Improving the Performance of Cellulose Acetate Reverse Osmosis Membranes

Clare H. Worthley, BSc. Nanotechnology (Hons)

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Dr Stephen Clarke
Dr Milena Ginic-Markovic
Dr Kristina Constantopoulos

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Summary

Reverse osmosis membrane desalination technology has come a long way since the Loeb and Souririjan 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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Personal thanks for their love and support, always, to my parents and parents-in-law, and my husband, Nick, to whom I dedicate this thesis.

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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	Celluloase acetate membrane grafted with pHEMA
$CDCl_3$	Deuterated chloroform
D_2O	Deuterated water
DMA	Dynamic mechanical analysis
DMAP	4-dimethylaminopyridine
DMF	Dimethyl formamide
DS	Degree of substitution
DTG	First derivative of the thermogravimetric curve
E.coli	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	*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine
PMMA	Polymethyl methacrylate
POSS	Aminopropylisobutyl polyhedral oligomeric silsesquioxane
POSS-TDI	TDI-modified POSS
ppm	Parts per million
PRT	Polymerisation reaction time
PRTxxIMVx	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