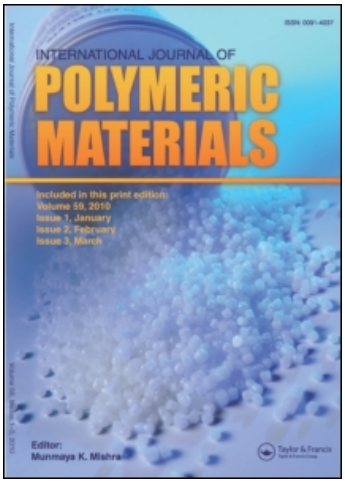


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# Modification of Cellulose Acetate by Aliphatic Isocyanates for Reverse Osmosis Studies

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In the present study an emphasis has been given to modify the commercially available cellulose acetate (CA) (39.9% acetyl) by aliphatic isocyanates to increase the mechanical resistance of the polymer. The transport properties of the cast membranes from these modified CA polymers have been studied. The work has been further extended to study the thermo oxidative degradation of these modified cellulose acetate polymers in dry state in air.

## INTRODUCTION

Reverse osmosis has already gained firm entry into the industrial world of water treatment and variety of wide separation, concentration and fractionation problems. Membranes prepared from secondary cellulose acetate (CA) have been the most successful for the

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reverse osmosis method of desalination. However, the major limitation of cellulose acetate reverse osmosis membrane is the membrane compaction and reduction of product flux rate under high operating pressures. Mechanically stabilized CA membranes have been prepared from cellulose acetate-styrene graft polymer.[1] In continuation of our earlier work[2] on the modification of CA by aromatic isocyanate, it would clearly be of interest to modify CA by aliphatic isocyanates as well as to study the potentiality of these modified polymers as reverse osmosis membranes for sea and brackish water desalination.

## EXPERIMENTAL

Cellulose acetate (39.9% acetyl) was procured from Mysore Acetate, India. Butyl and propyl isocyanates (98% pure) were obtained from M/s. Aldrich Chemical Co., USA. All other chemicals were distilled prior to use. The residual hydroxyl groups of cellulose acetate have been reacted partially with appropriate isocyanate as per the procedure reported earlier.[2] The isolated modified cellulose acetate polymers were in the form of whitish powder. After repeated precipitation with ethyl alcohol the modified polymers were dried in an oven at $100 \pm 5$°C for 6 h.

For modification of cellulose acetate different molar quantities of both butyl and propyl isocyanates have been used. The modified polymers thus obtained have been numbered as CABNCO (0.0125), CABNCO (0.025), CABNCO (0.050), CABNCO (0.075) and CABNCO (0.10) (for butyl isocyanate) and CAPRO (0.0125), CAPRO (0.025), CAPRO (0.05), CAPRO (0.075) and CAPRO (0.10) (for propyl isocyanate). The figures given in brackets show the molar quantities of each isocyanate used during partial modification of CA. The characteristics of these modified polymers have been given in Table III.

The procedure for preparation of membranes is the same as that described previously.[3] The casting solution was prepared by mixing the modified polymer:formamide:actone in 20:30:50 (weight ratio). This solution was cast on a glass plate at room temperature by using casting knife and an electric tape (0.4 mm thickness) as a guide. After an evaporation period of 60 s the membrane assembly

TABLE I

Reverse osmosis data on cellulose acetate modified with butyl isocyanate at different annealing temperature

| S. no. | Sample | Annealing temp. °C | Water flux gfd | % SR | Membrane constant $\times 10^5$ g/cm$^2$ s Atm. | Specific water content g/cm$^3$ | Av. pore diameter A° |
|---|---|---|---|---|---|---|---|
| 1 | CABNCO (0.0125) | 80 | 15.50 | 80 | 2.03 | 0.67 | 30.10 |
| 2 | CABNCO (0.025) | 80 | 14.00 | 82 | 1.75 | 0.64 | 28.30 |
| 3 | CABNCO (0.050) | 80 | 13.00 | 83 | 1.70 | 0.62 | 27.90 |
| 4 | CABNCO (0.075) | 80 | 6.50 | 90 | 1.20 | 0.56 | 23.80 |
| 5 | CABNCO (0.10) | 80 | 4.50 | 91 | 0.88 | 0.54 | 20.00 |
| 6 | Cellulose Acetate (CA) | 80 | 20.00 | 70 | 2.60 | 0.72 | 32.20 |
| 1 | CABNCO (0.0125) | 88 | 10.00 | 85 | 1.42 | 0.65 | 23.80 |
| 2 | CABNCO (0.025) | 88 | 9.60 | 89 | 1.26 | 0.60 | 23.60 |
| 3 | CABNCO (0.050) | 88 | 9.00 | 93 | 1.20 | 0.58 | 23.00 |
| 4 | CABNCO (0.075) | 88 | 6.00 | 95 | 1.15 | 0.52 | 22.00 |
| 5 | CABNCO (0.10) | 88 | 3.50 | 96 | 0.76 | 0.51 | 19.00 |
| 6 | CA | 88 | 10.50 | 83 | 1.50 | 0.70 | 23.80 |

TABLE II

Reverse osmosis data on cellulose acetate modified with propyl isocyanate at different annealing temperature

| Sr. no. | Sample | Annealing temp. °C | Water flux gfd | % SR | Membrane constant $\times 10^5$ g/cm$^2$ s Atm. | Specific water content g/cm$^3$ | Av. pore diameter A° |
|---|---|---|---|---|---|---|---|
| 1 | CAPRO (0.0125) | 80 | 17.00 | 74 | 2.20 | 0.66 | 30.50 |
| 2 | CAPRO (0.025) | 80 | 15.50 | 80 | 1.97 | 0.64 | 28.90 |
| 3 | CAPRO (0.050) | 80 | 14.00 | 82 | 1.75 | 0.61 | 29.00 |
| 4 | CAPRO (0.075) | 80 | 10.00 | 85 | 1.26 | 0.54 | 26.60 |
| 5 | CAPRO (0.10) | 80 | 7.50 | 88 | 0.98 | 0.53 | 21.10 |
| 6 | CA | 80 | 20.00 | 70 | 2.60 | 0.72 | 32.20 |
| 1 | CAPRO (0.0125) | 88 | 10.20 | 85 | 1.42 | 0.65 | 23.50 |
| 2 | CAPRO (0.025) | 88 | 9.80 | 90 | 1.26 | 0.63 | 23.00 |
| 3 | CAPRO (0.050) | 88 | 9.20 | 93 | 1.20 | 0.62 | 22.80 |
| 4 | CAPRO (0.075) | 88 | 8.50 | 95 | 1.13 | 0.58 | 20.20 |
| 5 | CAPRO (0.10) | 88 | 6.20 | 96 | 0.87 | 0.52 | 18.70 |
| 6 | CA | 88 | 10.50 | 83 | 1.50 | 0.70 | 23.80 |

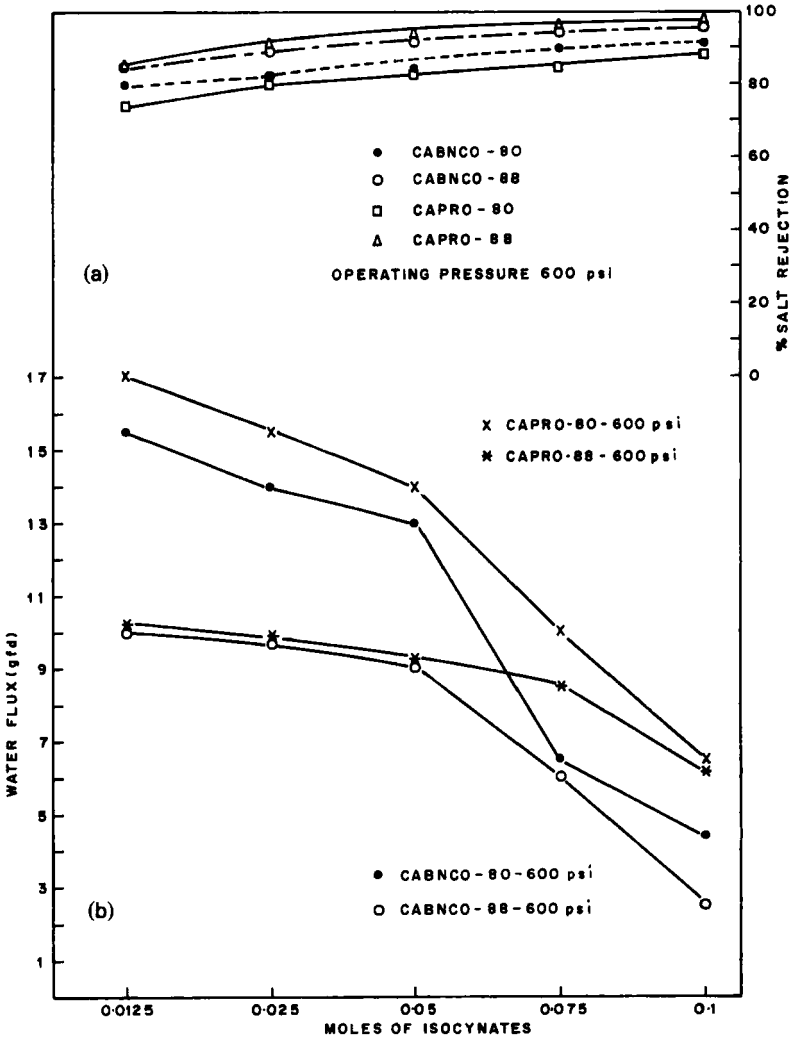


FIGURE 1(a) The effect of urethane modification on % salt rej.

FIGURE 1(b) The effect of urethane modification on water flux.

was immersed in ice-cold water for 1–2 h and then the plate was removed and the membrane was released from it. The membrane thus obtained have been annealed at 80/88°C, and was preserved in 0.2% formalin solution. The tensile strength measurements were made on Scott testing machine. The transport properties such as water flux and salt rejection have been tested on a Reverse Osmosis unit fabricated in our laboratory. The operating pressure used was 600 psi in all the cases with 5000 ppm of sodium chloride as a feed. The membrane surface which was in contact with air during casting was directed to the high pressure side of the feed solution. Thermogravimetric analysis has been carried out using MOM-BUDAPEST DERIVATOGRAPH. Microbial resistance was determined by ASTM designation D 1924-63 (1964) by using different cultures.

## RESULTS AND DISCUSSION

The IR spectra of the modified CA polymers show the characteristics bands for transamide group at 1650–1550 $cm^{-1}$. Reverse osmosis data have been summarised in Tables I and II. The effect of

TABLE III

Characteristics of modified cellulose acetates and cellulose acetate

| Sr. no. | Sample | Softening point °C | [η] Intrinsic viscosity* dl/g | Mol. wt.† | % N | Tensile strength of the membrane $kg/cm^2$ |
|---|---|---|---|---|---|---|
| 1 | CABNCO (0.0125) | 237–240 | 1.425 | 59 000 | 0.30 | 138 |
| 2 | CABNCO (0.025) | 245–247 | 1.55 | 64 800 | 0.38 | 134 |
| 3 | CABNCO (0.050) | 243–245 | 1.55 | 64 800 | 0.91 | 140 |
| 4 | CABNCO (0.075) | 240–242 | 1.60 | 65 920 | 0.99 | 134 |
| 5 | CABNCO (0.10) | 237–240 | 1.50 | 62 800 | 1.56 | 137 |
| 6 | CAPRO (0.0125) | 243–245 | 1.425 | 59 000 | 0.30 | 122 |
| 7 | CAPRO (0.025) | 248–250 | 1.45 | 60 200 | 0.50 | 150 |
| 8 | CAPRO (0.050) | 247–250 | 1.46 | 61 000 | 1.08 | 145 |
| 9 | CAPRO (0.075) | 248–250 | 1.475 | 61 400 | 1.43 | 162 |
| 10 | CAPRO (0.10) | 250–252 | 1.50 | 62 800 | 1.95 | 168 |
| 11 | CA | 242–243 | 1.40 | 57 800 | — | 105 |

* In acetone at 30 ± 0.1°C.

† $K = 1.56 \times 10^{-4}$ and $\alpha = 0.83$.

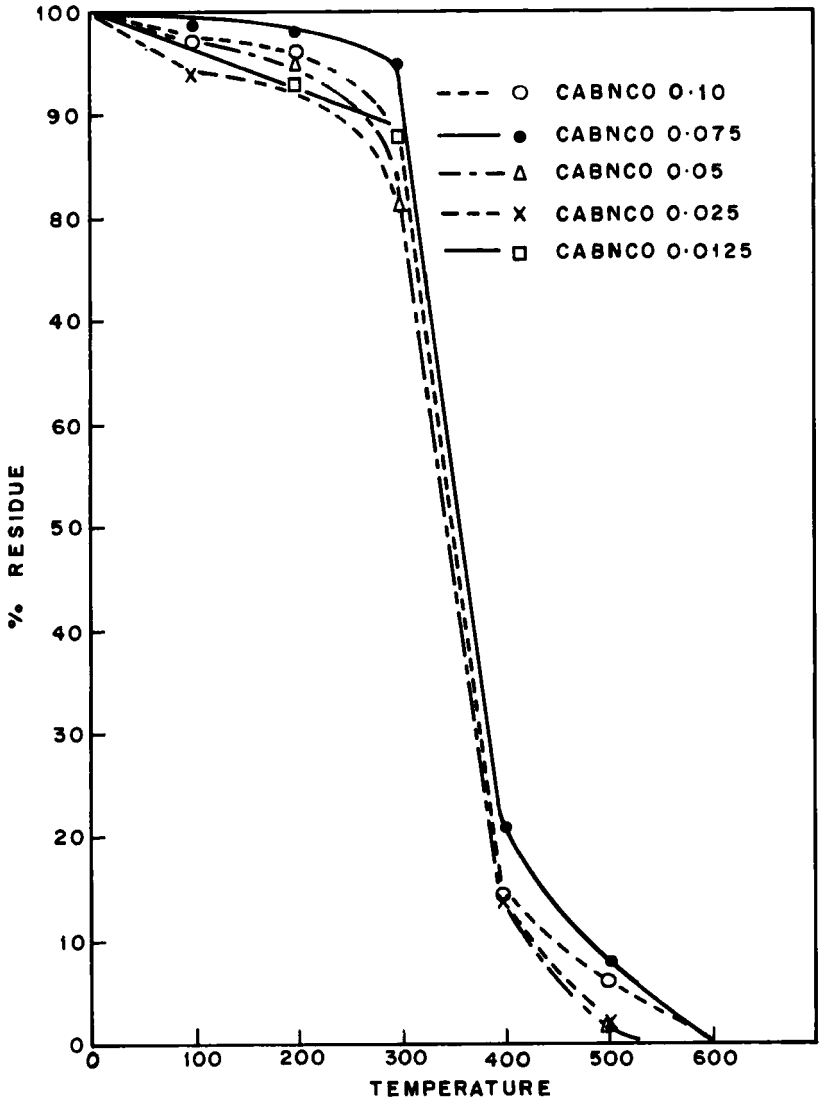


FIGURE 2 T.G. curves in air at 10°C/min for CABNCO samples.

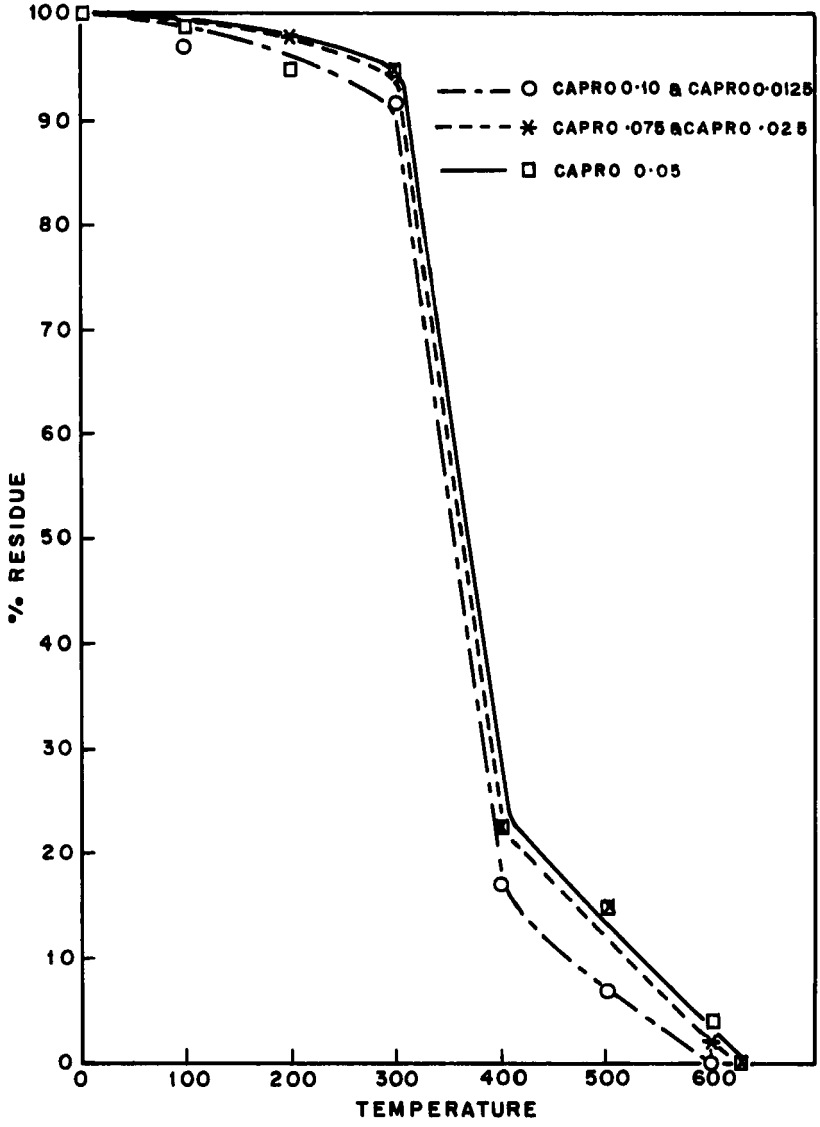


FIGURE 3 T.G. curves in air at 10°C/min for CAPRO samples.

TABLE IV

Percentage weight loss at different temperature for modified cellulose acetate

| Temp. °C | CABNCO (0.0125) | CABNCO (0.025) | CABNCO (0.050) | CABNCO (0.075) | CABNCO (0.10) | CAPRO (0.0125) | CAPRO (0.025) | CAPRO (0.050) | CAPRO (0.075) | CAPRO (0.10) | CA |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 100 | 6 | 2 | 4 | 1.5 | 3 | 4 | 0 | 0 | 1.5 | 3 | 6 |
| 200 | 7 | 2.5 | 5 | 1.8 | 4 | 4 | 1 | 1 | 2 | 4.5 | 7 |
| 300 | 12 | 7 | 9 | 5 | 12 | 8 | 5 | 5 | 5 | 8 | 15 |
| 400 | 86 | 80 | 85 | 79 | 84.5 | 84 | 77 | 85 | 78 | 83 | 84 |
| 500 | 98 | 90.5 | 96 | 92 | 94 | 94 | 91 | 87 | 85 | 93 | 91 |
| 600 | 100 | 100 | 100 | 99 | 100 | 100 | 95 | 96 | 98 | 100 | 100 |
| 620 | — | — | — | — | — | — | 100 | 100 | 100 | — | — |

urethane modification of CA by butyl and propyl isocyanate on % salt rejection and water flux has been shown in Figures 1(a) and 1(b). The lower annealing temperature for all the membranes studied exhibits higher water flux; however, % salt rejection is on the lower side. It can be seen from Figure 1(b) that the modification of CA effected by both the isocyanates upto 0.05 moles show nearly steady water flux at different annealing temperatures (80, 88°C); however, reasonable drop in water flux is observed where CA has been modified with more than 0.05 moles of the isocyanates. A higher % salt rejection has been observed with the increase of isocyanate quantities used during modification of CA (Figure 1(a)).

The decrease in specific water content, membrane constant and average pore diameter has been observed with the increase of amount of isocyanate used during modification. The tensile strength of the membranes (Table III) is found to increase with the increasing amount of isocyanate used.



Thermal stability of cellulosic materials has been studied in the past[4] and the data is available in the literature. In the absence of such data for partially modified cellulose acetate with aliphatic isocyanates, the present work was extended to study the thermal stability of these modified CA polymers in dry state by thermogravimetric analysis (TGA) method. TGA experiments were made in air at a heating rate of 10°C/min with MOM-BUDAPEST DERIVATOGRAPH. The thermogravimetric curves have been shown in Figures 2 and 3. The loss of weight of modified CA polymers at different temperatures has been determined from TGA curves and has been presented in Table IV. From the TGA data, it is clear that the modified CA polymers are fairly stable upto 300°C in air, however, rapid decomposition is observed in all the modified polymers beyond 300°C.

The microbial study on the modified CA membranes indicates that there is no fungi growth on the membranes.

## CONCLUSIONS

1. The modification of commercial CA with aliphatic isocyanates results in a polymer with high tensile strength as compared with CA.

2. The modified CA membranes exhibit higher % salt rejection with reduced water flux.

3. Optimum transport properties are obtained at higher annealing temperatures.

4. The modified CA polymers are fairly stable upto 300°C in dry state.

5. The membranes prepared from modified CA polymers show good microbial resistance.

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