Effects of surface crosslinking on sieving characteristics of chitosan/poly(acrylonitrile) composite nanofiltration membranes

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Effects of surface crosslinking on sieving characteristics of chitosan/poly(acrylonitrile) composite nanofiltration membranes[☆]

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Abstract

Effects of surface crosslinking of chitosan/poly(acrylonitrile) (PAN) composite nanofiltration membranes at different crosslinker (glutaraldehyde) concentrations and crosslinking times on their surface chemical composition and sieving properties such as pure water permeation, molecular weight cut-off and the rejection of mono/divalent salts and mono/oligosaccharides were investigated. Fourier transform infrared-attenuated total reflectance spectroscopy (FTIR-ATRS) and X-ray photoelectron spectroscopy (XPS) studies revealed the crosslinking of chitosan with glutaraldehyde as well as variations in chemical composition with glutaraldehyde concentration and crosslinking time. Pure water permeation/swelling in water decreased and rejection of salts and sugars increased with increasing glutaraldehyde concentration, indicating pore contraction and increase in hydrophobicity as well as pore tortuosity due to crosslinking. Molecular weight cut-offs of surface crosslinked membranes were in the range of 550–700 Da, a characteristic of nanofiltration membranes, whereas uncrosslinked membrane had cut-off of >1500 Da. The crosslinked membranes were found to be stable over 10-h operation for pure water permeation and the stability increased with increasing glutaraldehyde concentration. © 2000 Published by Elsevier Science B.V.

Keywords: Poly(acrylonitrile); Chitosan; Nanofiltration; Composite membranes; Crosslinking; Membrane preparation and structure

1. Introduction

Nanofiltration (NF) is relatively a new membrane process and is increasingly being used in a range of applications that involve removal of salts from small molecular weight organics or separation of small molecular weight solutes from macromolecules. Most of the NF membranes developed so far are composite in nature, with a selective layer on top of the microporous substrate. Various membrane materials have been used for a selective layer on polymeric or inorganic microporous substrates. The choice of materials depends on both chemical and physical

compatibility of selective layer with the substrate, which in turn determines the stability and performance of the resulting composite membranes. Poly(acrylonitrile) (PAN), one of the versatile polymeric materials, in addition to its well established use for asymmetric ultrafiltration (UF) membranes has been used as a microporous substrate for making composite membranes [1–3]. Chitosan, a natural hydrophilic biopolymer, has been used as a membrane material for reverse osmosis [4], pervaporation (PV) [1,5], and gas separation membranes [6], and recently we have demonstrated its use in composite UF membranes [7].

Since PAN is more hydrophilic compared to the commonly used polysulfone (PSF) substrate, the composite NF membranes of PAN with hydrophilic chitosan may be relatively more stable than chitosan/PSF composite membranes, during long-term operation. Although work on chitosan/PAN composite PV [1,2,8] and UF [7] membranes has been reported, to the best of our knowledge there is no literature on chitosan/PAN composite NF membranes. The hydrophilic chitosan/PAN composite NF membranes would be of interest in applications such as demineralization of whey, where hydrophilicity of the membranes would help to minimize fouling caused by protein adsorption. Most of the commercial NF membranes are charged, which is beneficial for removal of divalent salts by Donnan exclusion. However, charged membrane surface may cause significant fouling due to electrostatic interactions, particularly in processing protein containing feeds. Krajewska and Olech [9] have reported that crosslinking of chitosan gel membranes results in reduction in pore size and water absorption with increasing crosslinker (glutaraldehyde) concentration. Therefore it is of interest to study the formation of composite NF membranes with a hydrophilic and neutral (at pH $\geq$ 7.0) selective layer of chitosan on PAN substrate and subsequent surface crosslinking.

The present study reports the effect of surface crosslinking at different crosslinker (glutaraldehyde) concentrations and crosslinking times on surface chemical composition and sieving characteristics such as pure water permeation, molecular weight cut-off and rejection of model solutes, of chitosan/PAN composite NF membranes.

2. Experimental

2.1. Materials

PAN (MW $\approx$ 150 kDa) and chitosan (MW $\approx$ 116 kDa and degree of deacetylation (d.d.) $\approx$ 86%) were obtained from Polysciences, USA. Polyethylene glycols of different molecular weights and glutaraldehyde were obtained from Fluka, USA, and Aldrich, USA, respectively while all other solutes and reagents were obtained from Anachemia, Canada and used as received. Reverse osmosis treated water with a conductivity of $\approx$ 5×10^{-4} S m^{-1} was used for membrane preparation, swelling and permeation studies.

2.2. Preparation of chitosan/PAN composite NF membranes (PANCHINF)

The details of preparation of both base and composite membrane are described elsewhere [10]. Briefly, the PAN base membrane was cast from 14% solution in *N,N*-dimethyl-formamide and gelled in water at 20°C. The filtered and degassed chitosan solution in acetic acid (0.3 M)-sodium acetate (0.2 M) buffer was coated on the surface dried PAN UF base membrane by a finely polished glass rod. This membrane, after curing in a convection oven at 50°C for 24 h, was treated with aqueous (aq.) NaOH to convert chitosan acetate to chitosan. The NaOH treated membrane was washed several times with water and stored in water for 24 h before surface crosslinking. Since the mode pore size of PAN base membrane, determined by combined bubble point-solvent permeability method [11], was in the UF range (2×10^{-8} m), it is likely that chitosan chains might have penetrated into the pores of PAN base membrane.

2.3. Surface crosslinking of PANCHINF membranes

The surface crosslinking of PANCHINF membranes was carried out at 25°C using 0.02, 0.08

and 0.2% w/w aq. glutaraldehyde solutions for 0.5, 1 and 1.5 h with each solution. After crosslinking, composite membranes were washed several times with water before further characterization.

2.4. Surface characteristics

Samples of PANCHINF membranes for surface analysis were dried by solvent exchange with 50% aq. isopropanol, isopropanol and hexane in that sequence for 0.5 h in each solvent, followed by vacuum drying at 40°C for 3 days. The cross-sectional morphology of the representative composite membrane was characterized by scanning electron microscopy (SEM), whereas the variations in chemical composition on the surface at different crosslinking conditions were examined by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared-attenuated total reflectance spectroscopy (FTIR-ATRS) (also known as internal reflection spectroscopy). While the analysis conditions and instruments for SEM and XPS analysis were similar as reported previously [7], the FTIR-ATRS analysis details are as follows.

The coated surface of each membrane to be examined was placed in intimate contact on both sides of $(50 \times 20 \times 2)10^{-9}$ m^3 germanium (Ge) reflection element (refractive index = 4.0). Reproducible contact was achieved by using similar sample areas and identical membrane-to-plate force, achieved by pressure plates tightened by a torque wrench. The Midac spectrometer (model M-1700, USA) with a DTGS detector was used to detect the IR beam that enters and exits at 45° from the Ge element. The Ge element was cleaned by isopropanol and vacuum dried before recording each new spectrum. The spectra were recorded using GRAMS/32 program after ensuring that no peaks related to water vapor or CO$_2$ were observable. Both bare Ge element and membrane sample spectra were recorded after 100 scans. Surface spectra were ratioed to the stored spectrum of the bare, clean Ge reflection element.

2.5. Permeation characteristics

All permeation measurements including pure water permeation were carried out using a flow through cell (effective membrane area = 1.4×10^{-3} m^2) at a temperature, pressure and crossflow velocity of 25°C, 480 kPa and 0.75 m s^{-1}, respectively.

2.5.1. Molecular weight cut-off (MWCO)

Molecular weight cut-offs of all membrane samples were measured using 200 ppm aq. solutions of ethylene glycol and polyethylene glycols (PEG) (MW 200–1500 Da), separately. The concentrations of these neutral test solutes in feed and permeate samples were determined by Shimadzu 5000 Total Organic Carbon (TOC) analyzer.

2.5.2. Permeation of model solutes

The PANCHINF membranes were also characterized by determining the rejection of individual solutes (NaCl, MgSO$_4$, fructose, sucrose and raffinose) from their aq. solutions. The single solute concentrations in test solutions were 2000 ppm for salts and 1000 ppm for sugars. The concentrations of NaCl and MgSO$_4$ in feed and permeate samples were determined by conductivity measurements and atomic absorption spectroscopy (Varian, model SpectrAA 880), respectively, while those of sugars were determined by TOC analyzer.

3. Results and discussion

The average pore size of the composite membranes calculated using the PEG rejection data (Fig. 5) and Ferry's modified equation [12] was found to be of the order of $\approx 10^{-9}$ m. Therefore, after crosslinking the exterior surface, the diffusivity of glutaraldehyde molecules inside the top crosslinked chitosan layer may be reduced and hence we believe that crosslinking might have taken place only on the exterior surface of chitosan layer.

The reaction scheme for the crosslinking of chitosan with glutaraldehyde is shown below.

Chitosan

+

$$O=HC-(CH_2)_3-CH=O$$

Glutaraldehyde

Crosslinked Chitosan
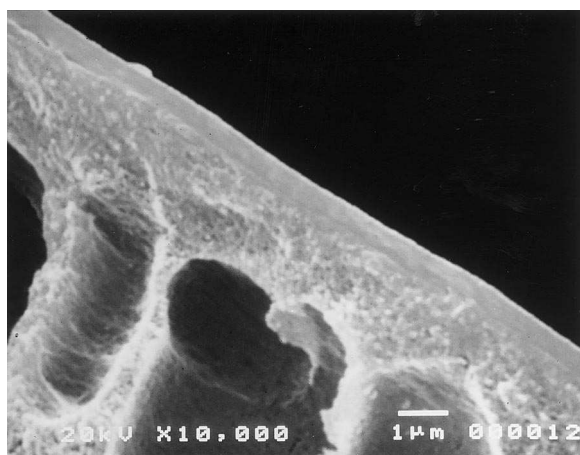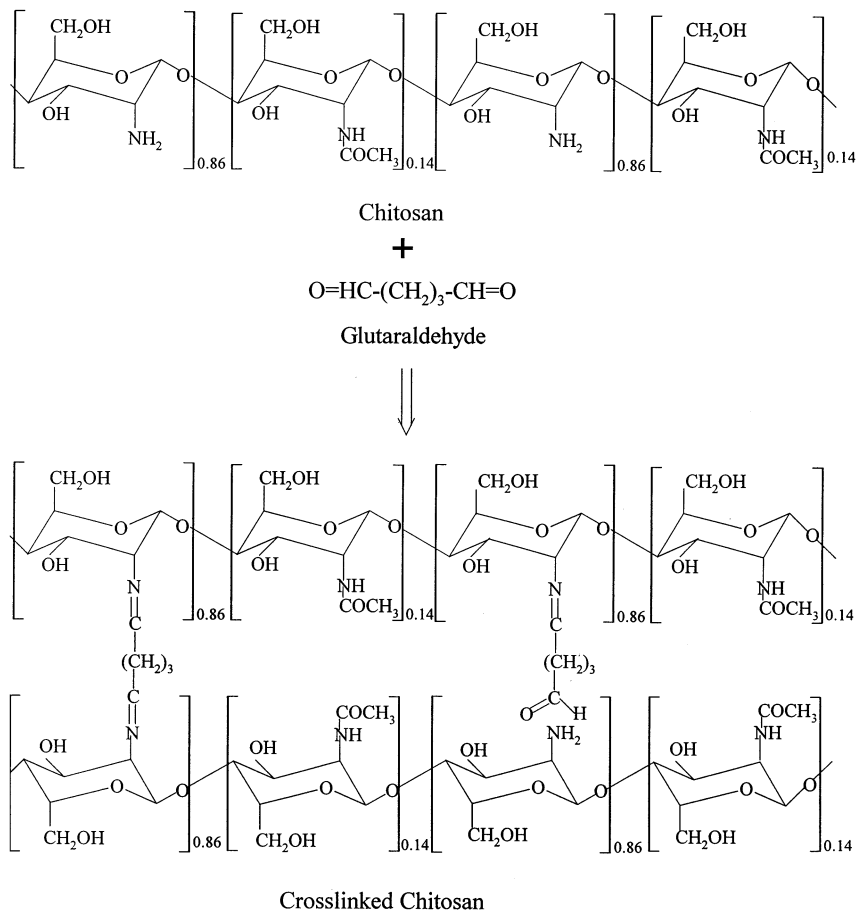
Fig. 1. Scanning electron micrograph of cross-section of a representative PANCHINF membrane.

However, it should be noted that molecules are presented without specific considerations to stereochemical conformations of various bonds.

3.1. Surface characteristics

3.1.1. SEM

The scanning electron micrograph of the cross-section of representative PANCHINF membrane (Fig. 1) clearly shows the presence of $\approx 5 \times 10^{-7}$-m thick, uniform coating of chitosan on the dense skin of PAN UF base membrane revealing the composite structure of the NF membrane prepared.

3.1.2. XPS

The effects of glutaraldehyde concentration and CT on the chemical composition of surface of
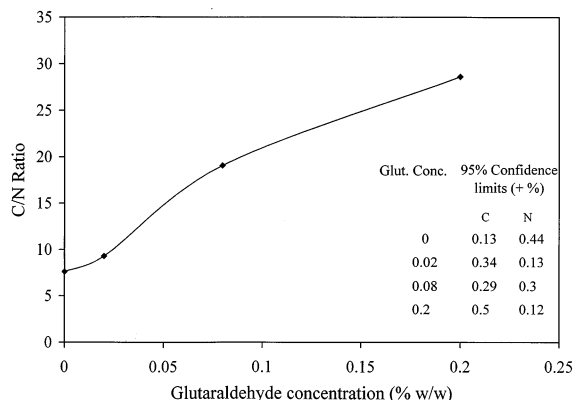
Fig. 2. Effect of glutaraldehyde concentration on the carbon/nitrogen ratio on the surface of PANCHINF membranes, determined by XPS studies, for 1 h CT.

PANCHINF membranes were studied by determining carbon/nitrogen (C/N) ratios. Fig. 2 shows the C/N ratios for control and representative crosslinked membrane as a function of glutaraldehyde concentration for 1 h CT. These data are the average of two measurements on two different spots on a single membrane and separate membrane for each glutaraldehyde concentration and CT. The 95% confidence interval limits for C and N are also shown in Fig. 2. It is apparent from Fig. 2 that the C/N ratio increases with increasing glutaraldehyde concentration as expected from reaction of chitosan with glutaraldehyde. This trend clearly indicates that the glutaraldehyde moieties were crosslinked to chitosan chains. The theoretical C/N ratios for chitosan (control), semi-crosslinked chitosan (only one aldehyde function unit) and fully crosslinked chitosan (two chitosan repeat units react with both aldehyde groups of glutaraldehyde molecule) are 6.28, 10.3 and 8.43, respectively. The increase in C/N ratios, however, is about two and three times higher at 0.08% and 0.2% glutaraldehyde, respectively than the theoretical ratio, even for fully crosslinked chitosan. This result indicates that more than one glutaraldehyde molecule reacted per chitosan repeat unit, however, under the crosslinking conditions used in this work only $-NH_2$ group of chitosan is likely to react with glutaraldehyde. There appears to be no plausible explanation for this unexpected result. Similar increase in C/N ratio with increasing glutaraldehyde concentration was observed with samples crosslinked for 0.5 and 1.5 h.

Table 1 shows the oxygen content on the membrane surface as a function of glutaraldehyde concentration and CT. These data are the average of two measurements on two different spots on a single membrane, and separate membrane for each glutaraldehyde concentration and CT. The 95% confidence interval limits are also shown in Table 1. It can be seen from Table 1 that the oxygen content on the surface generally increases with increasing glutaraldehyde concentration, the increase being clearer at 1.5 h CT. An oxygen value of 26.9 at 1 h CT and 0.02% glutaraldehyde is probably an error. This trend supports the increase in the concentration of pendant, unreacted aldehyde groups of bifunctional glutaraldehyde on the membrane surface. This may be due

Table 1
Effects of glutaraldehyde concentration and CT on surface oxygen content (atom %), as observed by XPS

Glutaraldehyde concentration (% w/w)	Crosslinking time (h)					
	0.5		1.0		1.5	
	Oxygen	Deviation[a]	Oxygen	Deviation[a]	Oxygen	Deviation[a]
0 (control)	18.1	0.2				
0.02	21.3	0.9	26.9	1.0	17.6	0.4
0.08	16.5	2.6	20.2	0	19.9	0.1
0.2	22.3	0.9	20.4	0.9	22.1	2.2

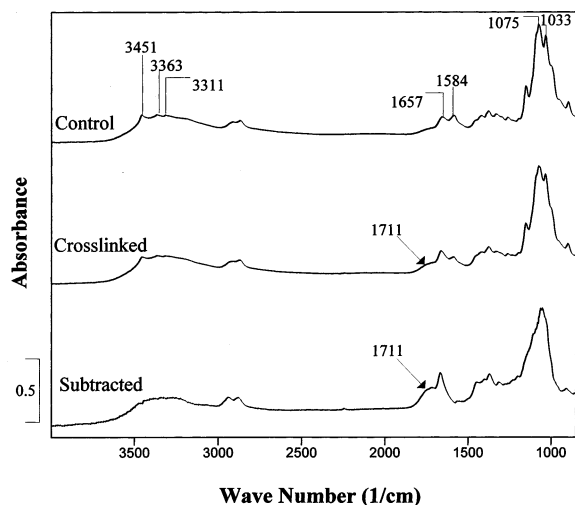[a] 95% Confidence interval limits ($\pm$%).

Fig. 3. FTIR-ATR spectra of (a) control, (b) representative crosslinked (0.2% glutaraldehyde, 1 h CT) PANCHINF membrane, and (c) subtraction of b from a.

to the fact that as crosslinking proceeds, the mobility of chitosan chains and hence the availability of reactive functional group ($-NH_2$) of chitosan chains may be decreased for further reaction with the second aldehyde group of glutaraldehyde. The presence of pendant aldehyde functionality is also evidenced by FTIR-ATR spectroscopy discussed in the following section. However, it should be noted that the theoretical oxygen content for semicrosslinked (one glutaraldehyde molecule per each chitosan repeat unit) is 15.1. Therefore, it appears from the oxygen content data (Table 1) also that more than one glutaraldehyde molecule reacted with each chitosan repeat unit.

3.1.3. FTIR-ATR spectroscopy

It is well known that the peak locations in FTIR-ATR (surface) spectra are identical to those in the transmission (bulk) spectra of the same material. Since the totally internally reflected beam penetrates to increasing depths of the sample with decreasing wave number, the FTIR-ATR spectral interactions are proportionately accentuated at smaller wave numbers.

The FTIR-ATR spectra for control and representative crosslinked (0.2% glutaraldehyde, 1 h CT) PANCHINF membrane are shown in Fig. 3

and are not corrected for the progressive increase in the absorbance due to increase in penetration depth at lower wave numbers. The penetration depths as a function of wave number were calculated as reported before [7,13] using refractive indices of these membranes and Ge element and angle of incident IR beam (45° in this case). The refractive indices of the control and crosslinked membranes were measured on samples prepared under similar conditions on glass plate instead of on PAN support and were found to be 1.6061 and 1.6066, respectively. Since the difference in the refractive indices of these two membranes was insignificant, the corresponding penetration depths were also similar and were found to be 7×10^{-7}, 3×10^{-7} and 2×10^{-7} m at 1000, 2240 and 3400 cm^{-1}, respectively.

Fig. 3 clearly shows the peaks corresponding to different vibrational modes of the functional groups of chitosan layer in case of control membrane. The major characteristic peaks observed in spectra of control and crosslinked membranes are shown in Table 2. It is important to note from Table 2 that the peak corresponding to $-C\equiv N$ stretching (2240 cm^{-1}) of PAN substrate is not observed in the control or crosslinked PANCHINF membranes. This is due to the fact that the chitosan coating thickness is $\sim 5 \times 10^{-7}$ m as observed by SEM, whereas the penetration depth at 2240 cm^{-1} as explained above is only 3×10^{-7} m. Thus observed peaks clearly reveal the presence of chitosan coating on PAN substrate.

In case of crosslinked membrane, it can be seen that in addition to all peaks present in the control membrane, there is a distinct peak at 1711 cm^{-1}, which may be due to the $>C=O$ stretching in H-bonded pendant aldehyde group of unreacted bifunctional glutaraldehyde. Another important observation from Fig. 3 is that the absorbance of the peak at 1657 cm^{-1} has increased in crosslinked membrane compared to that in the control membrane. This may be due to the overlapping of peak corresponding to $-N-H$ stretching in $-NHCOCH_3$ of original chitosan with that of $-C=N-$ stretching of newly formed Schiff's base between $-NH_2$ group of chitosan and $>CHO$ of glutaraldehyde. The formation of Schiff's

base between chitosan and glutaraldehyde has also been suggested by Uragami et al. [14]. In order to confirm the above two observations, we subtracted the spectrum of control membrane from that of crosslinked membrane and the resulting spectrum is shown in Fig. 3. It is clearly seen from the subtracted spectrum that the peak at 1711 cm^{-1} becomes sharp after subtraction, indicating the existence of a distinct peak at 1711 cm^{-1} in crosslinked membrane compared to the control one. Also, the area of the peak at 1657 cm^{-1} is 7.1 in crosslinked membrane spectrum and 6.6 in subtracted spectrum, indicating that at this frequency the two peaks corresponding to –N–H stretching (in –NHCOCH$_3$ of chitosan) and –C=N– stretching in newly formed Schiff's base do overlap, as mentioned above.

Thus, evidence of a distinct peak at 1711 cm^{-1} and overlapping of two peaks at 1657 cm^{-1} indicates the crosslinking of glutaraldehyde with chitosan. Similar observations were made in samples crosslinked at all other glutaraldehyde concentrations and crosslinking times.

3.2. Permeation characteristics

Crosslinking of chitosan chains may result in the insertion of hydrophobic glutaraldehyde moieties, which in turn might lead to decrease in both the hydrophilicity and swelling of chitosan layer in water and increase in pore tortuosity of membranes. It is expected that crosslinking of polymer chains may result in increase in mechanical constraints for chain mobility and hence increase in tortuosity. The effects of change in these membrane properties after crosslinking on the sieving characteristics are discussed below.

3.2.1. Pure water permeation/swelling studies

Table 3 shows the effects of glutaraldehyde concentration and CT on pure water flux. The table shows the average values of two measurements on two separate samples along with the corresponding 95% confidence interval limits. It is apparent from Table 3 that the pure water flux in crosslinked membranes generally decreases with increasing glutaraldehyde concentration and the decrease was more prominent at lower concentrations while gradual at higher concentrations. This may be attributed to the combined effects of increase in hydrophobicity, decrease in swelling (i.e. contraction of pores) and increase in pore tortuosity with increasing glutaraldehyde concentration. The swelling of membranes in water was measured by soaking the dried membranes in water for 24 h at 25°C and then weighing them after gentle blotting with tissue paper. The percentage swelling (S) calculated from dry (W_d) and wet (W_w) weights of membranes [$\%S = (W_w - W_d/W_d)100$] [15] is shown in Fig. 4 as a function of glutaraldehyde concentration at different CTs. The swelling data presented are average of two measurements taken on same sample after the interval of 24 h and the error bars corresponding

Table 2
Peak assignments in FTIR-ATR spectra of control and crosslinked membranes

Peak frequency (cm^{-1})		Peak assignments
Control membrane	Crosslinked membrane	
3451	3451	–O–H stretching (H-bonded)
3363	3363	–N–H stretching in –NH$_2$
3311	3311	–N–H stretching (H-bonded) in –NHCOCH$_3$
	1711	>C=O stretching (H-bonded) in pendant aldehyde
1657	1657	>C=O stretching (amide I) in –NHCOCH$_3$,
		–C=N– stretching in Schiff's base in crosslinked membrane
1584	1584	–C–N– stretching in –C–NHCOCH$_3$
1075	1075	–C–O–C– stretching in cyclic ether
1033	1033	–C–N– stretching in –C–NH$_2$

Table 3
Effects of glutaraldehyde concentration and CT on pure water flux ($1 \ m^{-2} \ h^{-1}$)[a]

Glutaraldehyde concentration (% w/w)	Crosslinking time (h)					
	0.5		1.0		1.5	
	Flux	Deviation[b]	Flux	Deviation[b]	Flux	Deviation[b]
0 (control)	8.9	1.2				
0.02	17.1	3.2	11.3	0.1	13.8	1.9
0.08	8.3	1.1	9.0	0.7	9.3	0.4
0.2	8.3	1.4	6.3	1.8	9.3	2.4

[a] Measured at temperature, pressure and crossflow velocity of 22°C, 480 kPa and 0.75 m s^{-1}, respectively.
[b] 95% Confidence interval limits ($\pm 1 \ m^{-2} \ h^{-1}$).

to 95% confidence interval limits are also shown in Fig. 4. It is clear from Fig. 4 that the swelling decreases with increasing glutaraldehyde concentration as expected from increase in hydrophobicity of membranes due to crosslinking. Krajewska and Olech [9] have observed similar trends in their study on chitosan (d.d. $\approx 70\%$) gel membranes. They have also reported the increase in pore tortuosity with increasing glutaraldehyde concentration. Although, in our study the d.d. of chitosan is higher ($\approx 86\%$) and chitosan is used as a selective layer in composite membrane, the trends in swelling with glutaraldehyde concentration seem to be similar to those observed by Krajewska and Olech [9]. Thus, reduction in swelling as well as increase in hydrophobicity and pore tortuosity leads to decrease in pure water flux. However, it should be noted that the swelling (water absorption capacity) at 1.5 h CT (Fig. 4) is higher than that at 0.5 or 1 h CT. This might be due to the formation of more tortuous path across the membrane thickness at these conditions of crosslinking.

3.2.2. Molecular weight cut-off

The effect of glutaraldehyde concentration on MWCO curves is shown in Fig. 5 for 0.5 h CT. These solute rejection data are the average of two replicates, with standard deviation of 3%. It is clear from Fig. 5 that the MWCO values are ≈ 1500, 700, 550 and 550 Da for samples crosslinked with 0 (control), 0.02, 0.08 and 0.2% glutaraldehyde, respectively. This trend clearly indicates that crosslinking with glutaraldehyde up to 0.2% concentration does result in contraction of pores and hence forms the membranes in nanofiltration range. Additionally, the MWCO curves have become sharper, i.e. pore size distribution has become narrower, in crosslinked membranes than in the control membrane. Similar results were obtained with membranes crosslinked for 1 and 1.5 h CT. Thus, these membranes have a potential for separation of monovalent salts from small molecular weight organics such as dyes and sugars.

3.2.3. Permeation of model solutes

NF membranes are generally characterized by the retention of mono/oligosaccharides and
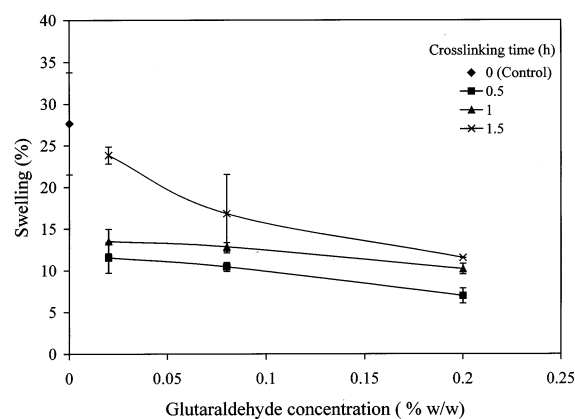

Fig. 4. Effect of glutaraldehyde concentration on swelling of PANCHINF membranes in water at 25°C for CT of 0 (♦), 0.5 (■), 1 (▲) and 1.5 h (×).
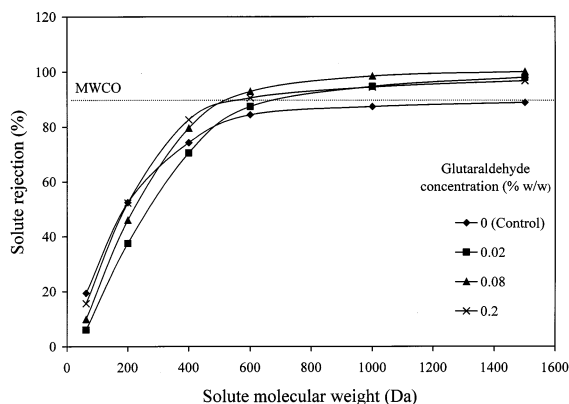
Fig. 5. Molecular weight cut-off curves for PANCHINF membranes crosslinked with 0 (♦), 0.02 (■), 0.08 (▲) and 0.2% (×) glutaraldehyde for 0.5 h.

mono/divalent salts. This information is very important for many industrial applications, especially for those involving separation of mono/divalent salts from small molecular weight organics. Table 4 shows the effect of glutaraldehyde

concentration on typical values of observed rejections of NaCl and $MgSO_4$ at different CTs, while Table 5 shows similar data for fructose, sucrose and raffinose. It can be seen from Table 4 that in case of crosslinked membranes the rejections of both NaCl and $MgSO_4$ increase with increasing glutaraldehyde concentration at all CTs while an increase at 1 h CT and then a decrease at 1.5 h CT for each glutaraldehyde concentration was observed. The increase in rejection of salts with increasing glutaraldehyde concentration might be due to the pore contraction caused by decrease in swelling and increase in pore tortuosity as explained previously in Section 3.2. It could also be due to the fact that the increase in hydrophobicity of membranes due to crosslinking, as evidenced by reduced swelling in water (Fig. 4), may result in repulsion of water of hydration of salt ions, which in turn may lead to increased rejection. However, there appears to be no plausible explanation at this time for the decrease in rejection at 1.5 h CT for each glutaraldehyde concentration. In order to explain the much higher rejections of

Table 4
Effects of glutaraldehyde concentration and CT on observed rejections (%) of mono/divalent salts

Glutaraldehyde concentration (% w/w)	NaCl			$MgSO_4 \cdot 7H_2O$		
	Crosslinking time (h)			Crosslinking time (h)		
	0.5	1.0	1.5	0.5	1.0	1.5
0 (control)	30.3	–	–	79.7	–	–
0.02	15.4	23.2	19.1	64.9	76.8	68.9
0.08	19.2	24.0	22.2	60.9	58.0	66.9
0.2	25.5	27.8	23.5	72.8	87.7	86.7

Table 5
Effects of glutaraldehyde concentration and CT on observed rejections (%) of mono/oligosaccharides

Glutaraldehyde concentration (% w/w)	Fructose			Sucrose			Raffinose		
	Crosslinking time (h)			Crosslinking time (h)			Crosslinking time (h)		
	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5
0 (control)	42.9	–	–	65	–	–	80.9	–	–
0.02	24.9	43.9	31.7	56.1	75.7	62.6	77.1	87.8	84.0
0.08	31.8	42.2	36.5	58.9	61.5	61.8	78.1	80.1	80.8
0.2	45.5	53.8	44.4	72.6	85.5	79.4	85.7	93.6	90.8

MgSO$_4$ compared to those of NaCl, we calculated the theoretical rejections of Na$^+$, Mg^{2+}, Cl$^-$ and SO$_4^{2-}$ ions using their hydrated ionic radii [16] and Ferry's modified equation [12] for a pore of 1-nm radius. The corresponding calculated rejections were 49, 59, 41 and 50%. It is clear from these values that the rejection of Mg^{2+} is higher by only 28% than that of Na$^+$ and rejections of Cl$^-$ and SO4^{2-} are not significantly different. Thus, based only on size exclusion mechanism the MgSO$_4$ rejection is not expected to be much higher than that of NaCl. Most of the commercial NF membranes are charged and hence Donnan exclusion is the principle mechanism of salt rejection. However, in the present case, the composite membranes are neutral, hence the Donnan exclusion mechanism is least likely and an increase in hydrophobicity due to crosslinking could be the main governing factor for the much higher rejection of MgSO$_4$ than that would be expected based only on the size exclusion mechanism.

An increase in fructose rejection with increasing glutaraldehyde concentration at all CTs (Table 5) can be explained similarly as above. The rejections of all three sugars increase with increasing CT up to 1 h and then decrease at 1.5 h CT (Table 5). We are not able to provide an explanation for this trend.

An important observation from Tables 4 and 5 is that the rejections of salts as well as sugars are higher for control membrane than for those crosslinked for 0.5 h, especially at 0.02 and 0.08% glutaraldehyde concentration. This is in spite of the fact that control membrane has higher MWCO (Fig. 5). The following hypothesis can explain this behavior. It is well known that the porous membrane is made up of void and solid portions. The crosslinking of the membrane material, i.e. chitosan, would result in increase in shrinkage of membrane material. This in turn could lead to two possibilities: (i) widening of some pores due to shrinkage of adjacent solid portion itself and (ii) contraction of some pores due to shrinkage of solid portion that surrounds these pores. The hypothesis that may work in a particular case will depend on the degree of crosslinking. In case of control membrane, chitosan is completely swollen, but with lower degree

of crosslinking (0.02 and 0.08% glutaraldehyde) the material contracts while expanding the pores, therefore salt rejections decrease compared to that of control membrane. However, at higher degree of crosslinking (0.2% glutaraldehyde) whole material including that surrounding the pores contracts, resulting in decrease in pore size and increase in pore tortuosity and subsequent increase in solute rejections.

After comparing the rejections of salts (Table 4) and sugars (Table 5) it can be concluded that these membranes have a potential for separation of mono/divalent salts from small molecular weight organics having molecular weights of $\geq$ 1000 Da.

3.3. Membrane durability

Although one can form a composite membrane from different combinations of substrate and coating materials, the performance of the resulting membrane would depend on the physical and chemical compatibility of the two materials. In order to study the long-term performance of the PANCHINF membranes, the effect of glutaraldehyde concentration and CT on change in the pure water flux after 10 h operation was measured and is shown in Table 6. It is observed from Table 6 that the percentage flux change decreases with increasing glutaraldehyde concentration as well as CT, indicating an increase in membrane stability, i.e. stronger adherence of chitosan layer with PAN substrate with increasing crosslinking. This may be attributed to the increase in hydrophobicity of chitosan layer with increased crosslinking and hence improved compatibility of chitosan with PAN substrate.

In a separate experiment, control and crosslinked membranes were incubated in water at 25°C for 24 h under static conditions and this water was then analyzed for total carbon by TOC analyzer. The objective of this experiment was to investigate any leaching of chitosan layer from PAN support. It was observed that the control membrane released 134 ppm total carbon while crosslinked membranes released only 2–11 ppm total carbon per gram of dry membrane. This observation also clearly indicates significant in-

Table 6
Effects of glutaraldehyde concentration and CT on membrane durability

Glutaraldehyde concentration (% w/w)	% Change in pure water flux after 10-h operation		
	Crosslinking time (h)		
	0.5	1.0	1.5
0 (control)	28.1	–	–
0.02	20.3	11.4	24.2
0.08	14.4	9.8	2.7
0.2	7.3	5.3	5.5

crease in the compatibility of chitosan layer with PAN substrate after crosslinking, which may be attributed to the increased hydrophobicity and tightening of the mechanical structure of chitosan layer. Thus, both the flux change and total carbon release data strongly suggest that crosslinking does ameliorate the stability of PANCHINF membranes.

4. Conclusions

This study concluded that crosslinking of top surface of chitosan/PAN composite NF membrane with glutaraldehyde could improve the membrane stability and lower molecular weight cut-offs.

The increase in C/N ratio on the membrane surface with increasing glutaraldehyde concentration as well as CT, observed by XPS spectroscopy, indicated an increase in crosslinking. FTIR-ATR spectra showed peaks characteristic of chitosan in the control membrane, whereas in case of crosslinked membranes, a distinct peak at 1711 cm^{-1} (due to $>C=O$ stretching of pendant unreacted H-bonded aldehyde group) and increase in the area of the peak at 1657 cm^{-1} (due to additional absorbance corresponding to $-C=N-$ stretching of newly formed Schiff's base) was observed. These two observations clearly revealed the crosslinking of chitosan on the surface.

Pure water flux/swelling in water decreased and rejections of salts and sugars increased with increasing glutaraldehyde concentration during crosslinking treatment and may be attributed to the increase in hydrophobicity as well as pore tortuosity and pore contraction. The NaCl rejections were between 15 and 35% while sugar rejections ranged from 45 to 90% depending on molecular weight of sugar. The molecular weight cut-offs of crosslinked membranes reduced to ∼ 600 Da from ≈ 1500 Da in uncrosslinked (control) membranes.

These composite membranes were found to be increasingly stable in aqueous medium at higher glutaraldehyde concentration and CT studied, indicating stronger adherence of chitosan layer to PAN substrate, after crosslinking. This study indicated that with a suitable combination of glutaraldehyde concentration and CT, composite membranes with desired MWCO in the nanofiltration range could be prepared. The membranes crosslinked for 1 h with 0.08–0.2% glutaraldehyde could be better candidates.

Based on the MWCO and model solute rejection data, it can be concluded that these hydrophilic NF membranes have a potential for the separation of mono/divalent salts from small molecular weight organics as well as to process streams which induce fouling of membranes due to protein adsorption, e.g. for demineralization of protein containing feeds.

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