Influence to the Performance of Cellulose Acetate Reverse Osmosis Membranes by Fibers Addition

A.P. Duarte,[1,2] J.C. Bordado,[1] M.T. Cidade[2]

[1]ICTPOL, IST, Departamento de Engenharia Química e Biológica, Torre Sul, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[2]Departamento de Ciência dos Materiais e CENIMAT, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal

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ABSTRACT: The asymmetric membranes based on cellulose acetate are mainly applied for separations in aqueous systems and in reverse osmosis processes, although they can also be used in the so-called salinity process of energy generation. These applications require membranes with considerable water permeability and high salt rejection. In this paper the improvements resulting from the addition of two different types of fibers on the permeability performance of the membranes (water permeability and salt rejection) as well as on mechanical properties are presented. Concerning the water permeability and salt rejection, the influence of four different contents of cellulosic fibers (CF) and anionic diethylaminoethyl cellulose (DEAE) fibers has been studied and the optimum value was chosen after measuring water permeability and salt rejection of the membranes. To study the mechanical performance, membranes with six different contents of these two types of fibers were produced. Both permeability and mechanical test results obtained for membranes with different contents of fibers were compared with the ones for the membranes produced from the same solution but without fibers. In terms of permeability tests, the membranes with 0.5 wt % CF fibers present the best results, with water permeability 22.8% higher than the membrane without fibers, while the salt rejection only decreases by 7.3%. Concerning the mechanical properties, the best membrane would be the one with 3 wt % CF fibers, however the membrane with 0.5 wt % CF fibers still present a toughness 18.9% higher than the membrane without fibers. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2321–2328, 2008

Key words: membranes; power production; fibers; permeability; mechanical properties

INTRODUCTION

Asymmetric cellulose acetate based membranes present outstanding properties for power production by reverse osmosis (RO), potential use for desalination of seawater,[1,2] as well as for salt separation in chemical process industries.

The cellulose acetate asymmetric membranes were the first to be used with success for RO processes,[3,4] mainly because they are relatively inexpensive, easy to produce and have good resistance to fouling as well as a high water permeability and salt rejection. However, they can only operate in a pH range of 4–6 and at low temperatures and they are susceptible to microbiological attack.[5]

The integrally asymmetric cellulose acetate based membranes are prepared in several steps, as follows: First, a solution of cellulose acetate is prepared in an appropriate solvent or system of solvents and the membrane is obtained by casting the solution with a film-drawing device with a precise slit width. In the second step, the volatile components of the solvent are partially vaporized, at room temperature and then the liquid film is immersed in a water bath, giving rise to the phase inversion, which leaves the membrane in the form of a water-swollen anisotropic gel of cellulose acetate.[6] In the last step, an optional one, the membrane can be submitted to an annealing post treatment in a warm water bath, solidifying in the previous described structure with a relatively low decrease in its water permeability.

Asymmetric membranes, prepared by phase inversion, consists of a very dense and thin active layer (0.1–1 μm) on the top of a highly porous and thick substrate (100–200 μm) and display the important feature of combining high salt rejection with high water permeability. The kind of active or ''skin'' layer structure, as well as hidrophobicity/hydrophilicity of the polymer surface, results in different polymer-water interactions and therefore in different selective permeation characteristics of the membrane.[7]

Correspondence to: M. T. Cidade (mtc@fct.unl.pt).

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The majority of the investigations concerning the cellulose acetate reverse osmosis membranes are mainly focused on the theoretical aspects that explains the permeability of the membranes. Dias et al.,[7] for example, studied the water structure in the pores of the membranes by ATR–FTIR spectroscopy including its correlation with the permeation properties of the membranes.

They showed that, for cellulose acetate membranes, a correlation between the permeation properties and the structure of water in the active layer is achieved, lower liquid-like water structures corresponding to lower values of salt (NaCl) rejection.

The results obtained for the membranes produced with cellulose acetate and cellulose butyrate[7] also show that membranes of the same material (i.e., same surface properties) and different permeation performance, present different adsorbed water structures in the active layer, whereas membranes that present different chemical composition but similar permeation properties (i.e., similar morphology) show similar adsorbed water structure in the active layer. So, it seems that the chemical composition is less important that the membrane's morphology.[7]

Kulkarni et al.[8] investigated the pore structure and the morphology of cellulose acetate RO membranes using Small-Angle Neutron Scattering (SANS). They analyzed a phase-inversion on the dry state of the annealed and nonannealed membranes.[8] The scattering of nonannealed membranes showed a presence of a discrete pore size distribution in the intermediate thickness and a region with a rather sharply defined pore size distribution, while the membranes submitted to an annealing treatment presented a much wider pore size distribution all over the membrane.[8]

The influence of the content of cellulosic fibers on water permeability and salt rejection of the membranes was already reported in Ref. 9. The obtained results indicate that the addition of cellulosic fibers to the membrane's solution influences the water permeability of the membranes. It increases consistently the water permeability until 0.5 wt % of fibers (in relation to dry weight).

Concerning the salt rejection, the addition of cellulosic fibers led to a slight decrease when compared to the membrane without fibers, independently of the content used. The mechanical properties confered by this type of cellulosic fibers was already studied for other cellulosic films by Borges et al.[10]

In this study, the mechanical properties of our integrally asymmetric membranes with cellulosic fibers are reported. In addition, DEAE fibers usually used as anion exchanger were also added to the membranes solution for study of their influence in the permeability and mechanical performance of the membranes.

Having in mind the comparison of permeability and mechanical characteristics of the membranes produced with the two different types of fibers, the membranes were prepared with the same starting casting solution described in the U.S. Pat. 4,340,428 published in 1982.[11] The permeability results for the membranes with the cellulosic fibers are reported once again (even though in a slightly different way) to be able to compare the results for the two different types of fibers.

To study the effect of the addition of CF and DEAE fibers, we comparatively analyzed the permeability performance (water permeability (A) and salt rejection (R) values) and the mechanical performance (Young's modulus (E), ultimate tensile strength (UTS), and elongation at break (ε_u)) for the membranes produced without fibers and with different contents of each type of fibers.

EXPERIMENTAL

Materials and methods

Cellulose diacetate ($M_w \sim 30{,}000$ g mol^{-1}, 39.8 wt % acethyl content) was received from Aldrich (180955; Madrid, Spain). The cellulose triacetate used was supplied by Sigma-Aldrich (181005; Madrid, Spain) with 46 wt % acethyl content (average).

The cellulosic fibers used were received from Sigma (S3504-Sigmacell R type 20) and are microcrystalline powder particles (average size 20 μm), usually used in chromatography columns.

The diethylaminoethyl cellulose fibers used were received from Sigma (DEAE-cellulose) and are microgranular cellulose weakly basic anion exchanger (size 60–130 μm). 1,4-Dioxan was supplied by Panreac Quimica S.A (Barcelona, Spain) and has a 99.5% of minimum purity. Methanol and acetone were used as received from Labsolve (Lisbon, Portugal). The methanol has a minimum purity of 99.5% and acetone of 99%. Acetic acid with a minimum purity of 99.8% was supplied by BDH Anala R (England).

The water permeability (A) of the membrane was measured at 8 bar with low pressure filtration cell mod. GN-10/400 from Berghof GmbH (Eningen, Germany).

The determination of the salt rejection was performed using inlet water with a concentration of the salt (NaCl) in water of 5 g/L and the conductivity of effluent water from the membrane was measured with Conductivity meter mod. HI 8733 of Hanna Instruments (Ronchi di Villafranca, Italy).

The morphology of DEAE and cellulosic fibers used were analyzed by observation of membranes made with both types of fibers with a polarizing optical microscope (POM) from Olympus model BH2

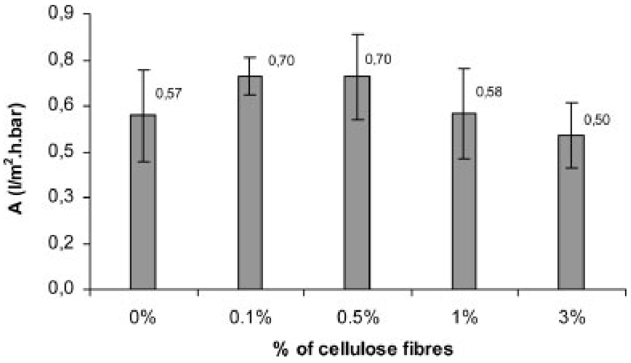

Figure 1 Average water permeability data for the membranes produced with different contents of CF.

TABLE I
Average Swelling Percentage of Membranes Produced with Different CF and DEAE Fibers Content

Fibers type	Fibers content (wt %)	% Swelling (*S*)	
		S	σ(*S*)[a]
Without Fibers	0.0	21.49	6.78
CF Fibers	0.1	19.33	3.40
	0.5	17.25	4.61
	1.0	17.01	3.71
	3.0	16.94	1.62
DEAE Fibers	0.1	19.87	6.65
	0.5	19.37	6.28
	1.0	17.40	4.86
	3.0	17.36	3.63

[a] Standard deviation.

and registered with a Digital video camera from Sony model SSC-DC50AP connected to a PC.

The mechanical tests were performed with membrane samples with 7.45 × 2.0 cm (length × height) on a tensile machine from Shimadzu, model AG-50KNG, with a load cell Shimadzu, model SBL 500 N. A cross-head speed of 5 mm/min and a load cell of 500 N were used.

Procedure

The membranes were produced with a casting solution prepared with the following raw materials: 45.77 wt % dioxane, 17.61 wt % acetone, and 8.45 wt % acetic acid as solvents; 14.09 wt % methanol as non-solvent, and 7.04 wt % cellulose diacetate and 7.04 wt % cellulose triacetate.

The membranes were obtained by spreading the solution (at room temperature $T \cong 25°C$) on a glass plate with a calibrated ruler whose thickness was previously selected, at a constant speed of 23 mm/s using an Automatic Film Applicator from Braive Instruments.

After 15 s for evaporation of the solvent, the polymeric film on the glass was immersed in an ice-water bath (0°C) during 15 min. After that, the film was placed in a water bath ($T \cong 4°C$) for 2 h. The last step of the process of preparation is the annealing post treatment with immersion for 15 min at 80–85°C.

Because the main objective of this work was to correlate the percentage of CF and DEAE fibers used with the permeability and mechanical properties of the membranes, we have analyzed comparatively water and salt rejection values of the membranes produced with 100-μm of thickness without fibers and with four different contents of the two types of fibers, as well as the mechanical characteristics (Young's modulus, ultimate tensile strength and elongation at break) of the membranes with 250-μm of thickness and produced without fibers and with six different contents of the two types of fibers.

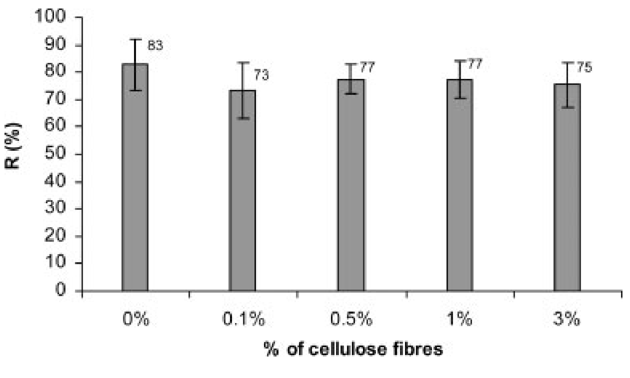

Figure 2 Average salt rejection data for the membranes produced with different contents of CF.

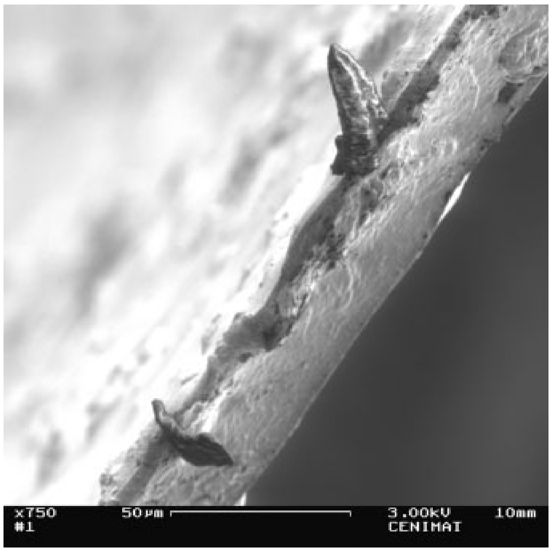

Figure 3 SEM image of a membrane produced with 10 wt % of CF fibers (average size = 20 μm).

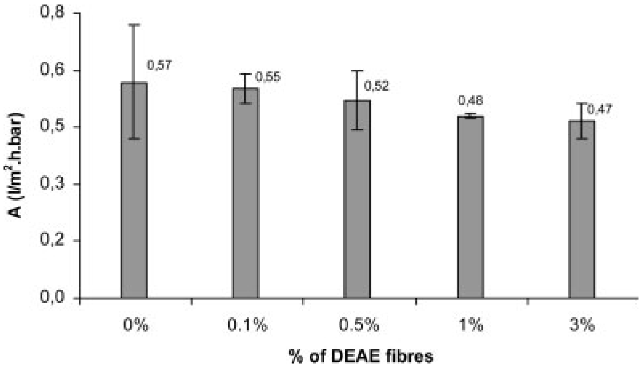

Figure 4 Average water permeability data for the membranes produced with different contents of DEAE fibers.

The use of the same thickness for both permeability and mechanical properties would be advantageous; however, it was found that for the mechanical tests a lower thickness, as the one used for the permeability tests, presented technical problems, namely lower reproducibility and higher experimental errors, so that it was decided to increase the thickness and not to compromise the results, because we were not interested in the absolute results but to be able to distinguish from different fiber contents, and, expectably, the membranes that presented better mechanical properties for the higher thickness, would be the same for the lower thickness.

The water permeability was calculated using the following equation (assuming that specific gravity is very close to 1):

$$A = \frac{V}{A_{\text{memb}} \times t \times p} \tag{1}$$

where A is the water permeability of the membrane (L/m^2 h bar), V is the volume of water though the membrane in a given time t (L), A_{memb} is the area of the membrane (m^2), t denotes time (h), and p is the pressure across the membrane (bar).

The salt rejection values (R) were calculated using the following equation:

$$R = \frac{C_0 - C_{\text{memb}}}{C_0} \times 100 \tag{2}$$

where R is the salt rejection (%), C_0 is the conductivity of salty water at the pressure side at the beginning of the experiment (mS), and C_{memb} is the conductivity of water that went through the membrane (mS).

The eq. (2) assumes that conductivity has a linear relationship with the salt concentration, and this is approximately correct for the relevant range of concentrations.

The water permeability and salt rejection values of the membranes produced with the following contents of cellulosic (CF) and diethylaminoethyl cellulose (DEAE) fibers (in relation to dry weight): (1) 0 wt %, (2) 0.1 wt %, (3) 0.5 wt %, (4) 1.0 wt %, and (5) 3.0 wt % were analyzed.

To measure the swelling capability, the membranes were weighted when dry and after 48 h in a salty water bath with 5 g/L of NaCl.

The mechanical performance (Young's modulus, ultimate tensile strength, and elongation at break) of the 250 μm membranes were analyzed for the following contents (in relation to dry weight) of both types of fibers: (1) 0 wt %, (2) 0.1 wt %, (3) 0.5 wt %, (4) 1.0 wt %, (5) 3.0 wt %, (6) 5.0 wt %, and (7) 10.0 wt %.

RESULTS AND DISCUSSION

The membranes were produced using the same casting solution but with different contents of both types of fibers and under the effect of similar external conditions (mainly temperature and humidity).

Permeability tests

The average value of the water permeability, (A), and salt rejection, (R), for five membranes obtained for each content of both types of fibers, along with the error bars, is presented in the following figures.

Figures 1 and 2 present the results of water permeability and salt rejection for the membranes produced with different contents of cellulosic fibers (CF).

The permeability measurements made with the membranes without CF and with four different CF contents, indicate that membranes with 0.1 and 0.5 wt % CF present better average water permeability values than the membranes without it. However membranes with 1 and 3 wt % have lower A values. So, it is possible to conclude that the addition of cellulosic fibers to the membrane solution influences

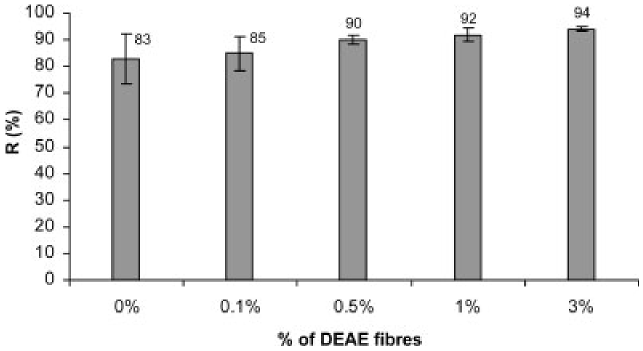

Figure 5 Average salt rejection data for the membranes produced with different percentages of DEAE fibers.

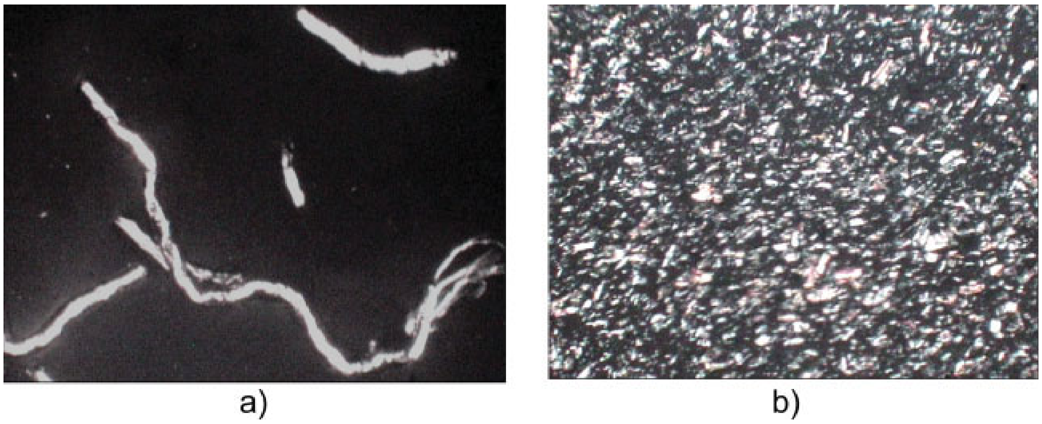

Figure 6 Optical microscopy photos of membranes produced with 10 wt % of DEAE fibers (a) and CF (b) (amplification of ×50). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the water permeability of the membranes; it increases consistently the water permeability until 0.5 wt % of fibers (in relation to dry weight) and then it starts to decrease, which may be due to a decrease of the swelling capability of the membrane, with the addition of the fibers.

In fact, the swelling capability of membranes produced without fibers and with different contents of both types of fibers (cellulosic and DEAE fibers), was measured using three membranes of each type, showing a decrease of the swelling capability of the membrane, with the addition of the fibers, specially for the smaller fiber contents (up to 0.5 wt % for the cellulosic fibers and 1.0 wt % for the DEAE fibers). The results obtained are presented in Table I.

It is worth to point out that the fibers are well distributed along the membranes (it is possible to find them in the skin layer as well as along the support layer), as can be seen in the SEM image of a membrane produced with 10 wt % of cellulosic fibers, presented on Figure 3, as an example.

Concerning *R* values, the addition of cellulosic fibers led to a slight decrease when compared to the membrane without fibers; for example the membranes with 0.5 and 1 wt% (R = 77% for both CF content) have a salt retention values close to the membranes without it (R = 83%).

Concerning the permeability, the membranes produced with 0.5 wt % of CF present the best performance, among the ones tested (the same *A* value than the membrane with 0.1 wt % fiber content, but with a slightly higher *R* value).

Figures 4 and 5 present the results of water permeability and salt rejection for the membranes produced with different contents of DEAE fibers.

The permeability results for the membranes with DEAE fibers indicate that, in average, water permeability decreases continuously with the DEAE fiber content, probably due to their size and morphology [see Fig. 6(a)]; they may tend to agglomerate reducing the free porosity of the membrane.

The fibers agglomeration phenomena on membranes produced with both type of fibers can be observed with the membrane at counter light.

In addition, the lower values of *A* in membranes with DEAE fibers can probably be explained by the fact that the fibers tend to reduce the swelling capability of the membrane.

Figure 6 presents the typical morphology of membranes produced with the same content (10 wt %) of DEAE fibers and cellulosic fibers.

Concerning the *R* values, it was proved that it increases continuously with the DEAE fiber content, as expected having in mind the *A* results.

Taking into account the results for water permeability and salt rejection 0.5 wt % of DEAE fibers seems to be the adequate choice because the mem-

TABLE II
Statistical Treatment of Membranes Thickness

Fibers type	Fibers content (wt %)	Thickness (T) (μm)	
		T	$\sigma(T)$[a]
CF Fibers	0	28.86	1.34
	0.1	33.66	2.23
	0.5	31.17	1.75
	1	28.46	1.19
	3	35.06	2.93
	5	36.83	2.28
	10	32.77	2.78
DEAE Fibers	0	28.86	1.34
	0.1	33.44	2.62
	0.5	30.33	4.34
	1	29.62	1.73
	3	30.66	2.94
	5	39.44	6.41
	10	40.52	1.84

[a] Standard deviation.

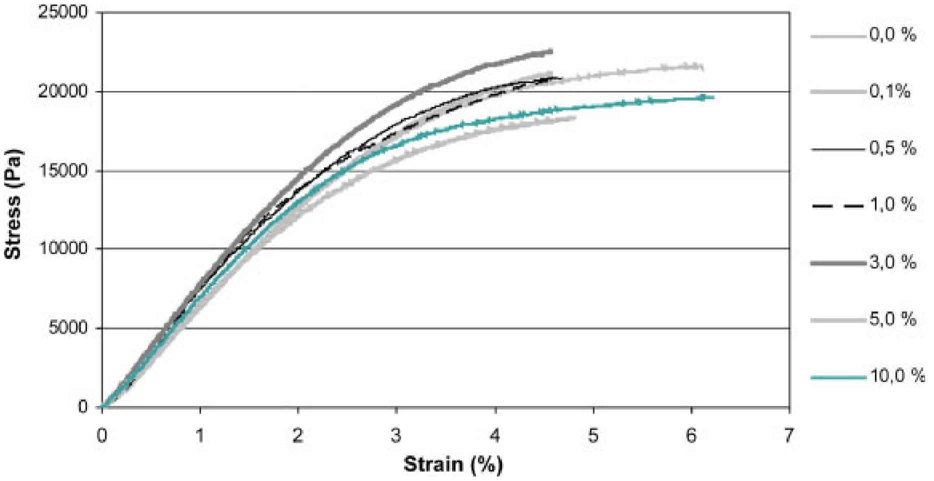

Figure 7 Curves Stress versus Strain for the membranes produced without fibers and with different contents of CF fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

branes produced with this fiber content present relatively good A and R values ($A = 0.52$ L/m^2 h bar and $R = 90\%$).

Concerning the effect of the addition of fibers on membranes permeability and salt rejection values, it is possible to conclude that membranes made with 0.5 wt % of DEAE fibers present A values 8.8% lower and R values 8.4% higher than membranes without fibers, while membranes made with 0.5% wt of cellulosic fibers present A values 22.8% higher and R values 7.3% lower than the membranes without them.

Although the addition of DEAE fibers increases the salt rejection of the membranes, contrary to what happens with the membranes made with cellulosic fibers, the last ones present a much higher increase in water permeability than membranes with DEAE on salt rejection values. Having in mind that for energy generation process the water permeability is a very important factor, and considering both salt rejection and water permeability, we conclude that membranes with cellulosic fibers are more efficient for this purpose. Because of anisotropy and noncontinuity of the material structure it is, for the moment, difficult to model the observed results.

Mechanical performance tests

Table II presents membrane thickness for all the membranes tested.

The stress versus strain curves for the membranes prepared without fibers and with six different CF content are presented on Figure 7.

The average value of Young's modulus (E), ultimate tensile strength (UTS), and elongation at break (ε_u), for five membranes of each content of both types of fibers, along with the error bars, is presented in the following figures.

Figures 8–10 present the mechanical properties of the membranes produced with different contents of CF and DEAE fibers.

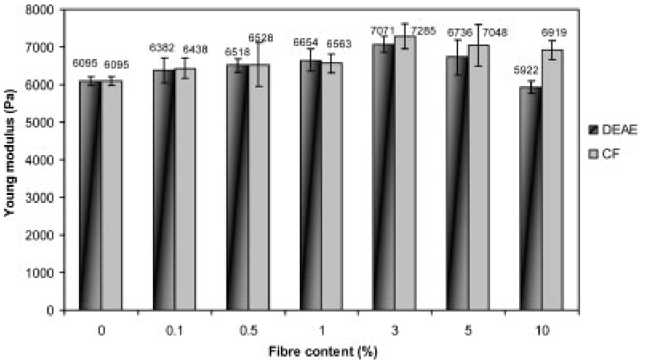

Figure 8 Average Young's modulus data for the membranes produced with different contents of DEAE and CF fibers.

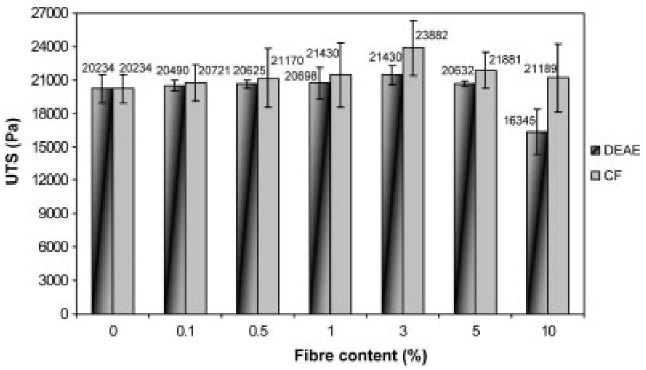

Figure 9 Average ultimate tensile strength data for the membranes produced with different contents of DEAE and CF fibers.

The Young's modulus results for the membranes with both types of fibers shows that E values increases with the fibers content reaching a maximum at 3 wt % of fibers for both DEAE fibers and cellulosic fibers. The decrease of the Young's modulus observed for contents of fiber higher than 3 wt % is probably due to the fact that the adhesion between the membrane matrix and fibers decreases with the fiber content owing to fiber's aggregation. So, the results indicate that the elastic deformation of the membranes is influenced, as expected, by the fiber content.

The results obtained for ultimate tensile strength are very similar to the ones obtained for the Young's modulus, as one should expect.

Mechanical experiments made with membranes produced with both types of fibers show that, as expected, the ε_u values decreases until a content of 3 wt % of fibers and then it increases.

The results presented above seem to show that concerning the mechanical reinforcement point of view, the cellulosic fibers perform better than DEAE fibers. Additionally, the membranes with the cellulosic fibers also present the best performance in terms of permeability. Considering that not only the mechanical strength but also the flexibility is an important characteristic for the application of this type of membranes in modules for desalinization and for energy generation processes, the toughness for the membranes with cellulosic fibers for the different fiber contents were determined. These results are presented in Figure 11.

The results indicate that, having in mind both mechanical strength and flexibility, the membrane with 3 wt % of CF content is the one with the best performance or, by other words, the one that present the higher toughness.

Finally, it is worth mentioning that the performance of the membranes do not change for long periods of time (several months), even with the addition of the fibers.

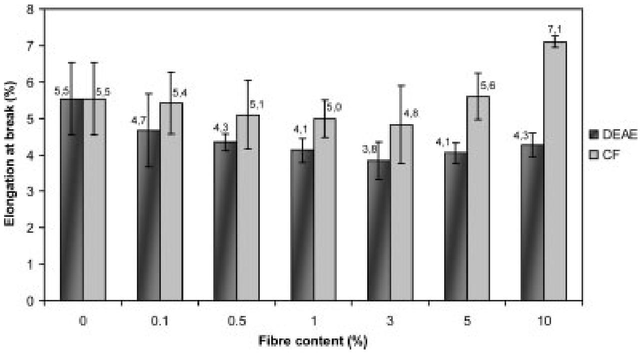

Figure 10 Average elongation at break data for the membranes produced with different contents of DEAE and CF fibers.

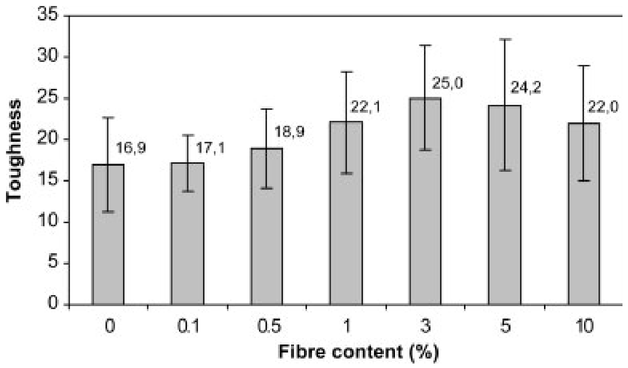

Figure 11 Average toughness for the membranes produced with different contents of CF fibers.

CONCLUSIONS

After the study of the influence of type and content of fibers on permeability and mechanical performance of the cellulose acetate asymmetric membranes, we can conclude that the membranes made with cellulosic fibers present the best performance concerning the studied parameters.

Having in mind the permeability results, the optimum value of CF content is 0.5 wt % because membranes made with these fibers content present A values 22.8% higher while R values decreases only 7.3% when compared with similar membranes without fibers.

Concerning mechanical results, the membranes with 3 wt % of CF present the best performance (E values ~20% higher and UTS values 18% higher than membranes without fibers), as confirmed by the results of the toughness of the membranes in function of cellulosic fiber content.

Taking into account the mechanical properties and the permeability results, a conflict in the choice of the CF content appears. However, having in mind the final application of these membranes, energy generation and desalinization processes, for which high water permeability and a high salt rejection are crucial, the correct choice seems to be the membrane with 0.5 wt % fiber content. The toughness for this membrane is only slightly higher (18.9) than the one without fibers (16.9).

The trends and correlations found will allow for further progress on energy production by membrane processes.

NOMENCLATURE

A	water permeability of the membrane (l/m^2 h bar)
V	volume of water though the membrane in a given time t (l)
A_{memb}	area of the membrane (m^2)
t	time (h)

p	pressure across the membrane (bar)
R	salt rejection (%)
C_0	conductivity of salty water at the pressure side in the beginning of the experiment (mS)
$\mathrm{C}_{\mathrm{memb}}$	conductivity of water that went through the membrane (mS)
E	Young's modulus (Pa)
UTS	ultimate tensile strength (Pa)
ε_u	elongation at break (%)
T	thickness (μm)
σ	standard deviation

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