environmental impacts caused by the existing membranes but also to improve membrane water flux and antifouling resistance.

1.2 Problem Statements

Natural organic matter (NOM) found in the water environment is ubiquitous and chemically complex organic compound. A study showed that NOM is one of the main pollutants in drinking water production mainly because of the generation of disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) when NOM interacts with chlorine in water [7]. Direct exposure to the DBPs can cause cancers, miscarriages and nervous system complications [1–3]. Therefore, effective removal of NOM is a significant and challenging research topic in the current development of water purification. Humic acid (HA) is the major species in NOM and accounts for 50–90% of the total freshwater organic matters [2,3]. Scientists always considered HA as a model compound in the studies of water treatment process using membrane-based technology [1–3].

UF membrane process receives a wider attention compared to other membrane technologies such as reverse osmosis (RO), nanofiltration (NF) and microfiltration (MF) due to its good balance between water flux and rejections against colloids, macromolecules and suspended particles [8–12]. One of the main polymeric materials that is widely used for the commercial UF membranes fabrication is polyvinylidene fluoride (PVDF). Compared to polysulfone (PSF) and polyethersulfone (PES), PVDF offers greater thermal stability and mechanical property as well as outstanding chemical and oxidation resistance [8,11,13–15]. However, PVDF is not made of biodegradable material and requires longer time to achieve complete degradation upon dump site disposal [16]. In view of this, it is a great significance if a novel membrane material is able to be developed using biodegradable polymer.

Biodegradable materials can be broken down by microorganisms, producing harmless compounds for nature. These kinds of materials have already been widely used in food packaging, daily necessities, containers, and medical instruments [13,16]. Among the biodegradable materials, polylactic acid (PLA, formula: $(C_3H_4O_2)_n$) - a polymer produced from natural sources like corn is widely reported in the literature [13,16]. Statistics from the SCOPUS reveal that there are more than 3,000 papers reporting the use of PLA for various applications over the past 10 years (2007–2018). PLA is possibly degraded in soil, compost or human body. In a composting environment the PLA is hydrolyzed into smaller molecules, e.g., oligomers, dimers and monomers after 45–60 days at 50–60°C. These smaller molecules are then degraded into CO_2 and H_2O by microorganisms in compost [17,18].

Incorporation of hydrophilic biopolymer like xanthan gum (XA) into PES membrane had been previously reported for HA removal. The modified PES membrane was reported to exhibit enhanced water permeability (24.8 L/m^2.h.bar) with HA rejection above 80% [19]. Similar to XA, PLA which is also a hydrophilic biopolymer has potential to be used for membrane modification. Previous studies have investigated the potential of using PLA and its derivatives for membrane fabrication. For instance, PLA/poly(lactic acid)-block-poly(2-hydroxyethyl methacrylate) (PLA–PHEMA) membranes with high PLA–PHEMA contents exhibited enhanced hydrophilicity, water permeability and anti-fouling resistance [20]. Upon addition of 15 wt% PLA–PHEMA, the water flux of the resultant membrane was reported to be about 236 L/m^2.h.bar with bovine serum albumin (BSA) clearance as low as 0.31 mL/min [20]. Shen *et al*. [21] on the other hand reported that the incorporation of PLA-based copolymer could improve the hydrophilicity of membrane by decreasing water contact angle from around 80° to 60°, leading to enhanced water permeability and greater antifouling properties.

Previous studies have shown that hydrophilic PLA could be used to modify the properties of PSF nanofiber membrane with respect to pore dimension [22] and oil sorption capacity [23], but using PLA as additive for asymmetric UF membrane fabrication has yet to be reported in the literature. It must be pointed out that the membranes made of pure PLA are not likely to be used for pressure-driven process owing to the poor mechanical properties of PLA film [16-17]. Thus, PLA can only be considered as additive to modify the existing membranes.

In view of this, the main objective of this work was to modify PVDF-based hollow fiber membrane using biodegradable PLA, aiming to produce environmentally friendly membranes with enhanced water flux and antifouling properties for water treatment process.

1.3 Research Objective

Based on the above-mentioned problems, the main objectives of this work were:

1) To characterize PVDF/PLA blend hollow fiber membranes with different properties by varying PLA:PVDF ratio in dope solution and air gap during spinning process.
2) To evaluate filtration performance of PVDF/PLA blend membrane as advanced treatment process in purifying water source containing organic foulants.

1.4 Scopes of the Study

In order to achieve the objectives of this research, the following scopes are outlined:

1) Preparing a spinning solution made of different ratio of PLA/PVDF ratio (0, 0.3, 1, 2 and 3) with the presence of 5 wt% polyvinylpyrolidone (PVP).
2) Fabricating hollow fiber membrane via spinning technique by varying air gap from zero to 8 cm using the dope solutions prepared.
3) Characterizing membrane properties using Fourier transform infrared (FTIR), scanning electron microscopy (SEM), contact angle measurement, atomic force microscope (AFM) analysis, thermogravimetric analysis (TGA), tensile machine and goniometer contact angle.
4) Evaluating PLA/PVDF hollow fiber membrane performance with respect to pure water flux, humic acid rejection and antifouling properties using bovine serum albumin (BSA) as foulant.
5) Investigating PLA leaching from the PVDF membranes by analyzing the water solution using total organic carbon (TOC) analyzer
6) Assessing performance of PLA/PVDF hollow fiber membrane towards river water treatment by measuring river water flux and reduction of turbidity, conductivity and chemical oxygen demand (COD).

1.5 Significance of Study

The significance of the current research was to develop a more environmentally friendly UF membrane for water application using biodegradable polymer - PLA. Besides being environmentally friendly, the PVDF-based hollow fiber membrane embedded with PLA as secondary polymer also exhibited greater water flux without compromising HA rejection. More importantly, the PLA-modified PVDF membranes required much lower temperature to decompose which minimizes environmental impacts. Owing to the improved surface hydrophilicity (lower water contact angle), the PLA-modified PVDF membranes also exhibited higher flux recovery rate than that of pure PVDF membrane, revealing the improved antifouling resistance against bovine serum albumin.

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LIST OF PUBLICATION

1. **N.S. Aseri**, W.J. Lau, P.S. Goh, H. Hasbullah, N.H. Othman, A.F. Ismail, Preparation and characterization of polylactic acid-modified polyvinylidene fluoride hollow fiber membranes with enhanced water flux and antifouling resistance, *J. Water Process Eng*. 32 (2019) 100912. (Impact factor: 3.173)