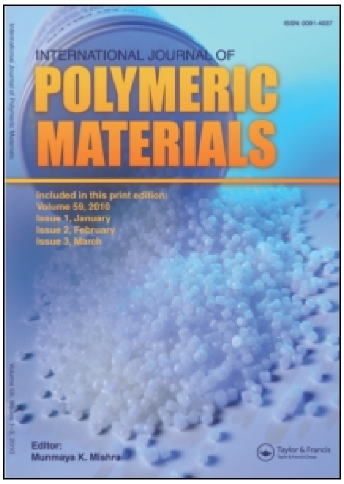

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Silylcellulose Acetate Membrane for Desalination of Water†

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Commercial cellulose acetate (39.9% acetyl) was partially modified with different proportions of Trimethylchlorosilane. The physical properties of modified polymers were studied. The membranes prepared from these polymers were evaluated for desalination of water by reverse osmosis. The thermal stability of modified cellulose acetate was also investigated.

INTRODUCTION

Membrane separation technique is industry's one of the major needs. Reverse Osmosis process (RO) is already well established technique for desalination of water and treatment of industrial effluents. Desalination of water by RO is simple, economic and practical hence gaining industrial importance. Cellulose acetate (CA) membranes are widely used for desalination of water by RO due to it's asymmetric characteristic.[1] Still it has certain drawbacks like poor chemical resistance and declination in high rate water flux under operating conditions. For improvement in the performance of

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RO membrane, modification of CA by chemical means is emphasised all over the world. In our previous work we have modified CA with isocyanates and the performance of the membrane were studied for desalination of water by RO.[2,3,4] This paper reports the partial modification of CA by Trimethyl chlorosilane (TMCS). The hydrophobic character of CA is further enhanced by introducing Si—O—C linkage.[5] The membranes obtained from Trimethylsilyl cellulose acetate (TMSCA) were evaluated for desalination of water by RO.

EXPERIMENTAL

Commercial cellulose acetate (39.9% acetyl and D.S. 2.4–2.6) was procured from M/s. Mysore Acetate (India), Trimethylchlorosilane was obtained from M/s. Fluka (West Germany) and was further purified by heating with sucrose and pyridine at 100–110°C for 1 hr.[5]

PREPARATION OF TMSCA

A 500 ml 4 necked flask fitted with a mechanical stirrer, a reflux condensor, a dropping funnel and a nitrogen gas inlet was flushed with nitrogen and 25 g of dry CA and 300 ml of pyridine were placed and stirred at 50–55°C till CA was completely dissolved. Then 1.016 g of TMCS in 25 ml of pyridine was added dropwise with stirring for 30 minutes. Temperature was raised to 100–110°C and the reaction mixture was refluxed for 6 hr. Unreacted TMCS was removed under reduced pressure (40°C/10 mm Hg). The slurry was filtered through a sintered glass funnel holding 1″ layer of alumina with a layer of tightly packed glass wool on top. The clear colourless filtrate was free of pyridine hydrochloride. The polymer was obtained in the form of white solid by precipitation with methanol and finally dried at 100°C/15 mm Hg.

CA was modified with different molar ratios of TMCS and were designated as TMSCA (0.2), TMSCA (0.4), TMSCA (0.6) and TMSCA (0.8). The number in parentheses denotes the molar proportions of TMCS used for partial modification of CA.

IR spectrum of the modified CA was recorded as film on Perkin-

Elmer Model 683 IR spectrophotometer from 4000 cm^{-1}–200 cm^{-1}.

The intrinsic viscosity of polymers was determined using Ubbelhode viscometer in acetone at 30° ± 1°C.[6] The percent acetyl content of the polymers was determined by ASTM Designation Number D 871-61T. The thermogravimetric analysis (TG) was carried out on MOM-BUDAPEST DERIVATOGRAPH at a heating rate of 10°C/minute in air. The tensile strength of the membranes was tested on Scott testing machine according to ASTM Designation D 882-527.

MEMBRANE CASTING

For preparation of membrane, a solution of polymer, formamide and acetone in 20:25:55 (wt. ratio) was taken and ball milled for 24 hrs. for uniform mixing. Then the flat membrane was cast on the glass plate of size 15 cm × 30 cm with a multiple electrical tape as a guide and casting knife at room temperature (30°C). The membrane was allowed to air dry by evaporating the solvent for one minute and then dipped in ice cold water (2°–4°C) for 1 hr. The membrane was released by removing the plate from the water and was annealed at 80°/88°C for 15 minutes. They were preserved in 0.2% formaline solution. The transport properties of the annealed membranes such as salt rejection, water flux rate, etc. were determined on the RO unit fabricated in this laboratory at operating pressure of 600 psi and 900 psi using 5000 ppm sodium chloride solution as feed. Specific water content of the membranes was determined according to Ferry's method.[7] Membrane constant and average pore diameter were determined by pure water permeability of membrane.

RESULTS AND DISCUSSION

Modification of CA

CA was reacted with different molar proportions of TMCS in pyridine at 100°–110°C. A highly pure TMCS was used to carry out the partial modification of CA and to get product partially soluble

TABLE I

Physical Characteristics of Trimethylsilyl Cellulose Acetate (TMSCA)

Compound	Softening Point °C	η [Intrinsic Viscosity] dL/g	Molecular weight	Total Degree of substitution	% of Acetyl content	% Si[8]	Tensile strength of membrane kg/cm^2
TMSCA (0.2)	232–235	1.45	60,200	2.392	39.20	0.14	120.2
TMSCA (0.4)	235–238	1.5	62,800	2.371	38.98	0.35	125.7
TMSCA (0.6)	238–242	1.55	64,860	2.327	38.57	0.42	132.8
TMSCA (0.8)	241–244	1.6	65,920	2.306	38.3	0.50	140.0
CA	243–245	1.4	57,800	2.446	39.9	—	105.0

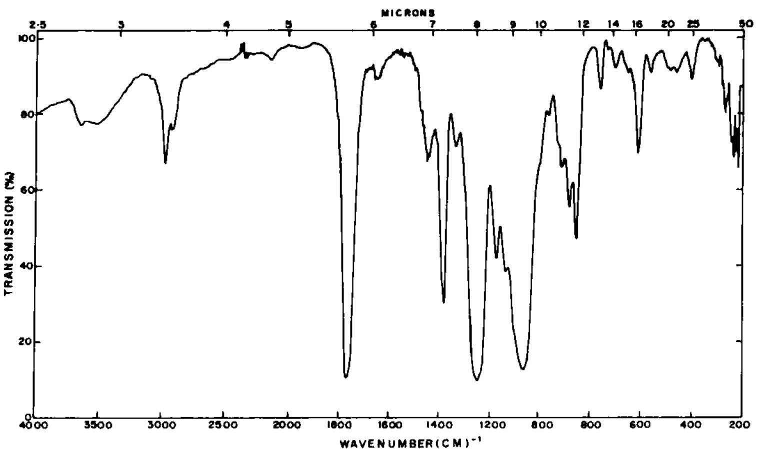

FIGURE 1 IR spectrum of TMSCA (4)

in hydrocarbon solvent. The modified polymers were characterised by softening point, viscosity and IR spectra (Table I). The molecular weight of TMSCA was determined according to the equation $\eta = kM^{\alpha}$ where $k = 1.56 \times 10^{-4}$ and $\alpha = 0.83$ in acetone at 30° ± 1°C. In the IR spectrum (Fig. 1) of partially modified CA, bands characteristic of Si-C stretching at 860 cm^{-1} and 845 cm^{-1} were observed. The tensile strength values obtained with TMSCA were higher than that of unmodified CA. This may be due to silyl groups in the polymer.

Thermal stability

The effect of silicon moiety on the thermal stability of TMSCA was studied by dynamic thermogravimetric analysis. The loss in weight of polymers at different temperatures was determined from primary theormograms and given in Table IV. Modified CA showed slightly higher thermal stability due to Si—O—C linkage.

Performance of modified CA membranes

The transport properties like water flux rate, percent salt rejection, specific water content and membrane constant of partially modified

TABLE II

Transport Properties of Membranes (Annealed at 80/88°C) at Different Operative Pressure

		Operative pressure 600 psi annealing temperature				Operating pressure 900 psi annealing temperature			
		80°C		88°C		80°C		88°C	
Sample No.	Membrane	Water flux (gfd)	Salt rejection %	Water flux (gfd)	Salt rejection %	Water flux (gfd)	Salt rejection %	Water flux (gfd)	Salt rejection %
1.	TMSCA (0.2)	18.0	69	12	77.8	19	72	13	80.9
2.	TMSCA (0.4)	14.5	74	10.9	80.2	16.5	77	12.4	82.5
3.	TMSCA (0.6)	13	78	9.4	83.1	14	81.5	11	85.1
4.	TMSCA (0.8)	11.1	83	8.1	85.8	12	86	9.8	87.6
5.	CA	20	67	12.1	76	34	71	15	80.1

CA membrane as well as that of unmodified CA were tested on RO unit at operating pressure of 600 psi and 900 psi with 5000 ppm of sodium chloride solution as feed. The percent salt rejection was calculated from the conductance of feed and permit solution, TMSCA membranes exhibited higher salt rejection compared to CA membrane. The percent salt rejection was increased as the

TABLE III

Membrane Characteristics of TMSCA and CA at 600 psi Operating Pressure

No.	Membrane	Annealing temperature °C	Specific water content g/cm^3	Membrane constant $\times 10^5$ g/cm^2 Atm	Average pore diameter A°
1.	TMSCA (0.2)	80	0.69	2.1	30.3
2.	TMSCA (0.4)	80	0.62	1.8	28.1
3.	TMSCA (0.6)	80	0.54	1.52	25.9
4.	TMSCA (0.8)	80	0.45	1.49	23.1
5.	CA	80	0.74	2.6	32.20
6.	TMSCA (0.2)	88	0.58	1.21	24.3
7.	TMSCA (0.4)	88	0.51	1.12	22.1
8.	TMSCA (0.6)	88	0.46	0.91	20.4
9.	TMSCA (0.8)	88	0.40	0.82	19.1
10.	CA	88		1.5	23.8

TABLE IV

Percentage Weight loss at Different Temperatures for TMSCA and CA

No.	Temperature °C	TMSCA (0.2)	TMSCA (0.4)	TMSCA (0.6)	TMSCA (0.8)	CA
1.	100	4	4	3.6	3	6
2.	200	4.5	4	3.5	3	6.5
3.	300	6	5.5	5	4.5	10
4.	400	85	80	80	75	85
5.	500	90	85	85	83	92
6.	600	100	97	95	92	100

molar proportions of TMCS for the partial modification of CA was increased (Table II). However, the water flux rate and specific water content of TMSCA membrane was less than that of unmodified CA (Table III). Membrane constant and average pore diameter of modified CA were lower than that of unmodified CA membranes. Annealing temperature of membrane has profound effect on the percent salt rejection. Higher annealing temperature for both TMSCA and CA membrane gave higher percent of salt rejection (Table II). Water flux rate was found to depend upon the operating pressure. While marginal increase in percent salt rejection was observed at higher operating pressure.

CONCLUSIONS

CA was partially modified with TMCS to obtain modified CA which were characterised by softening points, tensile properties and IR spectroscopy. RO membranes prepared from TMSCA exhibited better salt rejection than CA while water flux rate and membrane constant were reduced.

References

1. C. E. Reid and B. J. Breton, *J. Appl. Poly. Sci.* **1**, 133 (1959).
2. N. D. Ghatge, M. B. Sabne, K. B. Gujar and S. S. Mahajan, *J. Appl. Poly. Sci.* **29**, 1743 (1984).
3. N. D. Ghatge, M. B. Sabne, K. B. Gujar and S. S. Mahajan, *Intern. J. Polymeric Mater.* **10**(4), 284 (1984).

4. S. S. Mahajan, M. B. Sabne, K. B. Gujar and N. D. Ghatge, *Intern. J. Poly. Mater.* (in press).
5. J. F. Klebe and H. L. Finkbeiner, *J. Poly. Sci.* **A-1, 7,** 1947 (1969).
6. H. Kirk Johnston and S. Sourirajan, *J. Appl. Poly. Sci.* **16,** 3375 (1972).
7. J. D. Ferry, *Chem. Rev.* **18,** 373 (1936).
8. R. H. Meen and H. Gilman, *J. Org. Chem.* **23,** 314 (1958).