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Solvent and pH Resistance of Surface Crosslinked Chitosan/Poly(acrylonitrile) Composite Nanofiltration Membranes

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ABSTRACT: The resistance of novel surface crosslinked Chitosan/poly(acrylonitrile) (PAN) composite nanofiltration (NF) membranes to pH and organic solvents was studied with respect to the effects of crosslinking parameters, namely, glutaraldehyde concentration and crosslinking time. The pH resistance was determined by permeation of aqueous acidic (pH 2.5) and basic (pH 11) solutions as well as swelling studies in the pH range of 2.5–11. The solvent resistance was determined by swelling, immersion, and permeation studies with several industrially important organic solvents, namely methanol, ethanol, iso-propanol, methyl ethyl ketone, ethyl acetate and hexane. It was observed that the crosslinked composite membranes maintain the permeate fluxes for test solvents for 2 h of continuous operation without any significant change in flux. SEM studies on membrane samples after immersion as well as permeation with the above-mentioned solvents indicated that the membrane morphology was maintained. The results are explained in terms of solvent–membrane polar and hydrophobic interactions, using solubility parameters of membrane and solvents and dielectric constants of solvents. Pure water flux and polyethylene glycol transmission data indicated that at pH 2.5 and 11, the membrane stability increased with increasing glutaraldehyde concentration and was much better at pH 11 than at pH 2.5. All surface crosslinked membranes showed reduced swelling between pH 4–10. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1782–1793, 2000

Key words: poly(acrylonitrile); chitosan; nanofiltration; composite membranes; solvent resistance; nonaqueous

INTRODUCTION

Industries utilizing solvents and generating solvent laden waste streams are increasingly interested in waste minimization, solvent recovery and treatment of waste streams. In many instances, stringent environmental regulations and greater willingness of environmental agencies to enforce the law¹ drives this approach. These industries include petrochemical, food, biotechnology, fine chemicals, pharmaceuticals, paints and coatings,

electronics, and others. Conventional technologies such as incineration, distillation, steam stripping, biological treatment and activated carbon adsorption have been successful for minimization of solvent waste or solvent recovery in certain cases.¹ However, due to higher energy consumption in some of these processes, there is a great potential for new technologies such as membrane-based separations.

Membrane separation technology has proven to be very successful in processing aqueous streams. However, use of membrane-based separation schemes for processing nonaqueous streams has not been widespread. Many such schemes are still in a developmental stage. One of

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the main reasons for this is the lack of commercial membranes and modules that could withstand organic solvents for a reasonable time without decline in performance. Membranes made from ceramics and specialized polymers such as polyimides are available for selected applications; however, these are very expensive and generally not available in the lower molecular weight cutoff (nanofiltration) range.² Therefore, there is an immediate need for research in developing new economical solvent resistant nanofiltration membranes. Published literature^{3,4} on development of polymeric membranes and studies on their solvent resistance is lacking partly due to its industrial importance. There are some studies on permeation of either pure solvents or solutions in organic solvents using commercial membranes.^{5–12}

Polymeric membranes after contact with organic solvent may result in one of the following:¹³ (a) no chemical effect; (b) little swelling, membrane may be compatible for short-term use; (c) extensive swelling and slow dissolution of membranes; (d) complete dissolution or disintegration of membranes; or (e) the relaxation of polymer chains due to plasticization in solvent results in swelling with subsequent pore size reduction.

Therefore, it is of interest to study the formation of NF membranes that would offer resistance to swelling with a wider range of industrially important organic solvents. To achieve this goal, the selection of polymers and the membrane formation method is very important. Nanofiltration (NF) membranes are generally composite in nature, with an ultrafiltration (UF) membrane as a substrate and a thin layer of another polymer as a selective barrier. Poly(acrylonitrile) (PAN) is one of the versatile polymers that is widely used for making membranes, and offers good resistance to a wide range of solvents. Chitosan, a natural hydrophilic biopolymer, also possesses excellent solvent resistance. However, formation of homogeneous NF membranes is not feasible with either of these polymers.

Therefore, a composite NF membrane with PAN UF membrane as a substrate with a thin layer of Chitosan could offer resistance to a wider range of solvents. Additionally, a hydrophilic surface of these membranes would be desirable for protein separation. Proteins are known to reduce permeate fluxes due to adsorption on membranes by hydrophobic interactions.¹⁴

The aim of the present study was to investigate effects of surface crosslinking of Chitosan/PAN

composite NF membranes on their resistance to pH and industrially important solvents. Because Chitosan is soluble below pH 6.5, the main objective of crosslinking was to ameliorate pH stability below pH 6.5, reduce the swelling with polar solvents such as alcohols, and increase the affinity and hence permeation rates for nonpolar solvents such as hydrocarbons. The effects of crosslinking parameters, namely glutaraldehyde concentration and crosslinking time (CT) on solvent permeation and pH stability were also investigated.

EXPERIMENTAL

Materials

Poly(acrylonitrile) (PAN) and Chitosan were of the same characteristics and purity as reported previously.¹⁵ Methanol (MeOH), iso-propanol (IPA), methyl ethyl ketone (MEK), ethyl acetate (EtOAc), and hexane (a mixture of C₆ isomers) were procured from BDH, Canada, while ethanol (EtOH) was obtained from Commercial Alcohols Ltd, Canada. Glutaraldehyde was obtained from Aldrich, Milwaukee, WI, while all other reagents were obtained from Anachemia, Canada, and used as received. Reverse osmosis-treated water with a conductivity of 5×10^{-4} S m⁻¹ was used for membrane preparation, pH stability, and swelling studies.

Preparation of Surface Crosslinked Chitosan/PAN Composite NF membranes (PANCHINF)

The details of the preparation of Chitosan/PAN composite NF membranes and subsequent surface crosslinking have been reported previously.^{16,17} In brief, the Chitosan solution was coated on surface-dried PAN ultrafiltration base membrane. After drying and treating with aqueous (aq.) alkali, these membranes were surface crosslinked for 0.5 and 1 h each with 0.08, 0.2, and 0.5% w/w glutaraldehyde solution. The NF characteristics of these membranes such as pure water flux, molecular weight cutoffs, rejection of salts, and sugars were reported previously.^{16,17}

pH Stability

The pH stability of these membranes was determined from the change in pure water flux and polyethylene glycol (PEG, MW 600 Da) transmission measured before and after the filtration of aq. acidic (pH 2.5) or basic (pH 11) solution for 1 h.

The pH stability was also determined by measuring swelling¹⁸ (S) [$\%S = (W_w - W_d/W_d)100$] of these membranes in the pH range of 2.5–12 under static conditions, where W_d and W_w are the weights of dry and wet membrane samples, respectively. The wet weight, W_w , was obtained by incubating membranes at 25°C for 24 h in water adjusted to desired pH with 2 N HCl or NaOH, and gentle blotting by tissue paper before weighing.

Solvent Resistance

Static Swelling

The solvent resistance was determined from swelling studies of dried membranes in test solvents, measured at 22°C after 24 h under static conditions. For this study, membranes were dried by solvent exchange with 50% aq. IPA, IPA and hexane for 0.5 h with each solvent in that sequence, followed by vacuum drying for 24 h at 40°C. The percentage swelling was then calculated in a similar way to that of pH swelling study.

Immersion Studies

The solvent resistance was also determined from the change in pure water flux measured before and after immersing membranes in test solvents for 20 h at 22°C. In case of alcohols, the sequence of solvent immersion was: 50% aq. alcohol (0.5 h), corresponding pure alcohol (20 h), 50% aq. alcohol (0.5 h) and water. In the case of MEK, EtOAc, and hexane, the sequence was: 50% aq. IPA (0.5 h), IPA (0.5 h), MEK, EtOAc, or hexane (20 h), IPA (0.5 h), 50% aq. IPA (0.5 h) and water. The stirred cell assembly (Amicon, $1.3 \times 10^{-3} \text{ m}^2$, 600 rpm) was used for measuring pure water flux at 480 kPa and 25°C.

Solvent Permeation

The results of swelling and immersion studies were supported by measuring actual permeation rates of solvents through *PANCHINF* membranes as a function of time. To avoid the damage to pore structure of membranes due to higher difference in surface tension of water and test solvents, they were immersed in solvents with decreasing surface tension, prior to testing. In the case of alcohols (MeOH, EtOH, IPA), membranes were first immersed in 50% aq. alcohol and then twice in corresponding pure alcohol for 0.5 h in each sol-

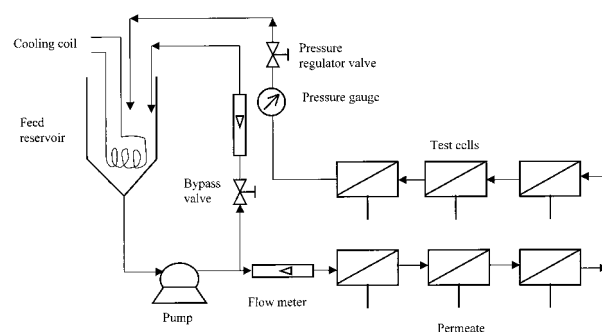


Figure 1 Schematic of membrane test setup for solvent permeation.

vent before placing the membrane in test cell. In the case of MEK, EtOAc, and hexane, the immersion sequence was 50% aq. IPA, IPA, and then twice in the test solvent for 0.5 h in each solvent. This was followed by measuring the solvent flux every 30 min up to 2 h at a temperature, pressure and crossflow velocity values of $23 \pm 0.3^\circ\text{C}$, 830 kPa, and 0.93 m s^{-1} , respectively. The solvent fluxes were measured after pressurizing membranes at 900 kPa for 20 min, to minimize the effects of membrane compaction. The membrane test setup shown in Figure 1 was used for solvent permeation. The materials of construction such as piping and fittings were chosen to be resistant to the test solvents. A diaphragm pump with PTFE (Teflon) diaphragm was used to pump the feed solution. Permeate vials were covered with aluminum foil to avoid the solvent losses due to evaporation at ambient conditions.

Membrane Morphology

The effect of solvent treatment on membrane morphology was investigated by taking Scanning Electron Micrographs (SEM) of the surfaces of membrane samples after static swelling and solvent permeation tests. The samples after solvent permeation were also investigated for morphological changes in their cross sections. The scanning conditions and equipment were same as used previously.¹⁵

RESULTS AND DISCUSSION

pH Stability

Because Chitosan is soluble in acidic solutions (pH < 6.5) due to protonation of $-\text{NH}_2$ groups, the surface crosslinking of *PANCHINF* mem-

Table I Membrane Stability at pH 2.5

Glutaraldehyde Concentration (% w/w)	Change in Pure Water Flux (%)		Change in PEG Transmission (%)	
	Crosslinking Time (h)		Crosslinking Time (h)	
	0.5	1	0.5	1
0 (control)	194	—	91	—
0.08	134	111	12	3
0.2	98	56	3	-2
0.5	29	44	-10	-15

branes is expected to reduce the number of —NH_2 groups of Chitosan and hence reduce the solubility below pH 6.5. Although PAN membranes are stable¹⁹ up to pH 10, composite membrane formation with Chitosan and subsequent surface crosslinking might improve the pH stability of composite membranes. Therefore, the pH stability was also investigated in basic solution (pH 11). Tables I and II show effects of glutaraldehyde concentration and CT on the change in pure water flux and PEG transmission after aq. acidic (pH 2.5) and basic (pH 11) solution treatment, respectively. The PEG with MW 600 Da was chosen as a test solute because most of the membranes crosslinked under present crosslinking conditions had molecular weight cutoff of about 600 Da.^{16,17} Both flux and PEG transmission values in Tables I and II are the average of two data sets with the standard deviation of 5 and 6% in case of fluxes and PEG transmission respectively.

It is clear from Table I that the changes in both pure water flux and PEG transmission after aq. acidic solution treatment decrease with increasing glutaraldehyde concentration at all CTs, indicating the higher stability at 0.5% glutaraldehyde concentration. This behavior is attributed to the increased crosslink density of Chitosan with less number of —NH_2 groups of Chitosan remaining for protonation, and hence dissolution, with increasing glutaraldehyde concentration. For the similar reasons changes in both flux and PEG transmission decreased at 1 h CT.

In general, Table II shows similar trends of changes in flux as well as PEG transmission as that observed in the case of pH 2.5 solution treatment (Table I). However, at pH 11, changes with glutaraldehyde concentration are not significant,

and changes in flux are about an order of magnitude smaller than those for pH 2.5. The slight changes in membrane performance after aq. basic solution treatment may be due to Chitosan swelling that is higher at lower glutaraldehyde concentration (lower crosslink density) and decreases with increasing glutaraldehyde concentration. The data from Tables I and II clearly indicates that the *PANCHINF* membranes are more stable at pH 11 than at pH 2.5 after crosslinking.

The typical data for swelling of *PANCHINF* membranes as a function of pH at different glutaraldehyde concentrations are shown in Figure 2(a) and (b) for CT of 0.5 and 1 h, respectively. It is apparent from Figure 2(a) and (b) that the swelling is higher at pH 2.5 and 12 among the pH range studied, while it is relatively constant between pH 4–10. The higher swelling at pH 2.5 may be due to protonation of —NH_2 groups, while at pH 12 it may be due to —NH^- group formation from the residual —NH_2 groups of Chitosan or slight hydrolysis of PAN and, hence, more water absorption in both cases. As expected, crosslinking has improved the pH stability below pH 6.5 up to pH 4; however, these membranes still could not be recommended for use below pH 4 and above pH 10.

Solvent Resistance

The four classes of organic solvents, namely alcohols, ketones, esters, and aliphatic hydrocarbons, which are commonly used in many chemical process industries, were selected for testing the resistance of *PANCHINF* membranes. The solvents selected from each class are listed with their relevant physical properties in Table III. It can be seen from Table III that the molecular weight

Table II Membrane Stability at pH 11

Glutaraldehyde Concentration (% w/w)	Change in Pure Water Flux (%)		Change in PEG Transmission (%)	
	Crosslinking Time (h)		Crosslinking Time (h)	
	0.5	1	0.5	1
0 (control)	6	—	-4	—
0.08	2	2	1	-1
0.2	4	2	-1	-1
0.5	0	-3	-6	-2

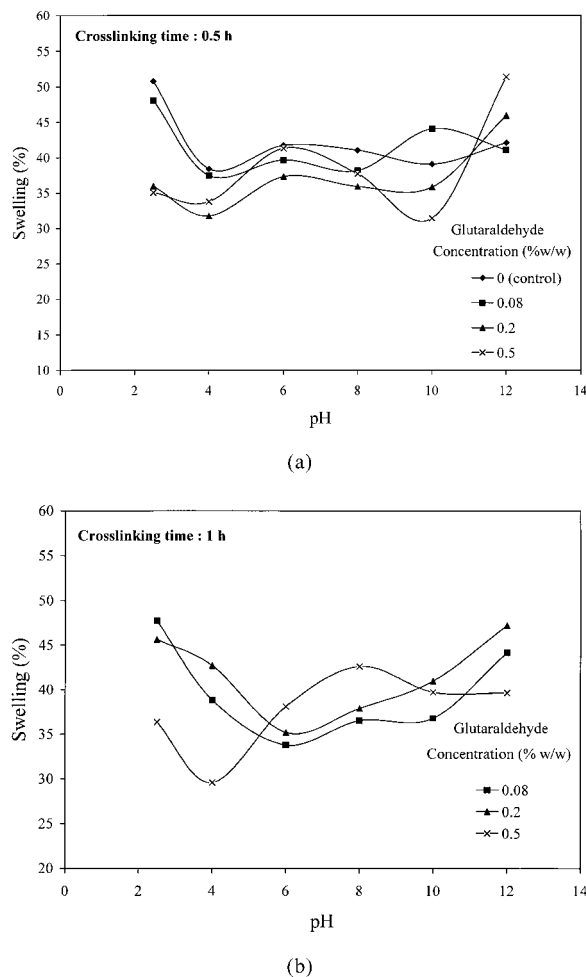


Figure 2 Effect of pH on swelling of membranes crosslinked with 0 (◆), 0.08 (■), 0.2 (▲), and 0.5% (×) glutaraldehyde for CT of (a) 0.5 and (b) 1 h.

increases in the order: MeOH < EtOH < IPA < MEK < EtOAc \approx hexane, while solubility parameter (δ) and dielectric constant (ϵ) show the opposite trend.

Swelling Studies

The swelling data of *PANCHINF* membranes in various solvents as a function of glutaraldehyde concentration are shown in Figure 3(a) and (b) for CT of 0.5 and 1 h, respectively. Each data point presented is the average of four replicates, and the corresponding average standard deviation for each solvent is also shown in Figure 3(a) and (b). It is apparent from Figure 3(a) and (b) that the swelling with each solvent is marginally lower at 0.2% glutaraldehyde; otherwise, it is independent of glutaraldehyde concentration. Figure 3(a) shows that swelling in the control membrane is lower than that in crosslinked membranes for each solvent. The slight increase in swelling after crosslinking may be due to an increase in hydrophobicity of membranes, caused by insertion of nonpolar $=\text{CH}-(\text{CH}_2)_3-\text{CH}=\text{}$ links between Chitosan chains, resulting in increased affinity with organic solvents.

However, further crosslinking results in pore size reduction and then formation of defects at 0.5% glutaraldehyde.¹⁶ Therefore, swelling (solvent holding capacity) initially decreases and again increases at 0.5% glutaraldehyde for both 0.5 [Fig. 3(a)] and 1 h [Fig. 3(b)] CT. Although there appears to be a trend in swelling with glutaraldehyde concentration, the overall change is not significant. However, there appears to be a trend among solvents studied, and is discussed below.

The top selective layer of Chitosan has polar hydroxy groups; hence, membrane–solvent polar

Table III Relevant Physical Properties of Solvents²²

Solvent	Molecular Weight (g/mol)	Absolute Viscosity at 25°C (cP)	Hildebrand Solubility Parameter (δ) (cal/cm^3) ^{1/2}	Dielectric Constant (ϵ) at 20°C
Alcohols				
Methanol	32	0.6	14.5	32.6
Ethanol	46	1.08	13.4	24.3
Iso-propanol	60	2	11.5	18.3
Ketones				
Methyl ethyl ketone	72	0.41	9.3	15.4
Esters				
Ethyl acetate	88	0.45	9.1	6.02
Aliphatic hydrocarbons				
Hexane	86	0.31	7.3	1.9

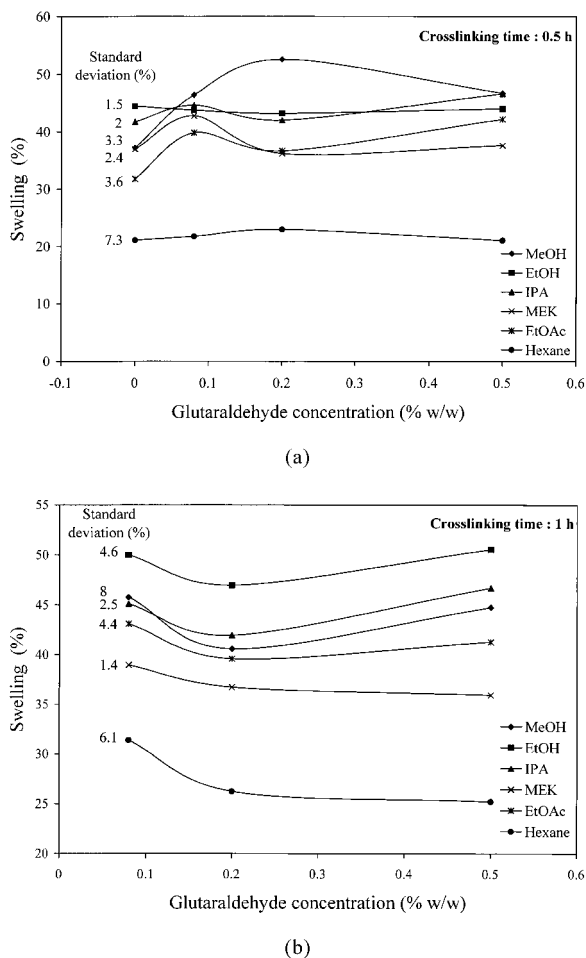


Figure 3 Effect of glutaraldehyde concentration on swelling of membranes in MeOH (◆), EtOH (■), IPA (▲), MEK (×), EtOAc (*), and hexane (●) for CT of (a) 0.5 and (b) 1 h.

interactions are more likely to govern the membrane swelling, and can be related to dielectric constant of solvents. Thus, the swelling is least in the case of nonpolar hexane ($\epsilon = 1.9$), while it is higher for relatively polar alcohols ($\epsilon = 18.3$ – 32.6) at both CTs. The swelling with MEK ($\epsilon = 15.4$) and EtOAc ($\epsilon = 6.02$) is between that with hexane and alcohols. This clearly indicates that swelling of membranes strongly depends on membrane–solvent polar interactions. Farnand et al.⁶ have also emphasized the importance of dielectric constant of solvent on the performance of cellulose acetate reverse-osmosis membranes for separation of inorganic salts from water, methanol, and ethanol solutions.

The trend in swelling of membranes with various solvents can also be correlated to solubility parameters of solvent (δ_s) and membrane (δ_m).

Solubility parameters for various solvents are reported in Table III, while that of Chitosan was calculated using group contribution to molar attraction constant (F) and molar volume of Chitosan, as explained in Appendix. The δ_m of Chitosan is likely to increase after crosslinking due to contribution from glutaraldehyde moieties; however, for discussion of results, δ_m of uncrosslinked Chitosan was used. The swelling of substrate material in composite membranes is also an important factor that determines the membrane performance. The difference between solubility parameters of membrane and solvent ($\Delta\delta$) was calculated for Chitosan ($\delta = 10.16$, Appendix) and PAN ($\delta = 12.5$, ref. 20), and are shown in Table IV. In general, more swelling would be expected for a membrane–solvent combination with a smaller $\Delta\delta$ value. It is clear from Table IV that $\Delta\delta_{\text{Chitosan}}$ is smaller for IPA, MEK, and EtOAc; therefore, these solvents are likely to have more affinity with Chitosan than MeOH, EtOH, and hexane. On the other hand, $\Delta\delta_{\text{PAN}}$ values indicate that alcohols are likely to have more affinity with PAN. Therefore, trends in swelling in Figure 3(a) and (b) indicate that contribution of PAN swelling could be higher in total swelling in the case of alcohols, whereas in the case of MEK and EtOAc, Chitosan is likely to swell more than PAN.

The importance of solubility parameters in membrane–solvent interactions has also been emphasized by Nomura et al.⁵ while studying the permeation of cyclohexane through various membranes.

Immersion Studies

The typical data for change in pure water flux of membranes after immersion in various test solvents is shown in Table V. It is observed from Table V that there are no definite trends in change in water fluxes with glutaraldehyde con-

Table IV Difference ($\Delta\delta$) in Solubility Parameters of Chitosan and PAN with Various Solvents

Solvent	$\Delta\delta_{\text{Chitosan}} (\delta_S - \delta_{\text{Chitosan}})$	$\Delta\delta_{\text{PAN}} (\delta_S - \delta_{\text{PAN}})$
MeOH	4.3	2.0
EtOH	3.2	0.9
IPA	1.3	−1.0
MEK	−0.9	−3.2
EtOAc	−1.1	−3.4
Hexane	−2.9	−5.2

Table V Change in Pure Water Flux (%) after Immersion in Solvent

Glutaraldehyde Concentration (% w/w)	Methanol	Ethanol	Iso-propanol	Methyl Ethyl Ketone	Ethyl Acetate	Hexane
Control						
0	0	4	5	2	1	1
Crosslinking Time: 0.5 h						
0.08	-4	4	11	-1	-2	1
0.2	12	8	11	1	-3	2
0.5	-5	-4	4	-1	-1	-1
Crosslinking Time: 1 h						
0.08	10	-5	-14	-3	-2	4
0.2	9	8	3	2	-1	1
0.5	8	12	-5	-1	-3	-1

centrations or CTs. However, it is important to note that there is no significant change in pure water flux after immersion in a test solvent with any of the membranes. It can be inferred from this observation that membranes do maintain their physical and chemical structure after immersion in solvents. To get corroborative support, changes in membrane morphology after immersion in solvents were studied using scanning electron microscopy. Figure 4(a) and (b) show scanning electron micrographs of surfaces of representative *PANCHINF* membrane before and after immersion in solvent (MEK), respectively. It is apparent that there is no significant change in the membrane morphology after immersing in solvent. A similar observation was made with membranes formed at all other glutaraldehyde concentrations and CTs, for each solvent. This observation supports the conclusion that membrane integrity was maintained even after immersing them in solvents for an appreciable time of 20 h.

Solvent Permeation

Based on the results of static swelling and immersion studies, actual solvent permeation rates were measured as a function of operation time to investigate the solvent resistance of membranes. The solvent fluxes as a function of operation time are shown in Figure 5(a)–(e) for membranes crosslinked with different glutaraldehyde concentrations and CTs, for permeation of MeOH, EtOH, IPA, MEK, and EtOAc, respectively. The values

presented are an average of two data sets with the corresponding standard deviation of 14, 9, 12, 9, and 14%.

Alcohols

Figures 5(a)–(c) show that solvent flux decreases in the order: MeOH > EtOH > IPA. This may be due to the combined effects of an increase in molecular weight, viscosity, hydrophobicity, and a decrease in the dielectric constant of alcohol (Table III) in that order. Another important observation from Figure 5(a)–(c) is that the magnitude of highest flux decreases with an increase in hydrophobicity of solvent as well as membranes. The increase in membrane hydrophobicity with increasing glutaraldehyde concentration in the case of *PANCHINF* membranes has been reported previously.¹⁶ Thus, the solvent–glutaraldehyde concentration pairs for the highest flux are—MeOH: 0.08%, EtOH: 0.2%, and IPA: 0.5%. This observation also supports the fact that solvent flux strongly depends on membrane–solvent polar and hydrophobic interactions.

As can be seen from Figure 5(a), the MeOH flux decreases with increasing glutaraldehyde concentration as well as CT. This may be attributed to a decrease in pore size and an increase in hydrophobicity of membranes with increasing glutaraldehyde concentration or CT.¹⁶ An increase in hydrophobicity of membranes results in reduced polar interactions, and hence, reduced affinity with MeOH. The MeOH fluxes in this study are of

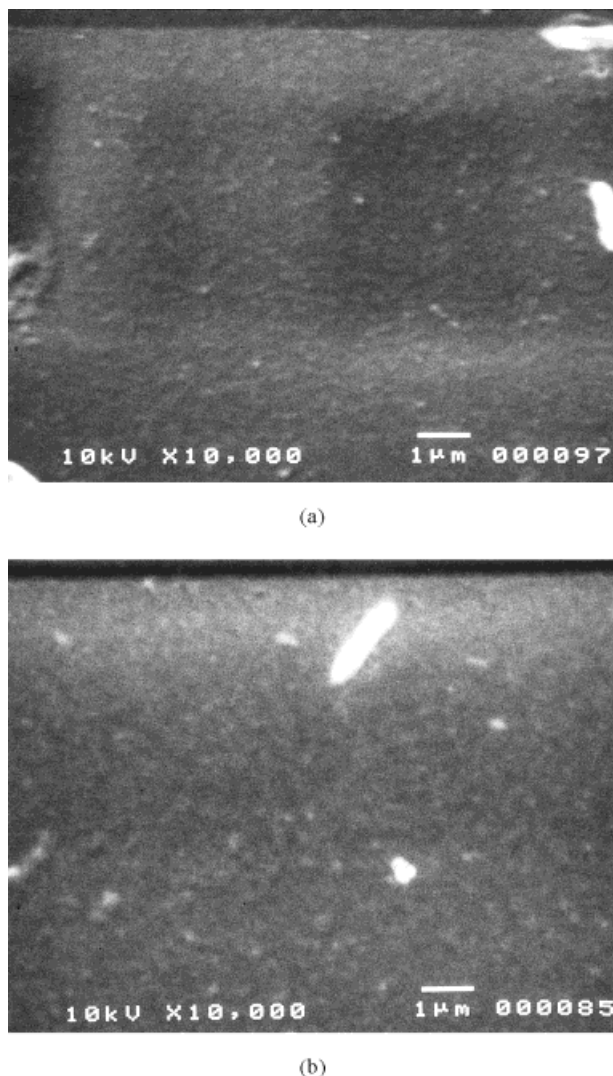


Figure 4 Scanning electron micrograph of surface of representative *PANCHINF* membranes (a) before and (b) after immersion in solvent (MEK).

similar magnitudes to those observed by Raman et al.¹⁰ for six commercial NF membranes under similar pressure and temperature conditions.

In the case of EtOH [Fig. 5(b)] and IPA [Fig. 5(c)], the solvent flux decreases with time for membranes crosslinked with 0.5% glutaraldehyde, the decrease being more in IPA than EtOH. This indicates strong hydrophobic interactions between relatively hydrophobic alcohols and membranes with maximum hydrophobicity¹⁶ in the present study. This may result in the loosening of the membrane structure and a subsequent change in pore geometry of the selective Chitosan layer. To verify this possibility, scanning electron

micrographs of membranes after EtOH and IPA permeation were taken, and are shown in Figure 6(a) and (b) for surfaces and 6(c) and (d) for cross sections, respectively. It is seen from Figure 6(a) and (b) that in the case of both EtOH and IPA permeation, the roughness of membrane surface has increased compared to that of the virgin membrane [Fig. 4(a)]. This observation clearly supports the above conclusion of a change in the surface morphology/pore geometry in the case of EtOH and IPA permeation, which in turn, may be due to lower $\Delta\delta$ values for these two solvents. It may be recalled that in static immersion studies with these solvents, there was no change in surface morphology. Therefore, changes in surface roughness observed in permeation experiments may be due to dynamic conditions of experiment, namely, the crossflow of solvent under applied pressure. Because $\Delta\delta_{\text{PAN}}$ values are smaller for both EtOH and IPA (Table IV), there is a slight change in swelling in the asymmetric layer of the PAN substrate, and this can be observed in Figure 6(c) and (d). These observations are consistent with relatively higher swelling observed in these alcohols [Fig. 3(a) and (b)].

It was also observed that the change in solvent flux from 0.5 to 1 h CT was higher for both EtOH and IPA than for MeOH. This indicates that hydrophobicity of both solvents as well as membranes does play an important role in the permeation performance of membranes.

MEK and EtOAc

Although molecular weights of MEK and EtOAc are higher and dielectric constants are lower than that of EtOH (Table III), the MEK and EtOAc fluxes [Fig. 5(d) and (e)] are similar to that of EtOH [Fig. 5(b)]. This may be attributed to the lower viscosities of both MEK and EtOAc than that of EtOH (Table III). The solvent flux for both MEK and EtOAc increases with increasing glutaraldehyde concentration at 0.5 h CT, while the opposite trend is observed at 1 h CT. It was reported that at 0.5 h CT, the hydrophobicity of membranes increased with increasing glutaraldehyde concentration,¹⁶ and both MEK and EtOAc are relatively more hydrophobic (less polar) than alcohols (Table III). Therefore, stronger affinity through membrane–solvent hydrophobic interactions leads to higher permeation of these solvents. The SEM studies showed no significant changes in either surface morphology or cross-sectional characteristics of membranes samples after MEK

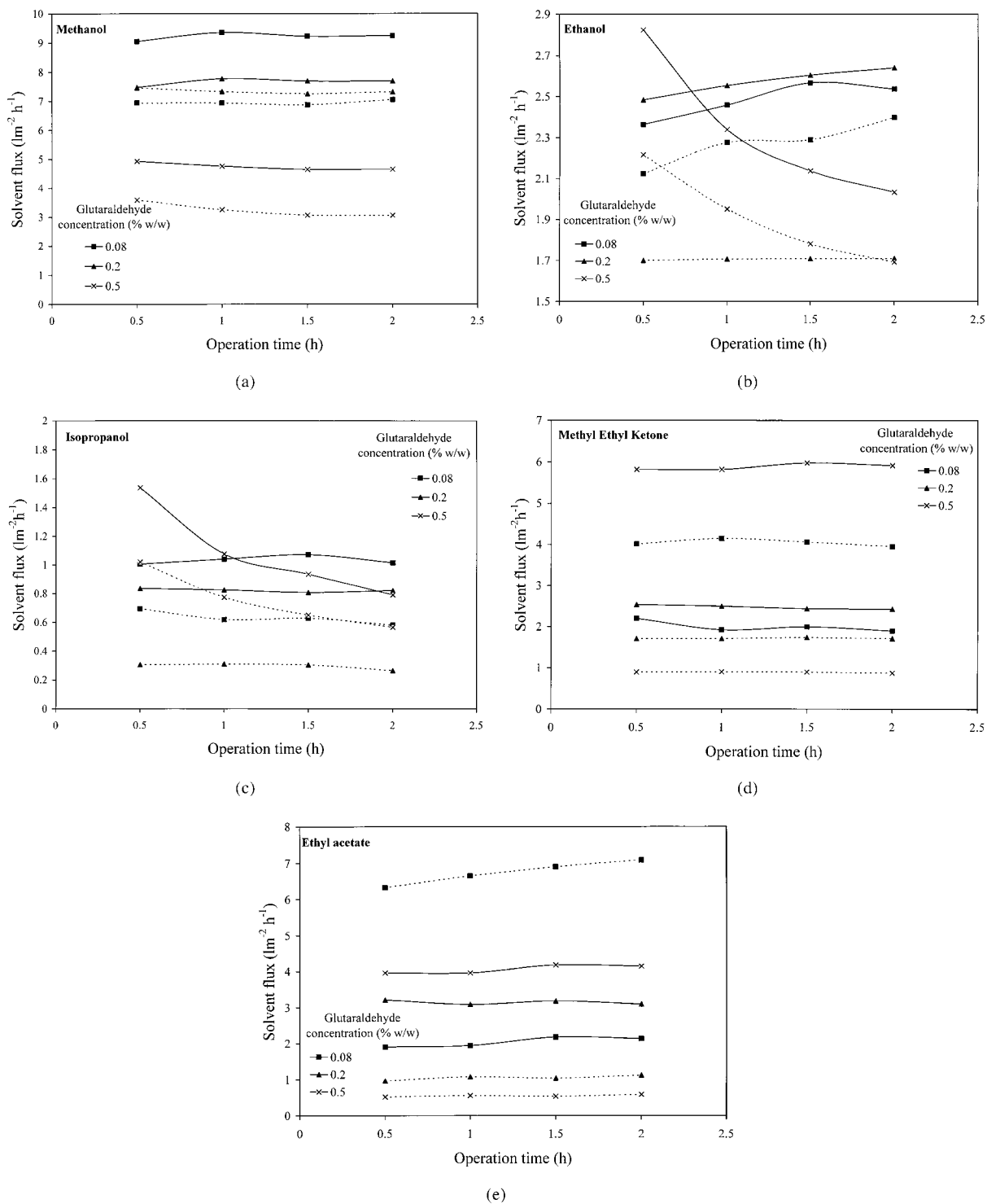


Figure 5 Effect of operation time on solvent flux for membranes crosslinked with 0.08 (■), 0.2 (▲), and 0.5% (×) glutaraldehyde for CT of 0.5 h (solid lines) and 1 h (dashed lines), for (a) MeOH, (b) EtOH, (c) IPA, (d) MEK, and (e) EtOAc.

or EtOAc permeation. This result is consistent with lower swelling in these two solvents compared to alcohols [Fig. 3(a) and (b)].

Hexane

Table III shows that molecular weight of hexane is similar to that of EtOAc and viscosity is lowest

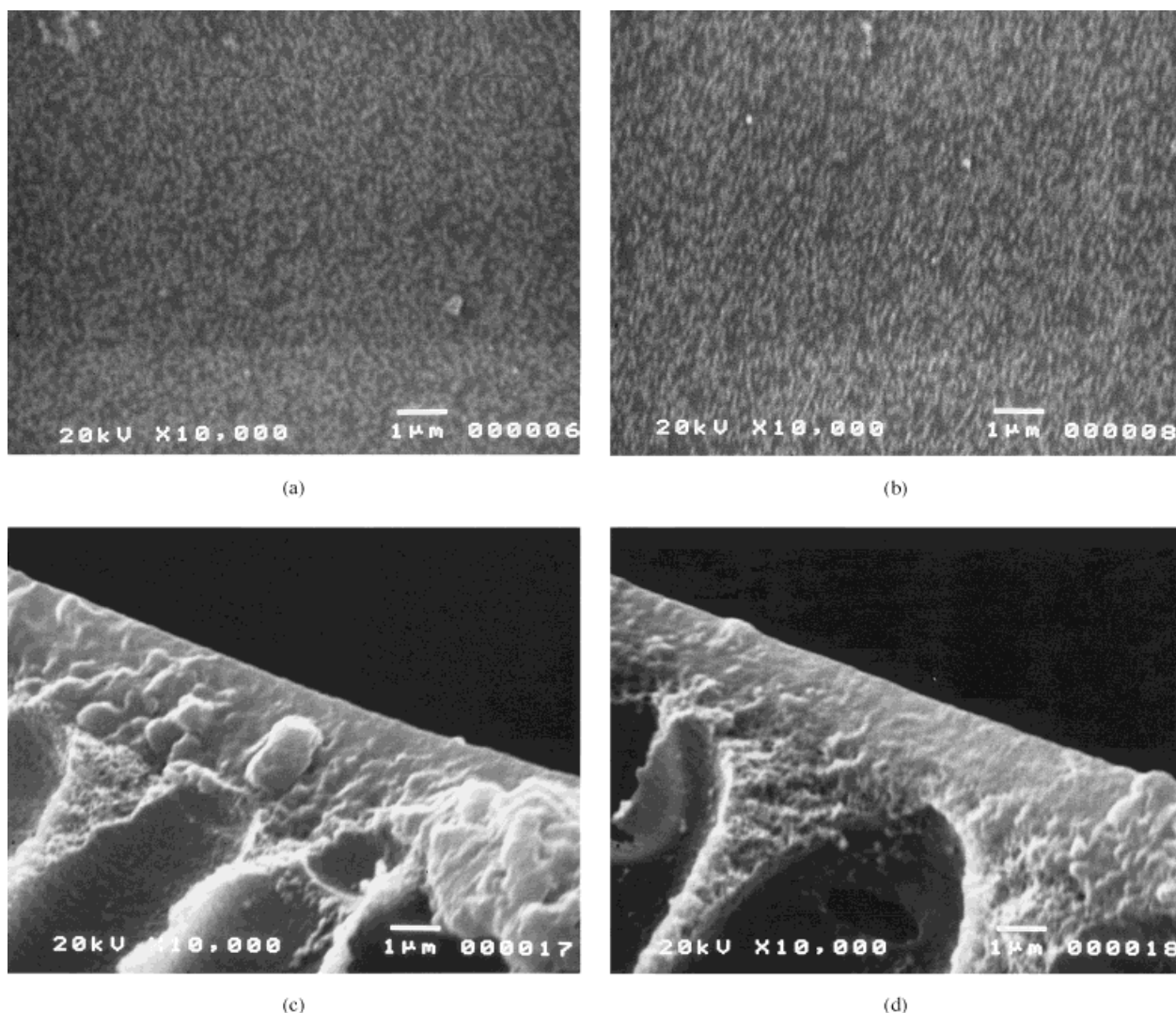


Figure 6 Scanning electron micrographs of surfaces of (a) EtOH and (b) IPA permeated membranes samples, while (c) and (d) show the corresponding cross sections, for membranes crosslinked with 0.5% glutaraldehyde.

among the solvents studied. Based only on molecular exclusion mechanism, one would expect the permeation of hexane through membranes in the present study, which have the molecular weight cutoff of ~ 600 Da.¹⁶ However, there was no significant permeation observable for hexane, even after the 2-h operation. This may be attributed to the lowest dielectric constant, maximum hydrophobicity and higher $\Delta\delta$ for hexane (Table IV). Although crosslinking increases hydrophobicity of the membranes, it seems that the increase is not adequate for nonpolar hexane, and hence, no permeation was observed.

The key observations from Fig. 5(a)–(e) are: (a) solvent flux remains almost constant with operation

for 2 h except for EtOH and IPA at 0.5% glutaraldehyde concentration and both 0.5 and 1 h CTs; (b) the decrease in solvent flux at 1 h CT relative to that at 0.5 h CT is an inverse function of dielectric constant of solvent as shown in Figure 7, i.e., higher the dielectric constant of solvent, the lower the flux decrease. This behavior also indicates the dependence of solvent permeation rates to solvent–membrane polar interactions.

Thus, swelling, immersion, and permeation studies with test solvents indicate that resistance of *PANCHINF* membranes to these solvents is excellent. It is also important to note that the membrane performance depends on the combined effects of solubility parameter, dielectric con-

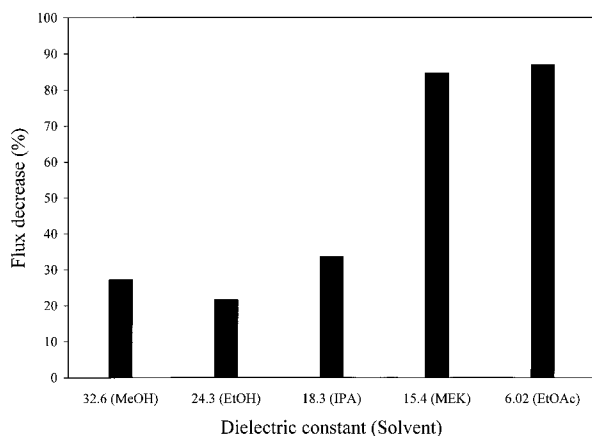


Figure 7 Effect of dielectric constant of solvent on flux decrease at 1 h CT relative to 0.5 h CT.

stant, and viscosity of solvents and the solubility parameter of membrane material.

This study has concluded that there is a potential for *PANCHINF* membranes for permeation of some industrially important solvents or waste streams containing traces of solvents. However, for developing practical applications, longer term permeation data with solvents needs to be collected and evaluated.

CONCLUSIONS

The novel surface crosslinked Chitosan/PAN composite NF membranes were found to be more stable at pH 11 than at pH 2.5 and the stability at

both pH values generally increased with increasing glutaraldehyde concentration. This was due to an increase in crosslinking, and hence, less of a number of —NH_2 groups of Chitosan remained available for protonation and subsequent dissolution at pH 2.5. At pH 11, the stability increased with glutaraldehyde concentration due to reduced swelling. Based on the swelling studies, the recommended usage of these membranes was in the pH range of 4–10.

The static swelling was least for nonpolar hexane, higher for alcohols, and in between for MEK and EtOAc. This trend indicated the strong dependence of membrane swelling on dielectric constant of solvents. The swelling was also found to depend on the difference between the solubility parameters of solvents and membranes. As expected, the swelling was higher in the case of solvents having comparable solubility parameter to that of membrane.

The solvent immersion studies and membrane morphology indicated that these membranes do maintain their structure after contact with test solvents for appreciable time. In flow-through tests, solvent fluxes were maintained up to 2 h, which indicated excellent solvent resistance of these membranes.

Generally, the solvent flux decreased with increased glutaraldehyde concentration or crosslinking time (CT). This might be due to decrease in pore size and increase in hydrophobicity of membranes with increasing glutaraldehyde concentration or CT. However, in the case of MEK

The Contributions of Different Groups to Molar Attraction Constant (F) are Tabulated Below^{20,21}:

Group	Molar Attraction Constant (F)	$[(\text{MPa})^{1/2} \text{ cm}^3 \text{ mol}^{-1}]$
	Chitosan- NH_2	Chitosan- NHCOCH_3
—C—O—C—	235×2	235×2
—NH_2	464	
Ring-6	–48	–48
$\text{—CH}_2\text{—}$	269	269
—CH—	176×5	176×5
—OH	462	462
—NH—		368
>C=O		538
—CH_3		303
Total (ΣF)	2497	3242

Therefore, actual total molar attraction constant (ΣF) for Chitosan = $(2497 \times 0.86) + (3242 \times 0.14) = 2601.3 (\text{MPa})^{1/2} \text{ cm}^3 \text{ mol}^{-1}$ Solubility parameter = $\Sigma F/V = 2601.3/125.1 = 20.8 (\text{MPa})^{1/2} = 10.2 (\text{cal/cm}^3)^{1/2}$

and EtOAc, the trends with glutaraldehyde concentration were opposite for 0.5 h CT.

MeOH fluxes were the highest and IPA fluxes were the least among the solvents studied. In the case of alcohols, the solvent flux decreased in the order: MeOH > EtOH > IPA. This may be attributed to the combined effect of increase in hydrophobicity, viscosity, and molecular weight of alcohol, in that order.

In the case of hexane, no measurable solvent flux was observed, despite its lowest viscosity and a molecular size comparable to EtOAc. This may be attributed to the lowest dielectric constant, maximum hydrophobicity, and higher difference in solubility parameter of hexane with membrane.

The membrane performance for permeation of nonaqueous solvents is governed by membrane-solvent polar and hydrophobic interactions as well as by viscosity of solvents.

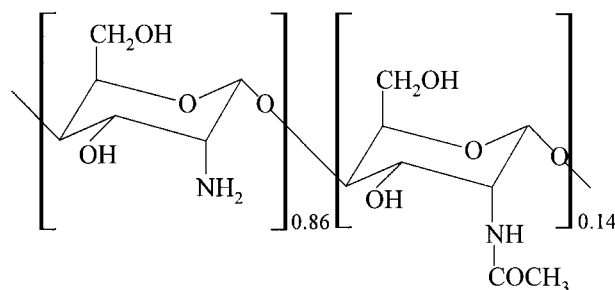
The results with test solvents indicate that these NF membranes have a potential for solvent recovery or treatment of waste streams containing traces of these solvents and other components of small molecular weights.

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APPENDIX

Calculation of Solubility Parameter of Chitosan

The repeat unit of Chitosan with the degree of deacetylation ~ 0.86 would be:



MW of repeat unit of Chitosan = $(161 \times 0.86) + (203 \times 0.14) = 166.88$ g/mol.

Density of Chitosan (determined on actual Chitosan film by buoyancy technique), $d = 1.3339$ g cm^{-3} at 25°C ,

Molar volume of Chitosan repeat unit, $V = \text{MW}/d = 166.88/1.3339 = 125.1$ $\text{cm}^3 \text{mol}^{-1}$.

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