MEMBRANE DEVELOPMENT AND FABRICATION FOR REVERSE OSMOSIS AND ULTRAFILTRATION

PARTS 1 & 2

Report to the
Water Research Commission

by

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FINAL REPORT TO THE
WATER RESEARCH COMMISSION

BY THE
INSTITUTE FOR POLYMER SCIENCE
UNIVERSITY OF STELLENBOSCH

PART 1:
EXECUTIVE SUMMARY TO FINAL REPORT

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THE REPORT IS PRESENTED IN FOUR PARTS:

PART 1: EXECUTIVE SUMMARY TO THE FINAL REPORT
EP JACOBS and RD SANDERSON

PART 2: STATISTICAL AND NUMERICAL TECHNIQUES IN THE OPTIMIZATION OF MEMBRANE FABRICATION VARIABLES
EP JACOBS and RD SANDERSON

PART 3: THE CHEMISTRY OF POLY-2-VINYLIMIDAZOLINE REVERSE OSMOSIS MEMBRANES
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PART 4: TECHNOLOGY TRANSFER:
THE DEVELOPMENT OF TUBULAR UF TECHNOLOGY FOR INDUSTRIAL USE
(CLASSIFIED - NOT AVAILABLE FOR DISTRIBUTION)
NKH STROHWALD, EP JACOBS and RD SANDERSON

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MEMBRANE DEVELOPMENT AND FABRICATION FOR REVERSE OSMOSIS AND ULTRAFILTRATION

INTRODUCTION

The purpose of this document is to highlight some of the research topics that received attention during the period under discussion, and how they affected progress towards the development of tubular thin-film composite (TFC) and ultrafiltration (UF) membrane fabrication technology. These findings will be discussed in detail in Parts 2, 3 and 4 of the accompanying documents.

The more pertinent topics are summarized as follows:

1. The bond strength between the poly(bisphenol-A sulphone) (PS) membrane (used either as UF membrane or as support for TFC membranes) and the support fabric was regarded as insufficient to ensure compatibility with the Membratek module design. The net result was that although no membranes failed during laboratory evaluation of single membranes, the membranes failed repeatedly once housed inside Membratek modules.

   After a study of flat-sheet membranes during which the effects of casting solution and quench-medium composition on the ultimate membrane/fabric bond-strength were investigated, this problem was solved. The modified casting-solution system which was developed from that study ensures the fabrication of membranes which adhere extremely well to the support fabric.

   A consequence of solving the problem was that poly(ether sulphone) (PES) UF-membrane technology became available to Bintech. Since then Membratek has proved by numerous bench and pilot plant UF studies that the PES UF membrane and epoxy-end module systems are completely compatible and that the membranes operate reliably.

2. The conductivity-rejection and waterpermeation rates of the TFC RO membranes fabricated on the newly developed PES-type support membranes were not equal to those obtained with the PS support membranes used earlier.

   TFC membrane performances were brought to the levels of earlier values after further modifications had been made to the support-membrane fabrication conditions. These alterations were made on the basis of the results of a statistically planned experiment conducted on nine support membrane fabrication variables.

Valuable information pertaining to the development of specific UF membranes can also be extracted from the results of the above experiment.

3. The limited dry-storage life of PVAM RO TFC membranes was reported. A noticeable deterioration in RO performance (increase in average flux and decrease in conductivity rejection) becomes apparent within a week of dry storage of freshly prepared membranes. Although the indications are that the deterioration can be arrested by chemical treatment of the desalting layer, the possibility that the support membrane itself might play a role should not be excluded. (The problem of dry-storage also arose with the previously used PS membranes).

   The various approaches made in attempts to arrest deterioration of the FD TFC membranes were met with limited success. The most successful of the approaches involved neutralization of the fresh membrane, followed by conditioning in an aqueous aromatic diamine solution (5 months storage). One month of dry-storage was obtained when fresh membranes were coated with poly(vinyl alcohol) and heat-cured at 110°C, after first neutralizing the membrane.

4. One of the approaches used in the study on improving the dry-storage capabilities of the FD TFC membranes, was to increase the cross-linking density of the desalting barrier to improve its mechanical stability, should that be the cause of deterioration.

   A di-functional aldehyde (glyoxal) was used for this purpose as amines and aldehydes react readily in aqueous acidic medium. The choice of reactant was fortunate since, although no improvement in dry-storage life of treated membranes was observed, drastic improvements in water permeation rates (up to 200%) were achieved, with no increase in solute passage. The standard method of treating and storing freshly prepared membranes now involves over-night conditioning of the membranes in an aqueous glyoxal solution followed by neutralization and storage in RO tap water, with pH corrected to 7.

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TUBULAR SUPPORT AND UF MEMBRANES

POLY(BISPHENOL A SULPHONE) (PS)

PS (Udel 1700P and 3500P) is widely used as a support for TFC RO membranes and as UF membrane material. The polymer was chosen for a number of reasons, the important ones being:

i) Films with an asymmetric structure can easily be obtained with simple binary casting solutions by the wet phase-inversion process, without the use of unusual solvents.

ii) The membrane fabrication procedures are simple.

iii) The polymer is relatively inexpensive.

iv) PS has a high Tg which ensures mechanical durability.

v) Films produced from the material show resistance to a wide range of common water-miscible solvents,

vi) It is hydrolytically stable and is not affected by oxidizing agents. [In fact, under harsh cleaning conditions, the integrity of the poly(ethylene terephthalate) (PET) membrane support fabric is suspect, rather than that of the PS membrane film].

There are, however, also negative aspects regarding the use of the polymer as a support membrane material.

vii) The polymer can be classed as hydrophobic. This causes densification of the prepared membrane film over a period in wet storage and some permanent loss in water transport capabilities if the film is allowed to dry out completely. (The latter possibility can be rectified by correct treatment).

viii) The molecular mass of the commercially available polymer is not high, and viscosities of binary casting solutions (i.e. polymer plus solvent) are generally low and are increased only slightly by increasing the polymer concentration over the practical range.

Although membranes can be produced from low-viscosity solutions, it is not the ideal for various reasons. Excessive penetration of the casting solution into the fabric will cause unwanted encapsulation of support-fabric fibres leading to increase in pressure drop on the low-pressure side of the membrane and lower hydraulic permeation rates. Bleed-through of the casting solution in areas where the fabric density is low will lead to the formation of blemished and imperfect membranes at those sites.

These problems can be solved by increasing the viscosity of the casting solution with quench-medium miscible additives. The addition of small proportions of low-molecular mass poly(vinyl pyrrolidone) (PVP) (10 000 to 40 000 mol mass) or $LiCl$ increases the viscosity of the casting solution markedly.

(Mixtures of polymers are, in general, not miscible in appropriate and common solvents, and will slowly separate into their respectively rich phases. Fortunately the water-soluble polymers, PVP and poly(ethylene glycol) (PEG) are exceptions and are completely compatible with PS in all proportions).

1. The surface free-energy difference between PS and the PET support fabric causes difficulty in establishing a casting environment that will facilitate good adherence between the cast membrane film and the support fabric.
2. The shelf-life of PS casting solutions is limited to a matter of days, depending on the solvent used. The low-molecular-mass fractions of the polymer are said to crystallize, which causes the formation of suspended particles. Conditioning the casting solution at 80 to 90°C will re-establish clarity of the solution depending on the age of the precipitant. N-N, dimethyl formamide (DMF) is one solvent particularly prone to the problem. NMP-based casting solutions do not show this tendency and such casting solutions are completely stable.

POLY(ETHER SULPHONE) (PES)

During a study on flat-sheet membranes which was planned to gain insight into the morphological behaviour of the support membranes and understanding of the membrane/support adherence problem, PES was introduced as a new candidate membrane material.

PES is structurally similar to one-half of the repeat-unit of PS, and although its solubility regime differs from that of PS, the same solvents are used in the preparation of casting solutions. The main reasons for including the material in the study were the advantages of the higher Tg (improved mechanical stability) and equilibrium water content (reduced hydrophobicity) listed for PES, as compared with those of PS. A further advantage proved to be the unlimited shelf-life of PES casting solutions irrespective of the solvent used. However, little reference could be found in literature with respect to its usefulness as a commercial membrane material.

MEMBRANE/FABRIC ADHERENCE

It was soon learnt during the above study that polyolefinic-type supports were a better proposition than PET with regard to membrane adherence. This posed a practical problem since the quality and strength of poly(propylene) and poly(ethylene) seam welds proved inadequate for the fabrication of single-ply support tubes; other problems concerned the stiffness of fabricated support tubes. This ruled out the possibility of producing reasonably robust single-ply polyolefin support tubes. The alternative, namely, the development and commercialization of a double-ply (polyolefin inner/PET outer wrap) support tube, was regarded as being too expensive and technically advanced from an economic point of view.

Two further findings highlighted the adherence studies:

1. PS adherence to polyolefin fabrics was, in general, better than that of PES and the reverse was true for PET, if the effect of solvents was disregarded.

2. Air-exposure, introducing partial gelation in the top skin before introducing the nascent membrane into the precipitation medium, improved adherence markedly. (One had to be careful, however, as non-skinned non-asymmetric membranes, with a honeycomb structure were obtained with certain solutions).

The final conclusions drawn were that adherence may be improved with the PES/PET system if the rate of precipitation of the membrane could be controlled. This was the only alternative to fabrication of a double-ply support tube.

In a statistically planned experiment in which the adherence of the PES membrane to the PET fabric was determined as response, evidence to substantiate the above conclusions was obtained.

The experiment is summarized in the table below.

Fabrication Variables		High/low level	Movement	Significance on adhesion of variable
Air drying	[ℓ/min]	0 - 1,1	+	95%
NaCl in leach	[g/ℓ]	0 - 5,0		n/s
Solvent in bath	[%v/v]	0 - 5,0	-	80%
Precipitant temp.	[°C]	5 - 20,0	-	90%
Surfactant	[g/ℓ]	0 - 1,0		n/s
PEG in dope	[%m/m]	0 - 2,0		n/s
PES in dope	[%m/m]	14 - 18,0	+	90%
PVP in dope	[%m/m]	0 - 5,0	+	99%
LiCl in dope	[%m/m]	0 - 0,2	+	90%

n/s: not significant

SUMMARY

The problems experienced in the past with consistency in membrane performance and membrane adherence to the PET fabric has largely been overcome by changing the membrane-forming polymer, reducing the rate of precipitation and increasing the viscosity of the casting solution. Adhesion values of as high as 15 kg/cm2 have been obtained, compared with values below 3,0 kg/cm2 for controls.

(NMP is currently used as the base solvent. The use of DMF as the base solvent was terminated because of its harmful dermatological and carcenogenic effect, as well as the toxicity of the solvent, although even better adherence has been obtained with DMF as the base solvent).

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PES SUPPORT MEMBRANE DEVELOPMENT

INTRODUCTION

Improvements of PVAM TFC membrane performance by formal optimization of fabrication variables have been obtained with PS support membranes in the past. In the original PVAM TFC membrane, PVAM-OD was deposited on PS (1700P) membranes produced from the PS/NMP/dioxane casting system. The support membrane originated from work conducted on the DETA RO membrane and was thought to have had adequate adherence to the support fabric. (Optimum PVAM-OD membrane performance achieved was: 97,1% rejection at 2MPa, 20°C, 2 000mg/ℓ NaCl feed, with a hydraulic flux of 730 lmd).

Quality assurance of the PVAM-OD material and cross-linking agent synthesized was a problem and the main cause of inconsistency in TFC membrane performance. Further research on the synthesis of PVAM led to modifications of the methods of synthesis and recovery of the final product. The new product proved to be chemically different and was renamed PVAM-FD (FD).

The whole procedure for TFC fabrication variable optimization was repeated with the newly developed precursor material (PVAM-FD) on the same support membrane as before. (Optimum PVAM-FD membrane performance: 98,2% rejection at 2MPa, 20°C, 2 000mg/ℓ NaCl feed, with a hydraulic flux of 560lmd).

Further improvements in TFC membrane performance were obtained when a higher molecular mass PS (3500P) was used instead of the 1700P, although the casting solution solvent system remained unchanged. The average membrane performance of six batches of six TFC membranes each, produced from four different support membrane fabrication batches were: 99,1±0,3% rejection and 440±63lmd flux. Unfortunately, the adherence of this PS support membrane to the PET support fabric was also inadequate.

OPTIMIZATION

At this stage of TFC membrane development all efforts were redirected from TFC membrane development to support and UF membrane development in a final attempt to solve the problem of support membrane adherence. This bore fruit as the problem of inadequate adhesion was mastered in six months.

[Following this, UF membrane technology was introduced into the Bintech group early in 1986 by appointment of a member from the water project team onto Membratek staff. Research and development of UF membranes continues at Membratek, where the development is more application-orientated. The work will be published in the form of an MSc thesis (Potchefstroom University)].

Work on TFC membrane development was restarted at that stage. However, with a new support membrane and without much knowledge of the casting system, it was decided not to optimize TFC membrane fabrication variables on a randomly selected PES support membrane. It was also decided rather to design an experiment around support-membrane fabrication variables and to find correlations between these variables and the performances of standard FD TFC membranes. The method of TFC membrane fabrication regarded as "standard" evolved from earlier optimization studies conducted on PS (1700P) support membranes.

A 1/16 replicate of a 2^9 factorial experiment was planned and the effect which nine support membrane fabrication variables had on TFC membrane performance was determined. The fabrication variables were:

Air-drying rate
Concentration of NaCl in precipitation medium
Concentration of solvent (NMP) in precipitation medium
Temperature of the precipitation fluid
Concentration of surfactant (SLS) in precipitation fluid
Concentration of poly(ethylene glycol) in casting solution
PES concentration in casting solution
PVP concentration in casting solution
LiCl concentration in casting solution

Only some of the above variables showed effects beyond the 95% level of confidence with regard to the pure-water flux response of the support membrane and RO rejection response and RO hydraulic flux response of the TFC membrane. These variables are given below.

Variable	PWP	Response RO Ret	RO Flux
Air drying	-[99]	+[99]	-[99]
Leach NaCl	-[95]		
Leach temp	+[99]	+[95]	-[99]
Leach Surfactant		+[99]	-[99]
PES	-[99]	+[99]	-[95]
LiCl	-[99]		

Note: The '+' and '-' signs indicate the effect of each variable on the response.
PWP: Pure water permeability
RO Rej: Reverse osmosis membrane retention
RO Flux: Reverse osmosis membrane flux

It is important to note that although not all variables are equally important, the range over which they are varied also plays a role. The fact that the effect of PVP, for example, is barely significant (-[80%] in the case of PWP, +[80%] in the case of RO Rej and not significant at all in the case of RO flux), holds true only for the range over which this variable was varied, namely 0 to 5%. The same holds true for PEG (range 0 to 2%) and it is quite possible that the case would be different if the upper level for this variable had been 5%, for example.

SUMMARY

The effects which air-drying, leach temperature, polymer concentration and LiCl have on the pure-water flux of the support membrane is to be expected. In general, all fabrication variables can be divided into one of two groups, that is, those that retard the onset or rate of phase separation and those that accelerate the process. Any variable that reduces the rate of membrane precipitation will cause the formation of a relatively more dense membrane with normally more, but smaller, skin-surface pores. The opposite will hold for variables that accelerate the precipitation of the membrane.

Any variable which has a positive effect on the salt rejection response of an RO membrane normally causes a reduction in the hydraulic permeability of the membrane. The opposing effects which fabrication variables have on the flux and rejection responses of a membrane must be balanced very carefully to produce an 'optimum' membrane. In order to accommodate these opposing responses, they are grouped together in the A^2/B-value, which to some extent aids the researcher in comparing two sets of data. One problem in using the A^2/B-value is its sensitivity to small changes when the salt rejection is very high (97% and higher). Below is a table which shows the effect which some of the support membrane fabrication variables have on the A^2/B-value of the TFC membrane. (Level of significance in square brackets, sign of the effect indicated by '-' or '+').

Variable	A^2/B-value
Leach NaCl	-[80]
Leach temperature	-[90]
Leach surfactant	+[99]
PES	+[99]
PVP	+[90]
LiCl	+[99]

Note: Level of significance in square brackets
Note: Sign of the effect on response indicated by '-' or '+'

It is interesting to note that while a specific variable (e.g. LiCl), does not seem to have any significant effect on the rejection and flux responses of the RO membrane, it becomes highly significant when the two responses are considered together. The same argument applies to the concentration of PVP which, when varied over the 0 to 5% mm range just becomes significant as a variable when the rejection and flux responses are considered together.

The composition of the support membrane casting solution that was evolved from the results of this work is given below.

The leach-tank temperature is maintained at 20°C, 50mg/ℓ Triton X-100 is used as the surfactant, and no air-drying is used. RO tap water is used as the precipitation medium. The membranes are rinsed continuously overnight before being used as TFC membrane supports.

Solution component	% by mass
PES concentration	19,0
DMF concentration	2,0
NMP concentration	68,8
PVP (40k) conc	10,0
LiCl concentration	0,2

The membranes (designated 719) have PWP-values of 900×10^{-5}, less than the values (3 000 to $3\,500 \times 10^{-5}$) said to be ideal for flat-sheet TFC membrane usage. TFC membranes with adequate performance have been produced on these support membranes (98,9±0,2%, 430±37lmd).

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FD TFC RO MEMBRANES

MEMBRANE INTEGRITY

SURFACE STUDIES

The geometry of tubular membranes hampers the inspection of the final product for the presence of micro-flaws and tiny blemishes. Evaluation of the membrane for RO properties remains the only means for determining the quality of the product. Even then it is sometimes not possible to establish beyond doubt the cause of poor performance. A dynamic dye test has been introduced recently which entails the addition of a minute quantity of Congo Red to the feed tank during evaluation of the membrane. The presence of any kind of flaw is revealed as a red mark.

It did not take long to find a correlation between poor rejection and the tiny red spots that appeared on the surfaces of some membranes. (The test is fairly sensitive. The probability that dye spots (micro-flaws, pin-holes) are present would be high if a membrane shows a rejection of 1 to 2% lower than the rest). On the other hand, membranes which give high salt rejection (98% and more) and high flux would not necessarily show these marks. No correlation could be found between PWP-values of support membranes and the presence of dye marks in the final TFC membrane.

The cause of these dye spots was sought by optical and electron microscopy by comparing fresh support membranes with dye-treated TFC membranes. The optical microscope revealed dye-coated cavities directly beneath the dye-spots, indicating inadequate mechanical support of the membrane top layer. Under the electron microscope the cause was more apparent. It is now almost certain that the large cavities are caused by air bubbles, similar to those known to exist within the CA membranes. This has never been noticed on cross-section micro-graphs. However, examination of the membrane skin revealed spherical humps with tiny concentric holes on the apices of some of them.

The stress that builds up in the membrane subsurface during phase-separation is relieved by visco-elastic flow of the still highly plasticized polymer. Further stress builds up during leaching and storage as remnants of the solvent diffuse from within the polymer matrix and the polymer becomes less plasticized. At this stage and during the drying process involved in fabricating TFC membranes, the stress could be relieved by rupturing the skin in already stressed areas, i.e., at the apices of the humps.

Air bubbles must be eliminated from the substructure, because their presence has been related to the high incidence of micro-flaws in the support membrane surface and because of the effect which these imperfections have on the permselectivity of the TFC RO membrane. It is obvious that the membrane would be mechanically weaker at those sites, increasing the probability of collapse under high hydraulic pressure.

DESALTING MATRIX

The basis of formation of TFC membranes is the cross-linking process which insolubilizes the water-soluble precursor (monomer or polymer) either by complete reaction with a cross-linking agent or partial reaction with the cross-linking agent, followed by thermal curing of the precursor. Increase in cross-linking density will improve the permselectivity of the membrane at the cost of a reduction in hydraulic permeability. In general, very high cross-linking densities will cause the formation of a brittle film, whereas insufficient cross-linking densities will allow excessive swelling of the hydrophilic precursor and physical rupture of the desalting barrier.

In all the optimization studies conducted on PVAM membranes, the final oven temperature and oven retention time can hardly be described as suitable to induce thermal cross-linking. (Primary amines will condense, and if contained in a polymer, cross-link, at 110°C). Experimentation with the PVAM/SCL system indicates a reduction in permselectivity and slight increase in hydraulic permeability as the curing temperature is raised from an optimum 4 min at 90°C to 10min at 120°C.

PVAM cannot cross-link thermally because of the absence of primary amines; the degree of cross-linking therefore depends completely on the reaction of SCL with the secondary amines of PVAM. Subjecting this film to high temperature treatment merely results in inducing stress-cracking caused by shrinkage of the composite membrane.

The remarkable degree to which the hydrophilic PVAM/SCL cross-linked film will swell in water was clearly illustrated on glass slides. These experiments also indicated, rather dramatically, how the introduction of drops of dilute acid onto the film induces uncontrolled swelling in areas, causing physical rupture. (Salts of the acid form at amine sites which further increase the water-uptake of the film).

PVAM TFC MEMBRANE CROSS-LINKING

It is concluded that the mechanical integrity of the membrane film can be improved by reducing the swelling capacity of the desalting matrix by increasing cross-linking.

The cross-linking reaction between the precursor (aqueous phase) and the cross-linking agent (organic phase) is believed to take place in the organic phase (Riley). This means that segments of the polymer must diffuse into the organic phase before reaction can take place. This becomes increasingly difficult as the reaction progresses. The net result is that the cross-linking density decreases from the aqueous/organic interface towards the support membrane surface. As idealized PVAM does not contain primary amines, cross-linking of the lower regions of the film will not occur as the result of thermal treatment.

In order to increase the cross-linking density of the thin film, the membranes are treated, after the initial SCL reaction, with an aqueous solution of glyoxal. This di-functional aldehyde reacts readily with secondary amines and there were definite reductions in the swelling capacity of the PVAM TFC films when the reaction conditions were duplicated on glass slides.

Even though the reaction increases the cross-linking densities, the functionality introduced into the membrane structure increases the hydrogen-bonding capacities of the matrix and thus the hydraulic permeability of the membrane.

The following two tables indicate how membrane flux is increased by conditioning the membranes for 21h in different glyoxal solutions. (The pH-value indicated is that of the glyoxal make-up water. The pH of aqueous glyoxal solutions slowly drifts towards final values of 4 to 6).

Treatment	Rejection	Flux	$A^2/Bx10^5$
Control	97,8±0,9	380±50	6,5
21h, RO tap	98,3±0,2	540±50	12,2
21h, RO tap + 1% GOXL	98,1±0,3	1110±216	26,3
21h, pH 9 + 1% GOXL	98,5±0,3	1090±220	33,5
21h, pH 11 + 1% GOXL	98,5±0,3	980±194	28,7
21h, 2% Na_2CO_3 + 1% GOXL	96,4±1,7	1230±81	15,6
Control	96,1±2,5	170±10	1,5
21h, RO tap + 1% GOXL	97,8±0,7	850±80	16,1
21h, pH 9 + 1% GOXL	98,5±0,5	670±30	17,9
21h, pH 11 + 1% GOXL	98,3±0,5	750±230	19,0
21h, 2%Na_2CO_3 +1% GOXL	97,3±1,5	840±150	13,4

The table below shows a comparison of membranes treated under different post-treatment conditions.

GOXL Conc [mass%]	GOXL make-up water pH			Condition Time [h]
	4	7	10	
1,0	98,7% 530 lmd [15,4]	98,4 550 [13,1]	97,2 500 [7,0]	1,0
0,5	98,5% 950 lmd [27,7]	98,6 940 [29,6]	98,3 850 [20,9]	21
1,0	97,8% 490 lmd [8,7]	97,6 560 [9,5]	97,0 540 [7,1]	21

The figure in the square brackets denotes $A^2/Bx10^{-5}$

DRY STORAGE

Since the introduction of the dye test, it has been noticed that there is a generally higher incidence of micro-flaws on the surfaces of dry-stored membranes than on those of directly tested membranes.

Membranes have been preserved in the laboratory for up to four weeks, simply by storing the membranes wet (immersed) in a buffer solution at pH 7. A 1m TFC membrane (0,5% GOXL, 21h) module which had a performance after 121h of operation of 98,5% rejection with a hydraulic flux of 552 lmd (16,5ℓ/h), had a performance of 98,3% rejection and a flux of 760lmd (23ℓ/h) after wet storage for 1 month.

In comparison, membranes from the same production batch had been stored in the open and in a closed-up air-tight container under conditions of high humidity. The membranes were not chemically treated after preparation, but were rinsed for 1h in RO tap water before storage. The results are given in the table below.

Stored	Days	Rej [%]	Flux [lmd]	A2/B-value
Control		97,7±0,9	360±95	5,8E^{-5}
Dry	7	97,4±0,3	210±37	3,0E^{-5}
	14	94,8±1,5	195±38	1,3E^{-5}
	21	93,8±2,4	207±17	1,2E^{-5}
Moist	2	98,5±0,3	280±77	7,1E^{-5}
	7	97,1±1,7	400±176	5,3E^{-5}
	14	97,0±2,2	470±193	5,9E^{-5}
	21	97,2±1,9	415±173	5,7E^{-5}

CHEMICAL CONDITIONING

Treatment of the membranes with glyoxal did not improve the dry-storage life of the membranes. However, post-treatment of the PVAM membrane with an aromatic diamine (1,3-phenylene diamine, PDA) did slow down deterioration, as was noticed in an experiment in which the membranes were stored for five months.

These membranes were deposited on PS supports, oven-dried and rinsed in RO tap water for two hours. After the rinse step, the membranes were immersed in an aqueous 0,7% (mm) solution of PDA for 20h, rinsed for one hour in RO tap water and stored open/dry. The membranes became discoloured in the PDA and the feed tank had to be rinsed thoroughly before evaluation to remove PDA from the system. The results of two experiments are shown below

	Rejection	Flux	A2/B-value
Control	98,9±0,3	270±51	8,0E^{-5}
Rx contro	98,9±0,4	270±17	9,3E^{-5}
14 days	99,3±0,2	300±35	16,6E^{-5}
Control	98,3±0,2	320±11	6,9E^{-5}
Rx control	94,7±1,6	230±19	1,5E^{-5}
7 days	97,2±0,3	230±9	2,9E^{-5}
5 months	97,0±0,6	300±21	3,6E^{-5}

Secondary amines react readily with glyoxal and an experiment was constructed to determine whether ethylene diamine (EDA) instead of PDA could be used in the post-treatment step, since EDA is less expensive. A Plackett-Burman balanced design, N=8, was used to study five variables in one experiment, leaving two for estimation of sum of errors. Below is a summary of the experiment; figures in square brackets denote levels of significance, and the '+' and '-' signs indicate the effect of the variable on the response.

Variables	Range	Rejection [%]	Flux [lmd]	A^2/B-value
GOXL conc	0,5 - 1,2%	-[70]	-[95]	
GOXL contact*	1 - 21h	+[80]	+[95]	+[99]
Dummy				
Diamine	EDA - TTDD	-[90]	-[80]	-[95]
Dummy				
Amine conc	0,5 - 0,9%	+[90]	+[80]	+[95]
Amine contact	1 - 21h	-[99]	+[90]	+[80]

Make-up water RO tap, pH 6,5
membranes were tested immediately after conditioning
TTDD: 4,7,10-Trioxatridecan 1,13-diamine
EDA: Ethylene diamine
*note: 15min drainage time after

It is concluded from the results of the above experiment that longer GOXL contact time at lower GOXL concentration improves membrane performance. EDA is preferred to the long-chain oxy-diamine. Higher amine concentration in the conditioning tank improves both the rejection and the flux performances of the membrane. In the case of rejection the exposure should be short, and the reverse applies to membrane flux performance.

In the earlier case where the membranes were reacted with PDA, the membranes were not treated with GOXL. The only reaction that can take place is that between free acids (i.e. the carboxylic and sulphonic acid that result from SCL hydrolysis) and the amines, forming the salt, thus effecting cross-linking. In the case of EDA conditioning, in which the membrane had been pre-reacted with GOXL to increase its cross-linking density, the EDA can react with unreacted aldehydes as well as form salts with free acids.

It is evident from the above that primary amine functionality can be beneficial. The PVAM-OD used earlier was a semi-hydrolyzed version of the vinylamidine polymer (containing various percentages of primary and secondary amines). Its use was discontinued since it was impossible to reproduce a polymer with a specific ratio of hydrolyzed-to-unhydrolyzed vinylamidines. Because of this inconsistency between various batches of polymer, membrane performance was inconsistent and it was difficult to relate to fabrication variables.

A simple way of introducing primary amine functionality into the precursor system, and of doing away with handling membranes coated with hazardous monomeric amine species, was the incorporation of fully hydrolyzed PVAM (HY) into the FD precursor system. The membranes were prepared in the standard fashion, after which they were dried for 4 min at 90°C. The membranes were then treated with GOXL before final heat treatment and storage. The membranes were stored dry for 16d before being evaluated.

The results obtained are indicated below. A Plackett-Burman plan, N = 12, was used in the design of the layout and three dummy variables were used for the sum-of-errors estimate in the analysis of variance. Again the '+' and '-' signs indicate the effect of the variables on the response and the figure in square brackets indicate the levels of significance of the variables.

Variable	Level	Rej [%]	Flux [lmd]	A2/B
Precursor conc	1,2 - 1,5%	-[95]	-[90]	
FD/HY mass ratio	FD - 10/1	+[95]	-[80]	+[90]
Glycerol	0 - 0,5%	-[70]	+[80]	
SCL contact	2 - 6min	+[70]	+[70]	
GOXL conc	0 - 1,0%		+[95]	+[90]
GOXL make-up	1% Na_2CO_3-pH 9	-[80]	+[70]	
Treatment time	1 - 48h	+[80]	-[90]	
Drying	15/55 - 5/110 min/°C	+[80]	-[80]	-[70]

The important finding in this experiment is that 1,2% (mm) is still the preferred concentration of the precursor, even though the precursor used in this experiment is a co-mixture of PVAM-FD and PVAM-HY. (Compare this with precursor concentrations of 1,2% obtained in the optimization of the PVAM-FD membrane and the 4,0% in the case of the PVAM-OD membrane). Also important is the indication that thermal treatment can influence rejection positively, even under mild curing conditions of 5 min at 110°C.

The best set of performance values obtained after the 16 days storage period was 98,0±0,6% rejection with a flux of 430±96 lmd.

CONCLUSIONS

Because of the structure of the FD material used as precursor, thermal cross-linking is ineffective. Cross-linking achieved by reacting the membrane with GOXL does not improve the dry-stability of the membrane. The incorporation of primary diamines (aromatic or aliphatic) results in effective cross-linking of the membrane structure by the formation of salts, without the use of thermal curing. Mixing of PVAM-HY and FD enhance cross-linking, and thermal post-treatment of the membrane is necessary. Increase in cross-linking obtained by the use of primary amines increases the dry-storage capabilities of the TFC membrane, depending on the subsurface structure of the support membrane and absence of micro-flaws on the membrane surface.

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MEMBRANE TECHNOLOGY TRANSFER

A new approach, with beneficial results, was made to introduce ultrafiltration membrane technology into Bintech. After the problem of adherence of the UF membrane to the support fabric had been solved, development of the membrane (from the Institute's point of view) narrowed down to the production of a range of PES UF membrane products. Membratek (Div of Bintech), on the other hand, required the know-how and facilities to enable them to produce UF membranes, to accommodate the membranes into their module concept and to operate the membranes on real effluent.

These requirements were met when Mr H Strohwald, a chemical engineer at the Institute, who is au fait with IPS UF technology, joined Bintech as a member of Membratek staff responsible for furthering UF membrane technology and development, module development and pilot plant evaluations. This approach appears to work well, and it effectively freed the Institute to enable it to concentrate on TFC membrane development.

PVAM TFC RO membrane know-how is slowly being introduced into the Membratek Division of Bintech. As a first step in the transfer of know-how, the economic viability of the membrane system was established. The positive outcome of these analyses led to the introduction of a member of Bintech R&D staff to techniques used in the synthesis of the necessary chemicals (SCL and PVAM-FD) as well as laboratory production (the traditional dip-coating approach) of 1m membranes.

The process of technology transfer is currently at the stage at which membranes (housed in 1m PCI modules) are being supplied to Membratek, for evaluation by them. Much larger quantities of 1m-length membranes will shortly be supplied to them for incorporation into their own module.

Both the organizations are presently at the learning stage regarding the TFC membranes. Unexpected results such as, for example, catastrophic deterioration of membrane performance after 120h of operation on Paarl tap water, after similar membranes had been operated for over 500h under standard laboratory test conditions without deterioration in performance, are difficult to understand, and will slow down the process of transfer. From the earlier text it is also evident that various types of PVAM membranes can be supplied; the important question is: which of such membranes is most suitable?

Although some of the present problems associated with the TFC membrane might give rise to misgivings about the membrane system, they have their positive aspects. It is fortunate that the final tailoring of the system will be concluded in collaboration with Membratek, which will introduce invaluable background information about the membrane into the Membratek group. It also creates the opportunity for members of their staff to acquire hands-on experience of the TFC membrane system which they lack at present.

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