

Modified Cellulose Acetate Membranes for Desalination*

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Synopsis

Residual hydroxyl groups of commercially available cellulose acetate (39.9% acetyl) have been reacted partially with phenyl isocyanate. The characteristics of these modified polymers have been studied. Membranes have been cast from these polymers to study their potentiality as reverse osmosis membranes. The work has been further extended to investigate the stability of these modified CA under the influence of high temperature and γ irradiation.

INTRODUCTION

The large scale research on desalting of brackish and sea water has shown that cellulose acetate (CA) membranes are extremely effective in desalting. This success of CA membranes indicates that it will be the material of choice in future reverse osmosis plants. In spite of several good features of these membranes, they have some drawbacks such as poor chemical resistance and fast biodegradability,¹ the rapid flux decay due to membrane compaction under the high influent pressure, etc. The effect of styrene grafting to cellulose acetate has been reported² as a possible technique for mechanically stabilizing CA membranes. Surely, modification of cellulose acetate resulting in improved performance will make it a more attractive polymer in the preparation of reverse osmosis membranes for sea and brackish water desalination.

In the present work the residual hydroxyl groups of cellulose acetate have been reacted partially with phenyl isocyanate, and this modified CA possessing urethane linkages has been utilized for the preparation of membranes.

EXPERIMENTAL

Cellulose acetate (39.9% acetyl) was obtained from M/s. Mysore Acetate, India. Phenyl isocyanate (98% pure) has been procured from M/s. Fluka, West Germany. Other chemicals like pyridine, acetone, formamide, and ethyl alcohol were distilled prior to use.

Modification of Cellulose Acetate. A mixture of 25 g of dried cellulose acetate and 300 mL of pyridine was placed in a 500-mL round-bottom flask fitted with a mechanical stirrer, a thermowell, and a reflux condenser. The cellulose acetate was dissolved completely, and then the required amount of phenyl isocyanate was added dropwise in 15 min time at 30–35°C with constant stirring. Then the temperature was raised to refluxing temperature and refluxing was

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continued for 4 h with constant stirring. The reaction mixture was then cooled to ambient temperature and diluted with small amount of acetone. The modified cellulose acetate was isolated by precipitation with the addition of ethyl alcohol. The polymer obtained was a whitish powder and was washed several times with ethyl alcohol.

The modification of cellulose acetate has been effected by using different proportions of phenyl isocyanate. These modified cellulose acetate polymers have been designated as CANCO 10, CANCO 5, CANCO 2.5, and CANCO 1.25. The numerical number stands for the quantity of phenyl isocyanate (mL) used for modification. The molecular weights of these modified CA polymers have been determined by viscosity measurements. Membranes have been cast from these polymers, and their suitability as reverse osmosis membranes has been studied. The tensile strength of the cast membranes has also been determined. The work has been further extended to investigate the stability of these modified polymers under the influence of high temperature and γ irradiation.

Casting Procedure. Casting solutions of different modified CA polymers have been prepared using the proportions of polymer:formamide:acetone in 20:30:50 (weight ratio), respectively, as reported by Rao et al.³ After the initial mixing of these three components, the entire mass was ball-milled for 24 h, and then membranes were cast in the form of flat sheet as per the method described by Loeb and Sourirajan.⁴ Film—15 cm wide and 30 cm long—was cast on a clean, dry glass plate with multiple electric tapes (15 mm wide, 0.4 mm thick) as guide and a casting knife. After evaporation of solvent for 1 min, the membrane cast plate was immersed in a cold water bath (2–3°C), and, after a period of 1 h, the plate was removed and the membrane released from it. The membrane annealing was carried out for 15 min at 80/88°C. The membranes thus obtained were preserved in 0.2% formalin solution. The tensile strength measurements were made on Scott testing machine. The IR spectrum of the representative membrane CANCO 5 has been recorded using a Perkin-Elmer Model 137-E Spectrophotometer. Thermogravimetric analysis has been carried out using MOM-BUDAPEST DERIVATOGRAPH.

RESULTS AND DISCUSSION

Transport Properties. The transport properties of the membranes were tested for water flux and percent salt rejection using a reverse osmosis (RO) unit fabricated in our laboratory (the photograph of the unit has been shown in Fig. 1) at operating pressure of 600 and 900 psi with 5000 ppm of sodium chloride solution as a feed. The percent salt rejection by the membranes was evaluated by measuring the conductance of feed and permeate solutions. The transport properties of various membranes prepared from modified CA polymer have been given in Table I.

Phenyl-isocyanate-modified cellulose acetate membranes show reduced water flux and increased salt rejection as compared to the cellulose acetate membrane. High annealing temperature (88°C) for all the membranes studied exhibits good salt rejection and decreased water flux; however, higher operative pressure improves the water flux of these membranes with marginal increase in salt rejection.

Molecular Weight and Tensile Strength. The molecular weights of

TABLE I
Transport Properties of Membranes (Annealed at 80/88°C) at Different Operative Pressures

Sample no.	Membranes	Operative pressure 600 psi, annealing temperature				Operative pressure 900 psi, annealing temperature			
		80°C		88°C		80°C		88°C	
		Water flux (gfd)	Salt rejection (%)	Water flux (gfd)	Salt rejection (%)	Water flux (gfd)	Salt rejection (%)	Water flux (gfd)	Salt rejection (%)
1	CANCO 1.2	15	72.50	6	81	17	73	8	84
2	CANCO 2.5	13	66	8.30	90	14.50	63	9.60	94
3	CANCO 5	10.50	85	9.50	88.20	13	87	11.50	91.50
4	CANCO 10	9	89	6	92	8.20	90	7.60	94
5	Cellulose acetate (39.9% acetyl)	20	70	10.5	83	38	63	13	84



Fig. 1. Reverse osmosis unit fabricated in NCL.

modified cellulose acetate samples were determined at $30 \pm 1^\circ\text{C}$ in acetone by viscosity method⁵ using $[\eta] = KM^\alpha$, where $K = 1.56 \times 10^{-4}$ and $\alpha = 0.83$. The tensile strength measurements of membranes have been carried out according to ASTM Designation D 882-52T. The comparative characteristics of various modified cellulose acetate along with cellulose acetate are given in Table II.

The tensile strength of the membranes (Table II) is found to increase with the increasing amount of phenyl isocyanate used during modification.

γ Irradiation Effect. One of the modified cellulose acetate membrane, namely CANCO 5 was exposed to Co^{60} source in wet condition with a dose rate of 8 krad/min at Bhabha Atomic Research Centre, Bombay, India.⁶ The radiation effects on membranes were studied in terms of changes in the transport properties, tensile strength etc. The CANCO 5 membranes are found to be relatively stable up to 1 mrad as compared to the cellulose acetate membrane.

Thermal Stability. To evaluate the effect of urethane group and aromatic ring on the thermal stability of the modified cellulose acetate the thermooxidative degradation of these polymers has been studied by the thermogravimetric analysis (TGA) method. Thermogravimetric analysis experiments were made in air at a heating rate of $10^\circ\text{C}/\text{min}$ with MOM-BUDAPEST DERIVATOGRAPH. The thermogravimetric curves have been shown in Figure 2. Loss of weight of polymers at different temperatures was determined from TGA curve and has been presented in Table III.

The results (Table III) indicate that the presence of phenyl ring and urethane

TABLE II
Characteristics of Cellulose Acetate and Modified Cellulose Acetate

Sample no.	Sample	Softening point ($^\circ\text{C}$)	$[\eta]$, Intrinsic viscosity (dL/g)	Molecular weight	Tensile strength of the membranes (kg/cm^2)
1	CANCO 1.25	232-235	1.45	60,300	156
2	CANCO 2.50	238-240	1.47	61,000	175
3	CANCO 5	238-240	1.55	64,860	187
4	CANCO 10	242-244	1.50	62,800	190
5	Cellulose acetate (39.9% acetyl)	242-243	1.40	57,800	105

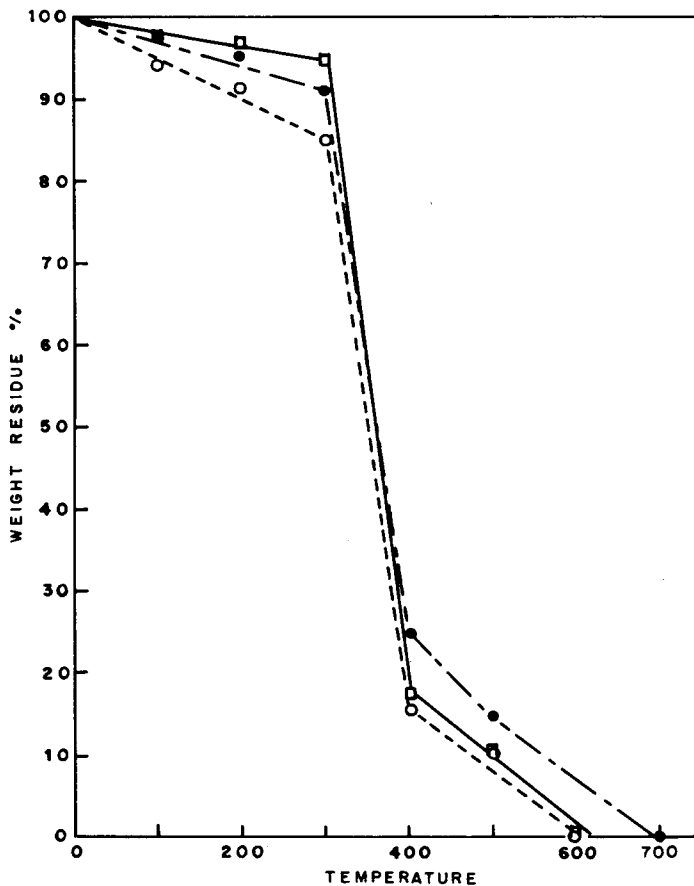


Fig. 2. T_g curves in air at 10°C/min for CANCO samples: (O) cellulose acetate; (□) CANCO 2.5; (●) CANCO 10.

group on the cellulose acetate backbone improves the thermal stability. The modified cellulose acetate polymers are stable up to 300°C. A further increase in temperature causes rapid decomposition of the modified cellulose acetate as has been observed in the case of cellulose acetate.

TABLE III
Percentage Weight Loss at Different Temperatures for Modified Cellulose Acetate and Cellulose Acetate

Temp (°C)	Modified cellulose acetate				Cellulose acetate
	CANCO 1.25	CANCO 2.50	CANCO 5	CANCO 10	
100	3	3	2	2.5	6
200	3	3	3	3.5	7
300	5	5	5	8.5	15
400	85	82	85	75	85
500	90	90	90	85	92
600	100	100	100	88	100
700	—	—	—	100	—

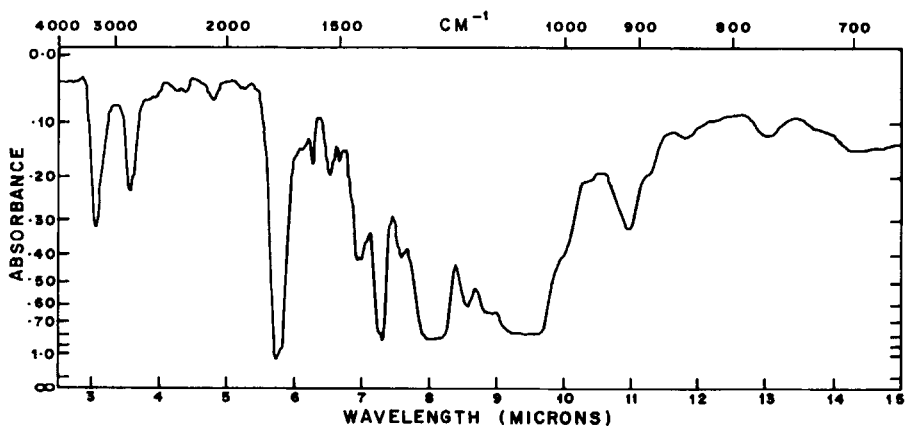


Fig. 3. IR spectrum of CANCO 5 sample.

IR Spectrum. A representative IR spectrum of CANCO 5 is shown in Figure 3. The spectrum shows the characteristic bands for transamide group at 1650–1550 cm^{-1} .

CONCLUSION

The modification of cellulose acetate with phenyl isocyanate results in a stronger polymer, which is more resistant to γ irradiation and thermal resistance, compared to cellulose acetate used in the present study. The reverse osmosis experiment on the modified CA membranes shows reduced water flux and increased salt rejection in comparison with CA membrane.

The work on modification of cellulose acetate with aliphatic isocyanate such as butyl and propyl isocyanates is in progress. The performance of these polymers as water desalination membranes becomes a separate study.

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