

Chemically treated polyethersulfone/polyacrylonitrile blend ultrafiltration membranes for better fouling resistance

A.V.R. Reddy^{a*}, Harshad R. Patel^{b*}

^aCentral Salt and Marine Chemicals Research Institute, Bhavnagar, India
Tel. +91 2782566511; email: avreddy@csmcri.org

^bChemical Engineering Department, Institute of Diploma Studies,
Nirma University of Science and Technology, Ahmedabad, India
Tel. +91 2717241911–15; email: harshadpinkii@yahoo.com

Received 20 December 2006; accepted 3 January 2007

Abstract

Membranes with high permeation combined with high rejection rate and high fouling resistance are in high demand in market. The stability of membrane is necessary in aqueous applications for separation of biological products such as proteins. Polyethersulfone (PES) is hydrophobic material hence it fouls rapidly during aqueous biological and macromolecular solute separations. Membrane with hydrophilic characteristics have drawn considerable attention in practical use in recent years because of its better fouling resistance.

This paper is an attempt to prepare hydrophilic PES membranes by blending polyethersulfone (PES) and polyacrylonitrile (PAN) in dimethylformamide (DMF) solvent in different proportions. Blend ultrafiltration membranes of PES and PAN were prepared on non-woven polyester fabric using motor driven prototype membrane casting machine according to phase inversion method. It has been observed that these membranes foul rapidly during ultrafiltration of macromolecular solutes. To improve fouling resistance membrane surfaces modified by treatment with aqueous alkali solutions of different concentration at room temperature. Unmodified and modified membranes were characterized using aqueous solution of inorganic solutes (NaCl & Na₂SO₄) and organic solutes (polyethyleneglycol [PEG], dextran [DXT], poly (sodium 4-styrene sulfonate) [PSSA]). Modified membrane had shown high flux recovery ratio compared to unmodified membranes, this improvement in the fouling resistance is due to hydrophilicity of membrane surface. Hydrophilicity was confirmed by advanced contact angle using DATA Physics direct contact angle tensiometer. Compatibility of polymer blends was confirmed by measuring glass transition temperature using differential scanning

*Corresponding authors (Research work carried out at R O Division, CSMCRI, Bhavnagar as ME Dissertation submitted at Chemical Engineering Department, The Maharaja Sayajirao University of Baroda, Vadodara).

Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

calorimetry (DSC). For measurement of rejection of macromolecular solutes gel permeation chromatography was used.

Keywords: Polyethersulfone (PES); Polyacrylonitrile (PAN); Hydrophilicity; Blend membranes; Flux recovery ratio (FRR)

1. Introduction

Hydrophobic membrane surface foul rapidly during macromolecular solute separation by adsorption or deposition and causing reduction in permeation rate. Membrane surface chemistry plays important role to enhance performance of ultrafiltration membrane [1,2]. Surface hydrophilicity can be improved by number of methods such as coating, grafting, surface treatment and so on [3–17]. An attractive method involves either tailoring the membrane material (polymer blends) to increase hydrophilicity or the use of pretreatment on existing membranes [4,6,14,17].

2. Experimental

2.1. Materials

Material	Supplier
PES	Gharda Chem. Ltd. (Ankleshwar)
PAN	Aldrich Chem. Co (USA)
PSSA	Aldrich Chem. Co (USA)
DXT	Aldrich Chem. Co (USA)
PEG	SD'S fine Chem. Co (Bombay)
DMF	Ranbaxy Ltd. (New Delhi)

All the chemicals were of AR grade and used as received from suppliers without purification.

2.2. Membrane casting

The Casting solution of desired proportion of polyethersulfone (PES) & polyacrylonitrile (PAN) were prepared separately (as presented in Table 1) in dimethylformamide (DMF) in hot condition and then mixed in hot condition with stirring [11].

Table 1
Composition of casting solution

Membrane code	PAN (%)	PES (%)	DMF (%)
17PAN0.0	0	17	83
17PAN0.3	0.3	16.7	83
17PAN0.5	0.5	16.5	83
17PAN0.75	0.75	16.2	83
17PAN1.0	1.0	16.0	83
20PAN0.0	0	20.0	80
20PAN0.3	0.3	19.7	80
20PAN0.5	0.5	19.5	80
20PAN1.0	1.0	19.0	80

2.3. Membrane preparation

The UF membranes were prepared according to phase inversion technique on non-woven polyester fabric (Holytex 3265) using prototype membrane casting machine [1,4,5].

2.3.1. Conditions

Thickness of membrane was kept: 180 μm using micrometer screw gauge, Gelation bath concentration: 0.02% SLS in water temperature: 25–30°C, Relative humidity: 30% by circulating hot air.

2.4. Membrane stabilization and modification

PES–PAN blend membranes were kept in freshly prepared double distilled water for 24 h for stabilization of membrane then modified by treating them with aqueous alkaline solutions of different concentration for 24 h at room temperature [15].

2.5. Analytical techniques

- Inorganic solutes and organic solutes (feed and permeate) were analyzed by systronic 2850 conductivity meter and gel permeation chromatography (water model 501 pump RI 2401 detector, ultrahydrogel column and millennium 32 software) respectively.
- Infrared spectra of unmodified and modified membranes were obtained with perkin elmer 16 PC FT-IR Spectrophotometer.
- Surface hydrophobicity/hydrophilicity of unmodified and modified membranes were determined by contact angle value (θ) of a water drop deposited on the membrane surface, using the DATA physics direct contact angle tensiometer (DCAT 21) [16].
- Miscibility of polymer blends were detected by glass transition temperature (T_g) measurements, using mettler differential scanning calorimetry (DSC) 820 – C cell at a heating rate of 10°C/min under argon [14].

2.6. Membrane characterization experiment

Cross flow ultrafiltration cell (Amicon model) fitted with an internal magnetic stirrer was used for evaluation of performance of modified and unmodified membranes. The active cell area was 38.5 cm². Initially water was permeated through membrane for about 30 min at transmembrane pressure of 4 kg/cm² at room temperature and then PWF measured at 3 kg/cm². Aqueous solutions of different inorganic and organic salt solutions were permeated through membrane are shown in Table 2.

3. Result and discussion

3.1. Effect of PAN blending on hydrophilicity

The data on advanced contact angle for membrane surface were measured.

It clearly indicates that the advanced contact angle decreased with increase of PAN compositions in polymeric solution, hence the hydrophilic nature

Table 2

Composition of salt solutions permeated through membranes

Salt solution	Molecular wt.	Concentration wt (%)
NaCl	58.5	
Na ₂ SO ₄	142	
Poly ethylene glycol	35,000	0.05
Dextran	77,000	
Poly sodium 4-styrene sulfonate	70,000	

of membrane surface increases with increase of % PAN in polymer solution. However important observation was that the advanced contact angle values for membrane series-2 were lower than that of membrane series-1 for same concentration of PAN. Contact angle values depend on surface chemistry, its roughness and its heterogeneity. Lower values for membrane series-2 may be due to the fact that PAN is pervading to the top layer of the membrane during membrane formation (before entering in to the gelation bath). This results in formation of a very thin skin layer of PAN on top of PES support, which ultimately produce more hydrophilic surface [13,15].

3.2. Thermal properties of membranes

Compatible polymer blend shows only one intermediate T_g between that of the homopolymers [14]. To study the miscibility of PAN in PES, 10 mg of blend samples were analyzed to obtain mid point T_g value. Data on mid point T_g values are presented in Table 3 clearly indicates that T_g of PES–PAN blends are in between that of homopolymers.

3.3. Membrane modification

PES–PAN blend membranes were modified by treating them with aqueous alkaline solutions of different concentration for 24 h at room

Table 3
Membrane characteristics

Membrane code	T_g	θ	Series
17PAN0.0	230	84.26	Membrane series-1
17PAN0.3	227.47	83.57	
17PAN0.5	226.96	83.08	
20PAN0.0	230	83.06	Membrane series-2
20PAN0.3	227.86	–	
20PAN0.5	–	82.34	
20PAN1.0	226.77	82.25	
PAN	85	–	

temperature. The chemical reaction likely to occur is shown in Scheme 1.

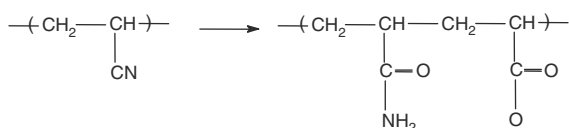
The structure of modified membranes were conformed by Perkin Elmer FT-IR spectra had shown new peaks developing at 1743 and 1662 cm^{-1} which are assignable to carbonyl stretching of carboxylic acid and amide group respectively, which arise due to hydrolysis of nitrile group on treatment with sodium hydroxide.

3.4. Effect of alkali treatment on hydrophilicity

It is very clear from Fig. 1 that contact angle decreases with increase of NaOH concentration, which imparts hydrophilic character to membrane surface due to formation of $-\text{COOH}$ and $-\text{CONH}_2$ group.

3.5. Effect on fouling resistance

After ultrafiltration of each solute the membranes were thoroughly washed with distilled water and then their PWP was measured at



Scheme 1. PAN reaction with alkali.

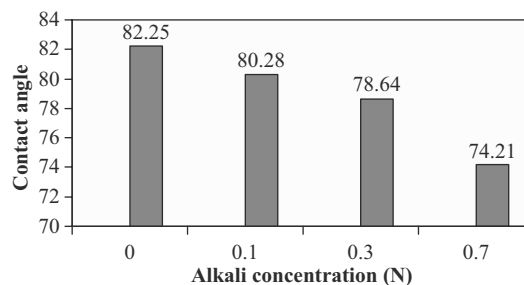


Fig. 1. Effect of alkali treatment on surface hydrophilicity.

3 kg/cm^2 . The flux recovery ratio (FRR) based on pure water flux was calculated according to following equation & results obtained are presented in Figs. 2 and 3.

$$\text{FRR (\%)} = \frac{\text{PWF}_{\text{UF}}}{\text{PWF}_0}$$

where,

PWF_{UF} = pure water flux after ultrafiltration of different solutes.

PWF_0 = initial pure water flux.

FRR is taken, as a measure of fouling resistance nature of membrane, higher the FRR higher will be the fouling resistance of membrane. All the chemically modified membrane shows higher value of FRR compared to unmodified membranes. Hence chemical modification imparts resistance to adsorption fouling during ultrafiltration of organic solutes. Figs. 2 and 3 shows alkali treatment & addition of PAN in PES, improves FRR of membranes and it provides somewhat resistance to adsorption fouling.

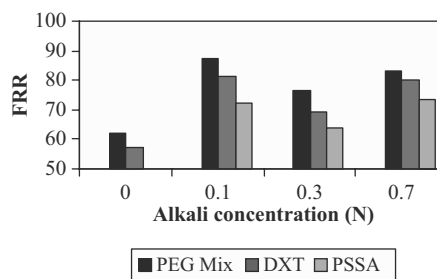


Fig. 2. Effect of alkali treatment on FRR.

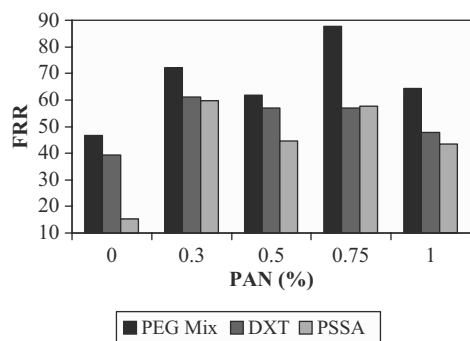


Fig. 3. Effect of PAN addition on FRR.

4. Conclusions

Hydrophilic surface treatment (PAN addition and alkali treatment) results in enhanced FRR at all experimental conditions. Hence all the modified membrane shows high resistance to adsorption fouling compared to virgin membranes, this is due to formation of hydrophilic functional group.

Nomenclature

PES	Polyethersulfone
PAN	Polyacrylonitrile
UF	Ultrafiltration
PEG	Polyethyleneglycol
DXT	Dextran
PSSA	Poly(sodium 4-styrene sulfonate)
gfd	Gallon per square ft per day
θ	Advanced contact angle
FRR	Flux recovery ratio

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