

# Cellulose Acetate Reverse Osmosis Membranes: Optimization of the Composition

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**ABSTRACT:** Membranes based on cellulose acetate for reverse osmosis can possibly be applied to the so-called salinity process of energy generation and water desalination. The requirements for membranes for these two different applications are a relatively high water flux and low salt permeability. In this article, we present the optimization of the composition of such membranes. We started by producing membranes with a patented casting solution with the following composition: 45.77 wt % dioxane, 17.61 wt % acetone, and 8.45 wt % acetic acid (solvents); 14.09 wt % methanol (nonsolvent); and 7.04 wt % cellulose diacetate and 7.04 wt % cellulose triacetate. The membranes produced with this solution were analyzed comparatively, with the membranes obtained by the introduction of modifications to

the following parameters: the solvent mix, the nonsolvent mix, the proportion of cellulose diacetate and cellulose triacetate in the casting solution, and the addition of reinforcing cellulose fibers. The results led us to conclude that the best membrane formulation had the following composition: 45.77 wt % dioxane, 17.61 wt % acetone, and 8.45 wt % acetic acid (solvents); 4.22 wt % cellulose triacetate and 9.86 wt % cellulose diacetate (polymers); 14.09 wt % methanol (nonsolvent); and 0.5 wt % cellulose fibers (with respect to the total polymer content). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4052–4058, 2006

**Key words:** fibers; membranes; selectivity

## INTRODUCTION

The word *membrane* is applied to a large diversity of structures that can perform a preferential permeation of chemical compounds. Selective permeation depends both on the molecular structure of the polymeric material and on the resulting texture of the dense layer. The integrally asymmetric membranes that are usually prepared by a phase inversion (wetting process)<sup>1</sup> are mainly applied in ultrafiltration and reverse osmosis.<sup>2</sup> With this process, in which salt water, if it is at a pressure above the osmotic one, is in contact with an appropriate semipermeable membrane, pure water can be recovered from the opposite side; this is particularly useful in separating solvents from solutions and attracts considerable interest as an economical process for the desalination and purification of water.

An integrally asymmetric membrane consists of a very thin, practically pore-free skin layer over a po-

rous carrier layer, which nearly extends to the large majority of the membrane. However, only the skin ensures the desalination selectivity. The very porous second layer acts mostly as a reinforcing support.

The production of integrally asymmetric cellulose acetate membranes comprises several steps. It starts with the preparation of a cellulose acetate solution in a suitable solvent or mixture of solvents. Membranes are then cast from the casting solution with a film-drawing device with a slit width of typically 100  $\mu\text{m}$ . After the subsequent partial evaporation of the volatile constituents at room temperature, the films are immersed in a cold water bath, which initiates a phase inversion that leaves the membranes in the form of water-swollen anisotropic gels of cellulose acetate. The last step of manufacturing the membranes is an annealing treatment in a warm water bath, in which the membranes set in the previously established structure with a relatively small reduction in the water flux (*A*).

With respect to the permeability characteristics of the resulting membranes, this process is controlled by the period of evaporation of the spread films in air and the temperature of the concluding warm-bath annealing treatment.

The objective of this work was to prepare reverse-osmosis membranes designed for use in the so-called

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salinity process of energy generation<sup>3</sup> or a salt separation process<sup>4</sup> (e.g., water desalination). These objectives required membranes with relatively high  $A$  values and low salt permeability, withstanding pressures up to 15 bar.

We started by producing membranes with a casting solution described in a U.S. Patent (4,340,428) published in 1982.<sup>5</sup> The casting solution was based on a solution of a mixture of cellulose diacetate and cellulose triacetate in a mixture of acetone, dioxane, and acetic acid, with methanol used as a nonsolvent in the preparation procedure. Acetone was included in the basic solution as a conventional vaporizable solvent for cellulose acetate, and dioxane was required to prepare homogeneous casting solutions with both cellulose acetates because cellulose triacetate is insoluble in acetone. Acetic acid was incorporated for its two-fold function: (1) a solvent for cellulose triacetate and (2) a softener that improved polymer mobility for the development of the polymer structure. Additionally, it froze the structure during coagulation through hydrogen bonding. Methanol acted as a nonsolvent for the polymer materials; this meant that it stimulated the absorption of water by the membranes and consequently tended to increase their flow performance.<sup>6</sup>

To prepare an optimized membrane, we comparatively analyzed the performance [ $A$  and salt rejection ( $R$ ) values] of the membranes produced from a patented casting solution<sup>5</sup> and that of modified ones obtained by the introduction of modifications to the following parameters:

- Solvent mix.
- Nonsolvent mix.
- Proportion of cellulose diacetate and cellulose triacetate in the casting solution.
- Addition of reinforcing cellulose fibers (CFs).

As already mentioned, the performance of the membranes was evaluated with the  $A$  and  $R$  values:

$A$  for the membrane ( $\text{l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ) was calculated with the following equation (assuming that the specific gravity was very close to 1):<sup>7</sup>

$$A = \frac{V}{A_{\text{memb}} t p} \quad (1)$$

where  $V$  is the volume of water through the membrane (l),  $A_{\text{memb}}$  is the membrane area ( $\text{m}^2$ ),  $t$  is the time (h), and  $p$  is the pressure across the membrane (bar).

The  $R$  values (%) were calculated with the following equation:<sup>8</sup>

$$R = \frac{C_0 - C_{\text{memb}}}{C_0} \times 100 \quad (2)$$

where  $C_0$  is the conductivity of salty water at the pressure side in the beginning of the experiment (mS) and  $C_{\text{memb}}$  is the conductivity of water that goes through the membrane (mS).

## EXPERIMENTAL

### Materials and methods

Cellulose diacetate (weight-average molecular weight  $\approx 30,000$  g/mol, 39.8 wt % acetyl) was received from Aldrich (180955). The cellulose triacetate was supplied by Sigma-Aldrich (181005; Madrid, Spain) and was 43–49 wt % acetyl. The CFs were received from Sigma (S3504 Sigmacell R type 20) and were microcrystalline powder particles (size = 20  $\mu\text{m}$ ) usually used in chromatography. 1,4-Dioxane was supplied by Panreac Quimica S.A. (Barcelona, Spain) and had a minimum purity of 99.5%. Methanol and acetone used received from Labsolve (Lisbon, Portugal). The methanol had a purity greater than 99.5%, and acetone had a purity of 99%. The acetic acid had a purity greater than 99.8% and was supplied by BDH Anala R (England). The chloroform had a purity between 99 and 99.4% and was received from Pronolab (Lisbon, Portugal). Methyl ethyl ketone (MEK) was received from Merck (Frankfurt, Germany) and had a purity greater than 99.5%. Tetrahydrofuran (THF) was supplied by Riedel-de Haen (33709; Seelze, Germany) and had a purity of 99.9%.

The determination of  $A$  for the membrane was measured at 8 bar with a low-pressure filtration cell (model GN-10/400) from Berghoff (Eningen, Germany).

The determination of  $R$  was performed with a salt concentration in water of 5 g/l, and the conductivity of water was measured with a conductivity meter (model HI 8733) from Hanna Instruments (Ronchi di Villafranca, Italy).

### Procedure

The patented membrane starting formulation<sup>5</sup> was 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 a nonsolvent.
- 7.04 wt % cellulose diacetate and 7.04 wt % cellulose triacetate.

The membranes were obtained through the spreading of the solution [at room temperature ( $\approx 25^\circ\text{C}$ )] on a glass plate with a calibrated ruler, whose thickness was previously selected (100  $\mu\text{m}$ ), at a constant speed of 23 mm/s with an automatic film applicator from Braive Instruments. After 15 s for the evaporation of the solvent, the polymeric film on the glass was immersed for 15 min in an ice-water bath ( $\approx 0^\circ\text{C}$ ).<sup>1</sup> After

that, the film was placed in a water bath around 4°C for 2 h. The last step of the process of the preparation of the membrane was the annealing post-treatment for 15 min at 80–85°C.

To study the influence of the solvents on the performance of the membranes, we prepared membranes with the following materials:

1. 17.61 wt % acetone, 45.77 wt % dioxane, and 8.45 wt % acetic acid (starting formulation).
2. 17.61 wt % MEK, 45.77 wt % dioxane, and 8.45 wt % acetic acid (the acetone was substituted by MEK).
3. 17.61 wt % acetone, 45.77 wt % dioxane, and 8.45 wt % acetic acid (the acetone and dioxane were treated with cork powder). Both solvents used in the membrane solutions were passed through a cork powder column to saturate the solvents with the oligomers of the cellular membranes of the tree cells. The objective of this treatment was the improvement of the separation between the water and salts as in natural processes.<sup>9</sup>

Concerning the nonsolvent, membranes were prepared by some of the methanol being replaced by other nonsolvents as follows:

1. 100 (methanol; starting formulation).
2. 80:20 (methanol/chloroform).
3. 80:20 (methanol/THF).

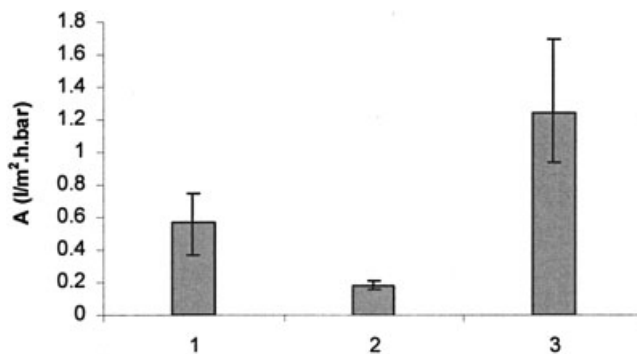
Considering the polymer, three situations were studied with the following proportions of cellulose diacetate and cellulose triacetate:

1. 50:50 (cellulose diacetate/cellulose triacetate; starting formulation).
2. 70:30 (cellulose diacetate/cellulose triacetate).
3. 100 (cellulose diacetate).

CFs normally used in chromatography processes were added to membrane starting solutions to act, expectedly, as reinforcements (even though this study had not yet been performed, the effect of these CFs in the resistance of other cellulosic films had already been studied).<sup>10</sup>

Membranes without CF and with four different CF concentrations (with respect to the total polymer content in the casting solution) were produced and compared:

1. Without CF.
2. 0.1 wt % CF.
3. 0.5 wt % CF.
4. 1 wt % CF.
5. 3 wt % CF.



**Figure 1** *A* values for the membranes produced with different solvent mixes: (1) 17.61 wt % acetone, 45.77 wt % dioxane, and 8.45 wt % acetic acid (starting formulation), (2) 17.61 wt % MEK, 45.77 wt % dioxane, and 8.45 wt % acetic acid (the acetone was substituted by MEK), and (3) 17.61 wt % acetone, 45.77 wt % dioxane, and 8.45 wt % acetic acid (the acetone and dioxane were treated with cork powder).

With the aforementioned solvent mix, nonsolvent mix, and composition of the polymeric mixture, membranes were produced, and their performance was analyzed; this allowed us to choose the one that presented the best combination of *A* and *R*.

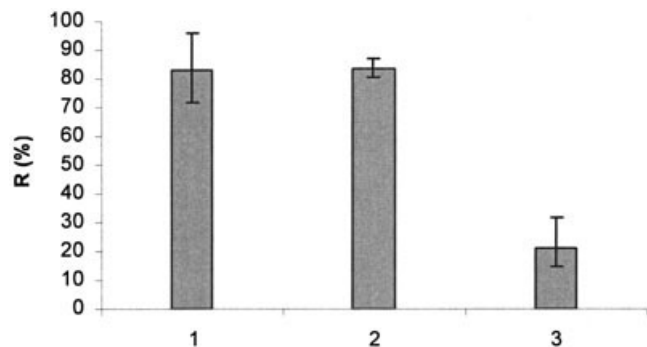
## RESULTS AND DISCUSSION

Five membranes of each type were produced with the same solution and under the same conditions but on different days; this allowed minimizing the effects of external conditions (mainly temperature and humidity) by the determination of average values of *A* and *R* and thus retained only the influence of the parameter under study.

The average values of *A* and *R* for the five membranes of each type, along with the error bars, are presented in the following figures, each one corresponding to the variation of one parameter at a time, whereas the others remained fixed.

Figures 1 and 2 present *A* and *R* for the membranes produced with different solvent mixes.

The solvent mix results indicate that membranes produced with dioxane and acetone present an average water flux ( $\langle A \rangle$ ) of approximately 0.6 l m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>. The replacement of acetone by MEK results in a significant decrease in  $\langle A \rangle$  (ca. 0.2 l m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>). The membranes produced with acetone in the solvent mixture, because of the higher vapor pressure, were expected to have, for the same evaporation time, a thicker superficial skin and thus a lower *A* value than membranes produced with MEK. However, the different solubilities of MEK in water, compared with that of acetone, result in a more rapid phase inversion with freezing of the top layer of microporosity and consequently in a slower process in the case of MEK, whose diffusion to the water phase would be slower. From the obtained results, we conclude that *A* is actually



**Figure 2**  $R$  values for the membranes produced with different solvent mixes: (1) 17.61 wt % acetone, 45.77 wt % dioxane, and 8.45 wt % acetic acid (starting formulation), (2) 17.61 wt % MEK, 45.77 wt % dioxane, and 8.45 wt % acetic acid (the acetone was substituted by MEK), and (3) 17.61 wt % acetone, 45.77 wt % dioxane, and 8.45 wt % acetic acid (the acetone and dioxane were treated with cork powder).

higher with acetone. The miscibility of acetone in water helps the diffusion to the water coagulation bath, increasing the porosity in the nonselective layer of the membrane.

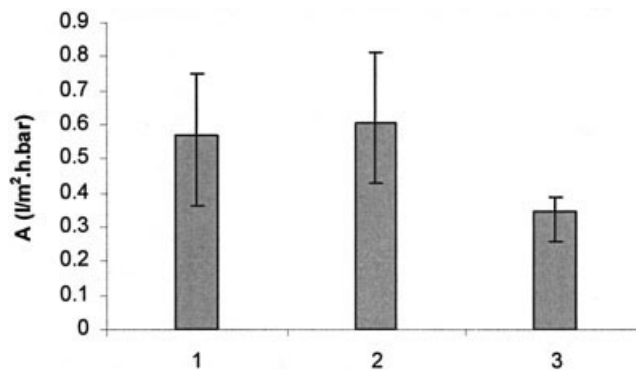
The  $R$  values are very similar for the membranes with acetone and MEK; the average salt rejection ( $\langle R \rangle$ ) is 83%. In the first ones, the  $R$  value is probably due to the thickness of the superficial skin, and in the second ones, it must be due to less porosity in the rest of the thickness.

The high  $\langle A \rangle$  value ( $1.25 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ) and low  $\langle R \rangle$  value (21%) of the membranes produced with the solvents treated with cork powder may be due to the presence of some extracted material in the treated solvents. These ramified molecules make difficult the migration of cellulose triacetate to the top of the membrane during the period of the evaporation of the solvent, decreasing the thickness of the superficial skin.

Figures 3 and 4 show the dependence of the nonsolvent mix used on the performance of the membranes in terms of  $A$  and  $R$ , respectively.

Membranes produced with 20% chloroform and 80% methanol as the nonsolvent present  $\langle A \rangle$  values around  $0.3 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ , whereas the membranes produced with 20% THF have  $\langle A \rangle = 0.61 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ . For the membranes with 100% methanol as the nonsolvent,  $\langle A \rangle$  is  $0.57 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ . The membranes produced with chloroform present the lowest  $\langle A \rangle$  values among the ones tested, probably because this nonsolvent has a very low solubility in water, which makes migration during coagulation difficult, and consequently the open porosity of the produced membranes is lower.

Concerning  $\langle R \rangle$  values, the membranes with chloroform present an  $R$  value of 83%, whereas the membranes produced with THF have  $\langle R \rangle = 79\%$ . The mem-



**Figure 3**  $A$  values for the membranes produced with different nonsolvent mixes: (1) 100 (methanol; starting formulation), (2) 80 : 20 (methanol/THF), and (3) 80 : 20 (methanol/chloroform).

branes produced only with methanol have, on average, an  $R$  value of 83%. An explanation for the small differences in these results could be the similarity between the boiling points of these three nonsolvents.

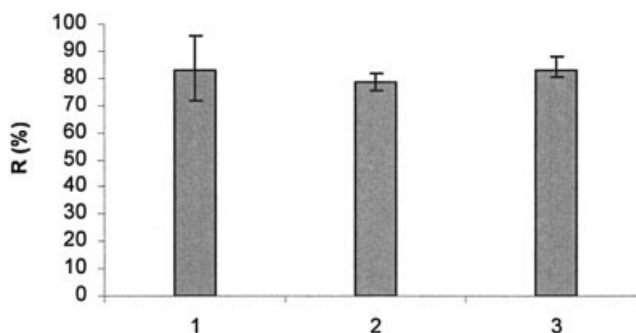
Therefore, the comparison between the results obtained for the membranes produced with the three nonsolvent mixes allows us to conclude that the membranes produced only with methanol as the nonsolvent present the best performance.

The dependence of the proportions of cellulose diacetate and cellulose triacetate on the performance of the membranes is presented in Figures 5 and 6 in terms of  $A$  and  $R$ , respectively.

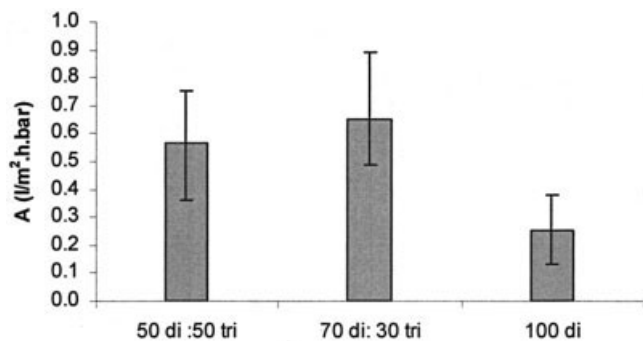
The membranes produced with 100% cellulose diacetate present a lower  $\langle A \rangle$  value ( $0.25 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ) than the membranes with both types of cellulose acetates. These differences are probably due to the differences in the quenching during the phase inversion.

The membranes produced only with cellulose diacetate present a low  $\langle R \rangle$  value of 72%.

The performances of the membranes with 50:50 and 70:30 cellulose diacetate/cellulose triacetate are simi-



**Figure 4**  $R$  values for the membranes produced with different nonsolvent mixes: (1) 100 (methanol; starting formulation), (2) 80 : 20 (methanol/THF), and (3) 80 : 20 (methanol/chloroform).

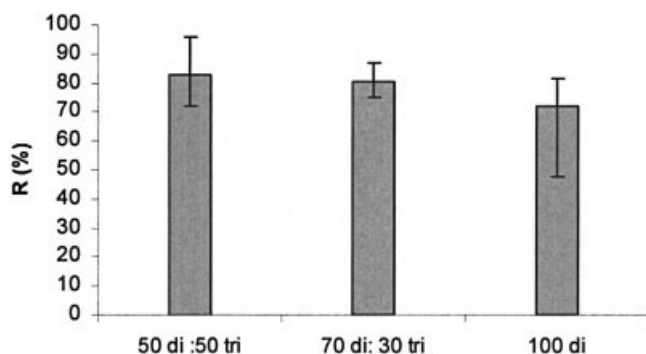


**Figure 5**  $A$  values for the membranes produced with different proportions of cellulose diacetate and cellulose triacetate.

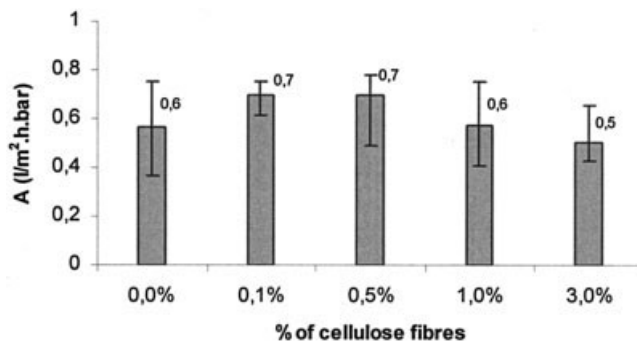
lar. The membranes with 50 : 50 have  $\langle A \rangle = 0.57 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  and  $\langle R \rangle = 83\%$ , whereas membranes with 70 : 30 present  $\langle A \rangle = 0.65 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  and  $\langle R \rangle = 80\%$ . The higher flux of the membranes containing cellulose triacetate could also be a result of a thinner selective layer that, once formed, prevents, to some extent, further evaporation of the solvent, leading to lower kinetics of selective film growth. The lower compatibility of cellulose triacetate results in faster quenching and preservation of the microporosity of the selective layer, which could be an explanation for the  $R$  results. Even the results are similar for the membranes made with 50 : 50 and 70 : 30 cellulose diacetate/cellulose triacetate; the ones produced with more cellulose diacetate present higher  $A$  values.

Figures 7 and 8 show the influence of the addition of CFs on the performance of the membranes in terms of  $A$  and  $R$ , respectively.

The measurements made with the membranes without CFs and with four different CF concentrations show that membranes with 0.1, 0.5, and 1.0 wt % CF present better  $\langle A \rangle$  values than the membranes without CF. However, membranes with 3 wt % CF have lower  $\langle A \rangle$  values.



**Figure 6**  $R$  values for the membranes produced with different proportions of cellulose diacetate and cellulose triacetate.



**Figure 7**  $A$  values for the membranes produced without CF and with four different concentrations of CF.

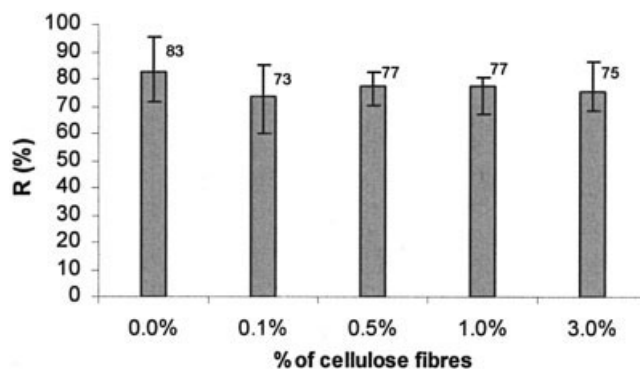
Therefore, we conclude that the addition of CFs to the membrane solution influences  $A$  of the membranes. It consistently increases  $A$  until 0.5 wt % fibers (with respect to the dry weight), and then it decreases, probably because in higher quantities the fibers tend to reduce the swelling capability of the membranes.

Concerning  $\langle R \rangle$  values, we can conclude that the addition of CFs seems not to have a significant influence on the performance of the membranes; the membranes with 0.5 and 1 wt % ( $\langle R \rangle = 77\%$  for both) have  $R$  values slightly lower than that of membranes without it ( $\langle R \rangle = 83\%$ ).

Concerning the additive used, the membranes produced with 0.5 wt % CF present the best performance.

Table I presents the statistical treatment of all the aforementioned results. The averages and standard deviations were determined by well-known equations that can be found in any book on statistics.

The statistical analysis of the results confirms that the external conditions have a significant influence on the membrane performance. As expected, the temperature and humidity are important and conditioning factors of the performance of the membranes because they have a significant influence on the solvent evaporation, which controls the thickness of the superficial skin and, as a result,  $A$  and the selectivity.



**Figure 8**  $R$  values for the membranes produced without CF and with four different concentrations of CF.

TABLE I  
Statistical Treatment of  $A$  and  $R$  Values

Modified parameter	$A$ ( $\text{l m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ )		$R$ (%)		
	$\langle A \rangle$	$\sigma$	$\langle R \rangle$	$\sigma$	
Solvent	Dioxane + acetone	0.57	0.15	82.89	9.33
	Dioxane + MEK	0.18	0.02	83.38	2.60
	Dioxane + acetone (treated with cork powder)	1.25	0.32	20.98	6.56
Nonsolvent	100% methanol	0.57	0.15	82.89	9.33
	80:20 methanol/THF	0.61	0.17	78.84	2.40
	80:20 methanol/chloroform	0.34	0.06	83.20	3.50
Cellulose polymer	50:50 diacetate/triacetate	0.57	0.15	82.89	9.33
	70:30 diacetate/triacetate	0.65	0.15	80.26	5.43
	100 diacetate	0.25	0.11	72.09	14.32
CF	0 wt %	0.57	0.15	82.89	9.33
	0.1 wt %	0.70	0.06	73.32	10.29
	0.5 wt %	0.70	0.14	77.41	5.48
	1.0 wt %	0.58	0.15	77.11	6.70
	3.0 wt %	0.50	0.11	75.29	8.31
Starting formulation		0.57	0.15	82.89	9.33
Optimized formulation		0.68	0.30	82.74	5.48

$\sigma$  = standard deviation.

Therefore, to minimize the influence of external conditions in the process of the optimization of the composition of the membranes, they were produced with the same solutions but on different days.

Figures 9 and 10 show the results for  $A$  and  $R$ , respectively, for the starting and optimized membranes for comparison.

Although the improvement may not seem very significant, both the averages and minimum values are higher for the optimized solution (for  $A$  and  $R$ ), and this means that our main objective, preparing a membrane with a higher performance than the ones patented, has been achieved.

## CONCLUSIONS

On the basis of the study, concerning the membrane casting solution, we can conclude that the best formulation has the following composition:

- 45.77 wt % dioxane, 17.61 wt % acetone, and 8.45 wt % acetic acid as the solvents.
- 4.22 wt % cellulose triacetate and 9.86 wt % cellulose diacetate.
- 14.09 wt % methanol as the nonsolvent.
- 0.5 wt % CF with respect to the total polymer content.

The membranes produced with the optimized formulation (70:30 cellulose triacetate/cellulose diacetate) present  $\langle A \rangle$  values approximately 19.3% higher than those of the membranes produced with the starting formulation, even though a slight decrease in  $R$  is observed ( $-0.2\%$ ). The main objective of the addition of CFs to a membrane solution is membrane reinforcement, but the results show that CFs have an influence on the membrane performance, especially with respect to the  $A$  values.

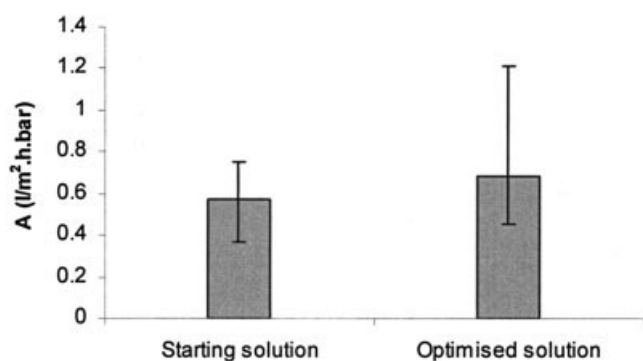


Figure 9  $A$  values for the membranes produced with the starting formulation and with the optimized formulation.

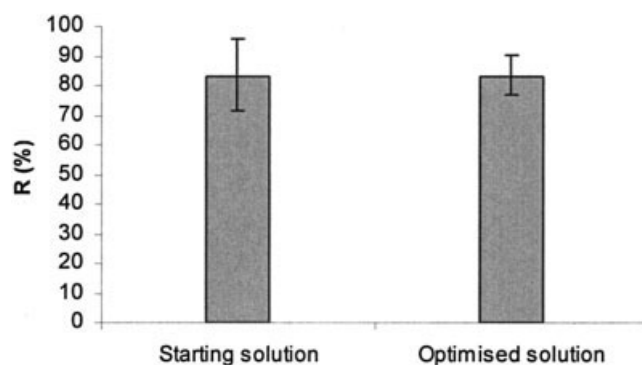


Figure 10  $R$  values for the membranes produced with the starting formulation and with the optimized formulation.

The calculated standard deviation is rather large, and this can be attributed to the presence of small microholes with a noticeable impact on  $A$  of the same membrane samples and also to the large number of parameters (temperature, humidity, vapor pressure, etc.) with direct and indirect influences on the membrane performance.

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