

Improving the Performance of Cellulose Acetate Reverse Osmosis Membranes

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Contents

SUMMARY	VI
DECLARATION	VIII
ACKNOWLEDGEMENTS	IX
LIST OF FIGURES	X
LIST OF TABLES	XIV
ABBREVIATIONS	XV
1 CHAPTER ONE – INTRODUCTION	1
1.1 BACKGROUND	2
1.1.1 Fresh water scarcity	2
1.1.2 Desalination	3
1.1.3 Thermal Distillation	4
1.1.4 Membrane-Based Desalination	4
1.1.4.1 Porous Membranes	4
1.1.4.2 Non-Porous Membranes	5
1.1.5 Reverse Osmosis Desalination Plant Set-Up	7
1.1.6 Critical RO Membrane Properties	9
1.1.6.1 Water Flux	9
1.1.6.2 Salt Rejection	10
1.1.7 Membrane Materials	11
1.1.7.1 Polyamide Composites	11
1.1.7.2 Cellulose Acetate (CA)	12
1.1.8 RO Membrane Limiting Factors	16
1.1.8.1 Concentration Polarisation	17
1.1.8.2 Membrane Compaction	18
1.1.8.3 Membrane Deterioration	18
1.1.8.4 Membrane Fouling	19

1.1.8.5 Biofouling Tests	22
1.1.8.6 Mechanical Detachment of Biofoulants	22
1.1.8.7 Organism Killing and Inactivation	22
1.1.8.8. Membrane Surface Modification	23
1.1.8.9 Nanocomposite Membranes	24
1.2 AIMS OF THIS THESIS	28
1.3 THESIS OUTLINE	29
2 CHAPTER TWO – MATERIALS AND METHODS	40
2.1 MATERIAL SOURCES – GENERAL SOLVENTS AND REAGENTS	41
2.2 MATERIALS SYNTHESIS	41
2.2.1 Synthesis of Tris[(2-pyridyl)methyl]amine (TPMA)	41
2.2.2 Synthesis of bromo-initiator-modified CAMs	42
2.2.3 2-hydroxyethyl methacrylate (HEMA) Purification	43
2.2.4 Surface grafting of HEMA polymers from CA membrane using SI-ARGET ATRP	43
2.2.5 Cell-fixing Solutions	44
2.2.6 Synthesis of cellulose acetate-grafted POSS	44
2.2.7 Membrane Casting	45
2.3 INSTRUMENTAL ANALYSIS AND CHARACTERISATION PROCEDURES	47
2.3.1 Delamination of CA from polyester backing	47
2.3.2 Nuclear magnetic Resonance (NMR)	47
2.3.3 Attenuated Total Reflection Fourier Transform InfraRed Analysis (ATR-FTIR)	47
2.3.4 X-ray PhotoSpectroscopy (XPS)	48
2.3.5 ThermoGravimetric Analysis (TGA)	49
2.3.6 Graft Density	49
2.3.7 Scanning Electron Microscopy (SEM) and Energy Dispersive	49

X-ray Microanalysis (EDAX)	
2.3.8 Atomic Force Microscopy (AFM)	50
2.3.9 Water Contact Angle (WCA)	50
2.3.10 Water uptake Experiments	50
2.3.11 Stirred-Cell	51
2.3.12 Dynamic Mechanical Analysis (DMA)	53
2.3.13 Static Aquarium Tests	53
2.3.13.1 Cell Fixing	54
2.3.13.2 Cell Counting	55
2.3.14 pH Resistance Tests	55
2.3.15 Membrane Hydrolysis	56
2.4 CALCULATIONS	56
2.4.1 POSS Content of Nanocomposites	56
2.4.2 Biofouling Resistance Calculations	58
2.4.3 Error Calculations	58
3 CHAPTER 3 – SYNTHESIS OF PHEMA-MODIFIED	61
CELLULOSE ACETATE MEMBRANES	
3.1 INTRODUCTION	62
3.2 RESULTS AND DISCUSSION	66
3.2.1 Synthesis of bromo-initiator modified CA membranes	68
3.2.1.1 ATR-FTIR Analysis	69
3.2.1.2 ¹ H NMR Analysis	72
3.2.1.3 XPS Analysis	73
3.2.2 Polymer Grafting	75
3.2.2.1 Thermal Analysis	78
3.2.2.2 Reaction Kinetics	82
3.2.2.3 Graft Density	83
3.2.2.4 ATR-FTIR Analysis	85
3.3 CONCLUSIONS	87

4	CHAPTER FOUR – THE PERFORMANCE AND BIOFOULING RESISTANCE OF PHEMA-MODIFIED CELLULOSE ACETATE MEMBRANES	92
4.1	INTRODUCTION	93
4.2	RESULTS AND DISCUSSION	94
4.2.1	Changes in morphology due to membrane compaction	94
4.2.1.1	SEM Analysis	95
4.2.1.2	AFM Analysis	99
4.2.2	Wettability Studies	100
4.2.2.1	Water Contact Angles	100
4.2.2.2	Water Uptake	101
4.2.3	Membrane Filtration Properties	103
4.2.3.1	Effect of polymerisation time	105
4.2.3.2	Effect of initial monomer volume	106
4.2.4	Changes in Hydrolysis due to Membrane Modification	108
4.2.5	Biofouling Resistance of Modified Membranes	110
4.3	CONCLUSIONS	116
5	CHAPTER FIVE – A STUDY INTO THE EFFECTS OF POSS NANOPARTICLES ON CELLULOSE ACETATE MEMBRANES	120
5.1	INTRODUCTION	121
5.2	RESULTS AND DISCUSSION	124
5.2.1	The Synthesis of a CA-POSS Additive	124
5.2.2	CA-POSS Characterisation	127
5.2.2.1	ATR-FTIR Analysis	127
5.2.2.2	Thermal Analysis	129
5.2.3	Nanocomposite Membrane Casting	130
5.2.4	Particle Dispersion in CA Membranes	132
5.2.4.1	ATR-FTIR Analysis	132
5.2.4.2	SEM and EDAX Analysis	134

5.2.5 Changes in RO membrane flux and rejection due to compaction	138
5.2.6 Changes in membrane morphology due to compaction	139
5.2.7 Nanocomposite Mechanical Strength	142
5.3 CONCLUSIONS	145
6 CHAPTER SIX – CONCLUSIONS AND RECOMMENDATIONS	150
6.1 CONCLUSIONS	151
6.1.1 Surface modification of CA RO membrane using commercially attractive radical polymerisation techniques	151
6.1.2 Optimisation of reaction conditions to achieve a range of polymer graft- densities	152
6.1.3 Biofouling resistance tests that more closely imitate actual fouling conditions	152
6.1.4 Characterisation of the modified membranes to determine ideal outcome: prevention of biofouling of the membrane whilst maintaining water flux and salt rejection properties	153
6.1.5 Synthesis of CA-anchored nanoparticles	154
6.1.6 Inclusion of anchored and unanchored nanoparticles in the CA matrix at different weight % to determine the effect of anchoring the nanoparticles on their dispersion in the membrane matrix	154
6.1.7 Investigation of the effect of nanoparticle inclusion on the filtration properties and mechanical strength of the membranes	155
6.2 RECOMMENDATIONS	155

Summary

Reverse osmosis membrane desalination technology has come a long way since the Loeb and Sourirajan type membranes of the 1960s. Advances in production and engineering processes have overcome many inherent system limitations, however some remain. Truly biofouling-resistant membranes are yet to be realised, and membrane compaction remains an issue.

In this thesis methods for mitigating these two membrane limiting factors have been investigated; polymeric modification and nanoparticle inclusion.

In the first part of the project, a detailed study of the polymerisation of poly(2-hydroxyethyl methacrylate) via activators regenerated by electron transfer atom transfer radical polymerisation was undertaken. Conditions were chosen to be commercially attractive. The modified membranes were studied with fourier transform infrared spectroscopy (FTIR), x-ray photospectroscopy, nuclear magnetic resonance, and thermogravimetric analysis. Results showed that by varying the initial monomer volume and/or the polymerisation reaction time it was possible to create a series of modified membranes with a range of polymer graft densities, thus indicating the livingness of the polymerisation reaction.

In order to evaluate the ideal graft density, the properties of the modified membranes were further investigated. The polymer coating was clearly visible using scanning electron microscopy and an increase in surface roughness was observed with atomic force microscopy, in both cases confirming the increase in polymer graft density. Water contact angle studies explored the relationship between surface morphology and wettability, indicating conformational changes in the polymer. Hydrolysis had little effect on modified membrane filtration properties when soaked at pHs outside the recommended range for pristine cellulose acetate membrane (CAM).

Unique aquarium biofouling tests were performed, and showed a decrease in biofouling for the modified membranes. Stirred-cell experiments were used to evaluate the filtration properties of the modified membranes. From the results it was possible to determine optimum conditions for membrane modification to obtain a polymer graft density with maximum biofouling resistance and minimum loss of filtration properties.

In the second part of the project, aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS) was investigated as a nanocomposite additive. Since nanoparticle agglomeration and leaching were identified as issues in nanocomposite materials, an anchored nanoparticle was synthesised using isocyanate chemistry to attach POSS to cellulose acetate (CA). This anchored nanoparticle was compared to un-anchored POSS as an additive in CA membrane casting solutions at loadings of 0.5, 1.0 or 5.0 wt%. FTIR and energy dispersive X-ray microanalysis showed the anchored nanoparticle to have better dispersion in the resulting membranes. The nanocomposite membranes showed greater flux of water and salt than an unmodified CA control. Membrane compaction was mitigated at low nanoparticle loadings. Dynamic Mechanical Analysis (DMA) results suggest POSS has a plasticisation effect on the CA matrix.

Declaration

'I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.'

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(C.H.Worthley)

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List of Figures

Figure 1.1 Relative amounts of Earth's water resources	2
Figure 1.2 Forward Osmosis / Reverse Osmosis	7
Figure 1.3 Schematic diagram showing the basic setup of a reverse osmosis desalination plant	7
Figure 1.4 Chemical structure of polyamide repeat unit	11
Figure 1.5 Representation of a cross-section of a TFC polyamide membrane showing the thickness of different layers	12
Figure 1.6 Chemical structure of the cellulose repeat unit	13
Figure 1.7 Formation of cellulose acetate from cellulose and acetic anhydride	13
Figure 1.8 Power consumption of RO processes from 1970 to 2008	17
Figure 1.9 Oxidation of cellulose acetate	19
Figure 1.10 Hydrolysis of cellulose acetate	19
Figure 1.11 The three phases of biofouling	21
Figure 1.12 Zeolite structures (a) A-type and (b) MFI-type	25
Figure 1.13 Schematic of the ideal aligned CNT nanocomposite membrane	27
Figure 2.1 Casting solutions for cellulose acetate membranes with nanofiller	46
Figure 2.2 Setup for membrane casting with doctor's blade and glass plate	46
Figure 2.3 Schematic representation of the stirred-cell apparatus	51
Figure 2.4 Calibration curve for the conversion of NaCl conductivity to concentration	52
Figure 2.5 Tension film clamp for the DMA apparatus	53
Figure 2.6 Schematic representation of the seawater aquarium setup and cell fixing	54

Figure 2.7 Schematic representation of the areas imaged for bacterial cell counting	55
Figure 3.1 Structure of the 2-hydroxyethyl methacrylate monomer	62
Figure 3.2 Proposed mechanism of ATRP	63
Figure 3.3 Proposed mechanism of ARGET ATRP	65
Figure 3.4 TGA and DTG curve overlays of pristine CAM and CAM cleaned with water or diethyl ether	67
Figure 3.5 Reaction scheme for surface modification of CAM	68
Figure 3.6 ATR-FTIR comparing the carboxylate to pyranose ring peak ratios for CAM-Br and pristine CAM	70
Figure 3.7 ¹ H-NMR of CAM-Br	72
Figure 3.8 XPS survey spectrum of CAM-Br, with inset showing high resolution Br3d scan	73
Figure 3.9 High resolution C1s scan of CAM-Br	74
Figure 3.10 TGA and DTG curve overlays of the HEMA monomer and homopolymer	78
Figure 3.11 TGA and DTG curve overlays of pristine CAM and CAM-g-pHEMA	79
Figure 3.12 TGA and DTG curve overlays of membranes with varying PRTs	81
Figure 3.13 Kinetic plot for the ARGET ATRP of HEMA with (a) varying PRT, and (b) varying IMC	82
Figure 3.14 Graft density for all CAM-g-pHEMA	84
Figure 3.15 ATR-FTIR in the range 800-1500 cm ⁻¹ for pristine CAM, CAM-g-pHEMA with increasing graft density, and pHEMA	85
Figure 4.1 Surface morphology and cross-sectional images of pristine CAM and low graft density modified membranes	96
Figure 4.2 Surface morphology and cross-sectional images of high graft density modified membranes	97

Figure 4.3 Surface-grafted polymers in the mushroom regime and low density, and the brush regime at high density	98
Figure 4.4 AFM image of the surfaces of pristine CAM and modified membranes	99
Figure 4.5 Sessile drop contact angles for pristine CAM and modified membranes	101
Figure 4.6 Proposed model for the reorientation of pHEMA during dehydration	103
Figure 4.7 Stirred-cell results for pristine CAM with pure water and 2000ppm NaCl solution at 15.5 bar and 26.0 bar	104
Figure 4.8 The effect of polymerisation time on CAM-g-pHEMA salt water flux	105
Figure 4.9 The effect of monomer concentration on CAM-g-pHEMA salt water flux	107
Figure 4.10 ATR-FTIR in the range 700-220 cm^{-1} , comparing pristine CAM soaked in different pH buffers to unsoaked CAM and fully hydrolysed CAM	109
Figure 4.11 Relative salt rejection for membranes after exposure to extreme pH	110
Figure 4.12 Bacterial varieties commonly observed during static aquarium testing, shown on the surface of pristine CAM	111
Figure 4.13 Typical SEM images after static aquarium tests for pristine CAM and CAM-g-pHEMA with increasing graft density	113
Figure 5.1 The Si-O cage structure of POSS nanoparticles	122
Figure 5.2 Synthetic method for preparation of CA-POSS	126
Figure 5.3 Absorbance spectra of aminopropylisobutyl POSS, POSS-TDI, CA-POSS and cellulose acetate	127
Figure 5.4 TGA and DTG thermograms of cellulose acetate and CA-POSS	129
Figure 5.5 ATR-FTIR of CA control membrane, CA-POSS additive, and	133

nanocomposite containing 5wt% CA-POSS	
Figure 5.6 SEM and EDAX results for different areas on cast CA	135
Figure 5.7 SEM and EDAX results for different areas on the cast POSS 1wt% nanocomposite membrane	136
Figure 5.8 SEM and EDAX results for different areas on the cast CA- POSS 1wt% nanocomposite membrane	137
Figure 5.9 Stirred-cell data showing 2000ppm NaCl solution flux over time for cast membranes with varying amounts of incorporated nanoparticles	138
Figure 5.10 Cross-sectional SEM images of unmodified CA membrane before and after compaction at 1000 KPa	140
Figure 5.11 Cross-sectional SEM images of nanocomposite membrane CA-POSS .5wt% before and after compaction at 1000 KPa	140
Figure 5.12 Storage modulus for POSS composites and CA control	143
Figure 5.13 Storage modulus for CA-POSS nanocomposites and CA control	144

List of Tables

Table 1.1 Feedwater characterisation by salt content	3
Table 1.2 Membrane filtration spectrum	5
Table 1.3 Comparison of TFC and CA membrane material properties	15
Table 2.1 Summary of spectral collection parameters used in ATR-FTIR experiments	48
Table 2.2 pH buffer solutions	56
Table 2.3 Calculations of the mass, mol % and wt% of CA-POSS and POSS additives, and CA in cast membranes	57
Table 3.1 The ratio of carboxylate to pyranose ring FTIR peak intensities with increasing initiator attachment reaction time	71
Table 3.2 Elemental surface composition of CAM and CAM-Br from XPS	74
Table 3.3 Key for pristine CAM and CAM-g-pHEMA membrane labels and reaction conditions	84
Table 3.4 Spectral band assignments comparing pristine CAM, CAM-g-pHEMA and pHEMA	86
Table 4.1 Water Uptake data for pristine CAM and CAM-g-PHEMA	102
Table 4.2 Summary of characterisation results of pristine CAM and CAM-g-pHEMA membranes with increasing graft density	115
Table 5.1 Spectral band assignments comparing POSS, POSS-TDI and CA-POSS	128
Table 5.2 Nanocomposite membrane casting variables and conditions	131
Table 5.3 Membrane casting solution formulations	132
Table 5.4 Relative peak intensities for nanocomposite membranes	134
Table 5.5 Compaction data for nanocomposite membranes	141

Abbreviations

AFM	Atomic force microscopy
AMPSA	2-acrylamido-2-methyl-1-propanesulfonic acid
APTES	3-aminopropyltriethoxysilane
ARGET	Activators regenerated by electron transfer
ATR	Attenuated total reflectance
ATRP	Atom transfer radical polymerisation
BiBBr	2-bromoisobutyryl bromide
BSA	Bovine serum albumin
CA	Cellulose acetate
CA-POSS	POSS-modified cellulose acetate
CAM(s)	Cellulose acetate membrane(s)
CAM-Br	Bromoinitiator-modified cellulose acetate
CAM-g-pHEMA	Cellulose acetate membrane grafted with pHEMA
CDCl ₃	Deuterated chloroform
D ₂ O	Deuterated water
DMA	Dynamic mechanical analysis
DMAP	4-dimethylaminopyridine
DMF	Dimethyl formamide
DS	Degree of substitution
DTG	First derivative of the thermogravimetric curve
<i>E.coli</i>	Escherichia coli
EBiB	Ethyl 2-bromoisobutyryl bromide
EDAX	Energy dispersive X-ray microanalysis

EPS	Extracellular polymeric substances
FO	Forward osmosis
FTIR	Fourier transform infrared
HBr	Hydrobromic acid
HEMA	2-hydroxyethyl methacrylate
IMC	Initial monomer concentration
IMV	Initial monomer volume
KBr	Potassium bromide
Me6TREN	tris[2-(dimethylamino)ethyl]amine
MED	Multiple effect distillation
MeOH	Methanol
MF	Microfiltration
MMM	Mixed-matrix membrane
MgSO ₄	Magnesium sulfate
MSF	Multi-stage flash distillation
MWCNT	Multi-walled carbon nanotube
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NF	Nanofiltration
NMR	Nuclear magnetic resonance
OEG	Oligo(ethylene glycol)
OGMA	Polyglycidyl methacrylate
OH	Hydroxyl group
PC	Phosphorylcholine
PEG	Poly(ethylene glycol)
PEGMA	polyethylene glycol methacrylate
PES	Polyethersulfone

pHEMA	Poly(2-hydroxyethyl methacrylate)
PMA	Polymethacrylate
PMDETA	<i>N,N,N',N',N''</i> -pentamethyldiethylenetriamine
PMMA	Polymethyl methacrylate
POSS	Aminopropylisobutyl polyhedral oligomeric silsesquioxane
POSS-TDI	TDI-modified POSS
ppm	Parts per million
PRT	Polymerisation reaction time
PRT _{xx} IMV _x	pHEMA-modified CA membrane with PRT of xx minutes and IMV of x mL.
PVF	Poly(vinylidene fluoride)
qDMAEM	quaternized 2-(dimethylamino)ethyl methacrylate
RO	Reverse Osmosis
SEM	Scanning electron microscopy
SI	Surface initiated
SQRT	Square root
SR	Salt rejection
STDEV	Standard deviation
TDI	Toluene-2, 4-diisocyanate
TDS	Total dissolved solids
TEA	Triethylamine
TFC	Thin film composite
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TiO ₂	Titania
TPMA	Tris[(2-pyridyl)methyl]amine

UF	Ultrafiltration
UV	Ultraviolet
WCA	Water contact angle
wt%	Weight percent
XPS	X-ray photospectroscopy