

Development and Characterization of Cellulose Acetate Benzoate Flat Osmotic Membranes

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SYNOPSIS

Different parameters of casting solutions and casting conditions were studied for the development of cellulose acetate benzoate flat osmotic membranes. Casting solutions were prepared with different concentrations of the polymer, the additive, and the solvent; viscosity of the casting solution; and the thickness of the membrane developed. The membranes were given different evaporation periods and annealing temperatures under different RH. Different annealing baths were also used. Based on these, conditions were optimized for the development of cellulose acetate benzoate flat osmotic membranes. These membranes were characterized with respect to bound water content, specific water content, transport properties by direct osmosis, salt intake by direct immersion, water permeability coefficient of the dense membrane, diffusion coefficient, salt permeability, and salt distribution by electrical conductivity. Also, cellulose acetate benzoate membranes were compared with conventionally used cellulose acetate membranes. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The intrinsic salt rejection of the dense film of cellulose acetate (CA) increases rapidly with increasing acetate groups for the free hydroxy group of cellulose.¹ In the case of mixed esters, such as cellulose acetate benzoate (CABz), the increasing substitution with the benzoyl radical should increase the intrinsic salt rejection of dense film of CABz. No basic chemical difference exists between the dense film and asymmetric membranes and, hence, an increasing degree of substitution in CABz should also increase the intrinsic salt rejection in asymmetric CABz membranes as in CA membranes. Hence, conditions were optimized for development of CABz flat osmotic membranes of a higher degree of substitution (d.s.), i.e., d.s. 2.6–2.7 CABz was prepared in the laboratory.² The CABz membranes were also characterized for complete evaluation and compared with conventional cellulose acetate membranes.

EXPERIMENTAL

Development of Membrane

Polymer Concentration

The casting solution consisted of three components, i.e., (i) polymer (CABz), (ii) additive formamide (F), and (iii) solvent acetone (A). Various casting solutions were prepared in which the concentration of the additive was kept uniform while the concentration of CABz was varied. The concentration of A was changed accordingly. Viscosity of the casting solution was determined by a Brookfield viscometer at 25°C. Tensile strength of the treated membrane was determined by the ASTM method.³

Additive Concentration

The concentration of F in the casting solution was varied, keeping the ratio of additive to polymer between 0.43 and 1.73. The concentration of CABz was kept constant while the concentration of A was changed accordingly.

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Table I Studies on Polymer Concentration and Membrane Properties

No.	Casting Solution			Viscosity of Casting Soln (cp)	S.R. (%)	Flux (gfd)	Membrane Strength (psi)
	CABz (%)	F (%)	A (%)				
1	15	30	55	14,300	61.9	34.6	900
2	17	30	53	21,200	77.2	29.4	1100
3	19	30	51	28,400	84.1	24.5	1250
4	21	30	49	35,600	89.3	21.3	1400
5	23	30	47	42,200	94.4	14.5	1700
6	25	30	45	48,100	94.6	13.9	1900

Thickness of the Membrane

Membranes of desired thickness were drawn using an appropriate paper strip with a doctor's blade during casting of the membranes.

Evaporation Period

The casting of the membrane was done at ambient temperature in an open area. A definite evaporation time was given to the membrane after casting and later it was submerged into ice-cold water.

Annealing Treatment

Annealing treatment was given by immersing the gelled membrane into hot water of a particular temperature for a specific period.

Annealing Treatment in Different Baths

This was done by immersing the gelled membrane in annealing baths of different types of alcohols in place of water.

Membrane Casting in Different RH

Small chambers of different RH were maintained and the membranes were cast in these chambers.

Characterization of the Membrane**Bound Water Content**

The method of Vincent et al.⁴ was adopted for determination of bound water content.

Specific Water Content

This was determined by finding the total water content of the membrane at constant weight by drying at 105°C.

Transport Properties

This was determined by the direct osmosis method.⁵

Salt Intake

This was determined by the immersion method.⁶

Table II Studies on the Effect of Additive on Membrane Properties

No.	CABz (%)	F (%)	A (%)	F/CABz (ratio)	S.R. (%)	Flux (gfd)
1	23	10	67	0.434	95.2	4.3
2	23	20	57	0.869	94.8	7.8
3	23	30	47	1.300	94.4	14.2
4	23	35	42	1.520	93.6	16.6
5	23	40	37	1.730	92.2	17.3
6 ^a	23	35	42	1.520	90.2	15.5
7 ^a	25	30	45	1.200	91.0	11.2

^a Nos. 6 and 7 are data of CA for comparison.

Table III Studies on Membrane Thickness (as Cast)

No.	Membrane Thickness (mm)	S.R. (%)	Flux (gfd)
1	0.05	85.3	7.4
2	0.10	89.5	8.8
3	0.15	93.2	12.2
4	0.20	94.4	14.1
5	0.25	91.3	10.2
6	0.30	89.2	8.6

Water Permeability Coefficient of the Dense Membrane and Active Layer Thickness of the Asymmetric Membrane

The method of Lonsdale was adopted.⁷

Diffusion Coefficient (D), Salt Permeability (D₂K), and Salt Distribution (K)

The method of Saltanstill et al. was adopted.⁸

RESULTS AND DISCUSSION

Experimental data for all above aspects are presented in Tables I–XIV. Polymer concentration in the range of 15–25% was studied. The concentration of 23% of the polymer CABz in the casting solution was observed to be optimum to obtain a casting solution viscosity of 42,200 cps, the strength of the membrane of 1700 psi, and the membrane salt rejection (S.R.) of 94.4% with the flux of 14.5 gallons per square foot per day (gfd).

An additive concentration in the range of 10–40% of formamide in the casting solution was studied to obtain an F/CABz ratio of 0.43–1.73. The optimum range was 1.3–1.5.

Table IV Studies on Membrane Performance at Different Evaporation Periods

No.	Evaporation Period (s)	S.R. (%)	Flux (gfd)
1	0	24.7	61.2
2	15	78.6	28.4
3	30	94.4	14.3
4	60	94.5	11.6
5	80	94.6	10.6
6	120	94.8	9.2
7	150	94.8	4.3
8	180	94.9	4.1

Table V Effect of Annealing Temperature on Membrane Performance

No.	Annealing Temp (°C)	S.R. (%)	Flux (gfd)	Percent Shrinkage in Area
1	25 (RT)	10.1	80.2	Nil
2	40	18.2	65.5	1.52
3	50	25.4	42.6	1.94
4	60	60.8	39.2	2.52
5	70	86.6	20.4	4.46
6	80	94.4	14.2	6.81
7	85	94.6	10.5	7.93
8	90	94.8	8.1	8.21
9	95	95.3	5.3	9.12
10 ^a	80	91.0	11.2	7.32
11 ^a	90	92.3	6.8	9.76

^a Nos. 10 and 11 are data of CA membranes for comparison with CABz membranes.

Though the effective part of the membrane is its active layer, the total thickness of the membrane has some effect on the membrane water content. The CABz membrane with a total cast thickness of 0.20 mm gave a very good performance.

Table VI Desalination Properties of CABz Membranes After Annealed in Different Annealing Baths

No.	Alcohol	Concentration of Alcohol (%)	S.R. (%)	Flux (gfd)
1	Methanol	10	94.3	14.4
		20	94.5	14.3
		30	94.3	14.3
		40	94.3	14.4
		50	94.2	14.5
2	Ethanol	10	94.3	14.4
		20	94.2	14.5
		30	94.3	14.3
		40	94.2	14.5
		50	94.1	15.6
3	Ethylene glycol	10	94.3	14.3
		20	94.2	14.4
		30	94.0	14.8
		40	93.8	15.2
		50	92.7	16.4
4	Glycerol	10	93.1	16.5
		20	92.6	20.8
		30	90.8	24.6
		40	88.7	27.3
		50	86.4	30.2

Table VII Studies on Osmotic Properties of Membrane Cast Under Different Relative Humidities

No.	RH (%)	S.R. (%)	Flux (gfd)
1	85	78.9	27.5
2	75	93.9	14.9
3	65	94.3	14.3
4	55	94.3	11.3
5	45	94.4	8.4
6	35	94.5	7.1
7	25	94.6	6.2

Table VIII Membrane-bound Water Content for Different Annealing Temperatures

No.	Annealing Temp (°C)	Bound Water Content (%)
1	60	22.8
2	70	22.4
3	75	21.6
4	80	19.8
5	85	19.2
6	90	18.6
7	95	17.2

Table IX Specific Water Content at Different Annealing Temperatures

No.	Annealing Temp (°C)	Specific Water Content (g/cm ³)
1	60	0.78
2	70	0.73
3	75	0.68
4	80	0.63
5	85	0.58
6	90	0.54
7	95	0.51

An evaporation period from 0 to 180 s was studied. The evaporation period of 30 s at ambient temperature (25°C) was observed to be the optimum period. This period is the lesser compared to that for conventional CA membranes⁹ (60 s). This is probably because CABz has a higher d.s. value than that of CA; hence, CABz is less amorphous than is CA and therefore it gave tougher membranes than did CA.

The annealing treatment was observed to be optimum at lower temperature (80°C) compared to that for CA (90°C). This is because CA is less crys-

Table X Solvent and Solute Fluxes by Direct Osmosis

No.	Solvent Flux (g/cm ² s)	Solute Flux (g/cm ² s)
1	4.92×10^{-5}	1.34×10^{-8}
2	4.91×10^{-5}	1.32×10^{-8}
3	4.93×10^{-5}	1.36×10^{-8}
Average	4.92×10^{-5}	1.34×10^{-8}

Table XI Membrane Salt Intake by Immersion

No.	Salt Absorbed (g/cm ³)
1	0.74×10^{-2}
2	0.72×10^{-2}
3	0.75×10^{-2}
4	0.75×10^{-2}
Average	0.74×10^{-2}

Table XII Pure Water Flux and Water Permeability Coefficient of Dense CABz Membrane

No.	Thickness (Microns)	Distilled Water Flux (g/cm ² s)	Water Permeability Coefficient (g/cm/s)
1	11.2	7.48×10^{-6}	3.78×10^{-7}
2	16.6	5.50×10^{-6}	4.05×10^{-7}
3	22.1	3.90×10^{-6}	3.89×10^{-7}
Average			3.906×10^{-7}

Applied pressure = 480 psi.

talline than is CABz and, hence, CA membranes are more open or dense. Similarly, the percent shrinkage in area of the CA membrane was greater than that for the CABz membrane during the annealing treatment.

In an alcoholic series, flux-inducing properties were observed to increase with increasing hydroxy groups. Thus, ethylene glycol, a dihydric alcohol, gave better flux than did methanol or ethanol, whereas glycerol, a trihydric alcohol, gave better results than did ethylene.

Table XIII Pure Water Flux and Thickness of Active Layer of CABz Asymmetric Membranes Annealed at Different Temperatures

No.	Annealing Temp. (°C)	PWP (g/cm ² s)	Gross Thickness (mm)	Thickness of Active Layer (microns)
1	70	16.2×10^{-4}	0.16	0.074
2	80	15.4×10^{-4}	0.14	0.078
3	85	13.8×10^{-4}	0.17	0.083
4	90	12.1×10^{-4}	0.18	0.094

The bound water of the membrane is lost to a certain extent during the annealing treatment. The decrease in bound water in the membranes annealed from 60 to 95°C was 5.6%. The annealing treatment at optimum temperature is necessary to develop the membrane with a proper bound-water content, which was optimum at 80°C when the bound-water content was 19.8%.

The specific water content of the membrane gradually decreased on increasing the temperature of annealing. The gradient was more or less uniform at uniform humidity from 60 to 80°C; however, above 85°C, there was very slight decrease in membrane-specific water content, as it became considerably tight.

The values of solvent and solute flux obtained by the direct osmosis method for CABz asymmetric membranes indicate that these membranes would be high-salt-rejecting membranes with considerably good water flux, as indicated by very low solute flux and high solvent flux.

Asymmetric membrane is composed of a dense active layer formed on a porous layer. The solute selectivity is attributed to this dense active layer. The characteristic properties of dense membranes are expected to be applicable to the asymmetric membranes. This is understood from the fact that asymmetric membranes have a greatly reduced effective thickness of a dense membrane.

The active layer thickness of the CABz membrane was 0.078 μ , whereas that of CA membrane¹¹ was 0.13 μ . This accounts for higher flux for CABz mem-

branes than for CA membranes. Similarly, the data obtained for salt diffusion, distribution coefficient, and salt permeability for CABz membranes clearly support the better data obtained for CABz membranes with respect to salt rejection and flux.

CONCLUSION

The CABz osmotic membrane was developed using indigenously prepared CABz. The membrane was fully characterized and compared with conventionally used CA membranes. CABz membranes showed better properties than those of CA membranes, mainly, the flux is better than that of CA but with comparable salt rejection.

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Table XIV Salt Diffusion Distribution Coefficient and Salt Permeability for CABz Membrane

Sodium Chloride	Membrane	$D_2 \times 10^9$ (cm ² /s)	$D_2 \times 10^{12}$ (cm ² /s)	$K \times 10^3$ (cm ² /s)
	Thickness (mm)			
0.5 m	0.16	1.6	48.0	30.0