

Studies on Polyurea-Amide Membranes

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SYNOPSIS

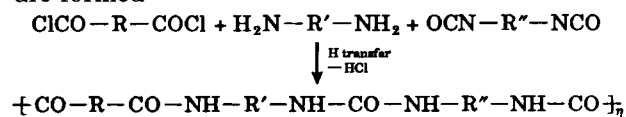
Different polyurea-amides were synthesized by interfacial polymerization of acid chloride, diamine, and diisocyanate. The polymers and the membranes were characterized for their RO/UF applications. Highly porous membranes could be prepared from the sulfuric acid-based casting formulation and the membrane casting conditions were established. The resulting membranes are not asymmetric as they give high permeability to water and salt solutions. They are found to be resistant to many organic solvents, thus making them useful in concentration/separation applications. Whole milk, egg albumin and Na-alginate were found to be rejected 100% by these membranes, while solutes of about 20,000 M_w are found to be rejected to the extent of 70–80%.

INTRODUCTION

From the knowledge of interfacial parameters (α_p , α_n , and β) generated for characterizing different polymeric materials, nitrogen-containing polymers are envisaged as suitable polymeric materials for reverse osmosis application.^{1–3} Structural groups like NH–CO and –NCO– are preferable in polymers as they exhibit positive contributions to interfacially sorbed water resulting in high flux and high salt rejection membrane. As a result polyamides, polybenzhydrazides, polyurea and polybenzimidazole membranes have been studied extensively.⁴ Polyamides and polyureas are excellent sources for producing thin film composite membranes.^{5–7} Studies on polyurea-amide membranes for reverse osmosis/ultrafiltration have not been reported thus far.

Six polyurea-amides have been synthesized in this laboratory by an interfacial polymerization method. The polymers thus obtained have been developed as porous membranes and are found useful in ultrafiltration applications.

The reaction route is shown below, wherein the isocyanate and acid chloride terminated polymers are formed



EXPERIMENTAL

Synthesis of Polyurea-Amide Polymers

Solvents and monomers were purified as described by Morgan.⁸ Forty millimoles of acid chloride and 40.0 mmol of diisocyanate were dissolved in 150 mL dried toluene or methylene chloride and charged into a three-necked 250-mL flask fitted with a thermometer, separating funnel and a high-speed stirrer. A 200-mL solution of 80.0 mmol diamine in 0.5 normal sodium hydroxide was added gradually over a period of 15 min under rapid stirring. The reaction temperature was maintained at 5°C for 1 h. The resultant polymer mass was washed successively with hot water and methanol several times, and filtered and dried under vacuum at 70°C. Table I shows the six polymers synthesized from different monomers.

Viscosity

Polymer viscosity was measured by an Ostwald Capillary Flow Viscometer at a constant temperature of $25 \pm 1^\circ\text{C}$ and expressed as reduced viscosity, η_{red} (0.5 g/100 mL of 98.08% H_2SO_4). The viscosity of the casting solution was measured by a Brookfield Synchroelectric Viscometer at $25 \pm 1^\circ\text{C}$ and expressed in centipoises (cp).

Membrane Porosity

Membrane porosity was measured by adopting the following relation

$$\text{Porosity \%} = \frac{W_1 - W_2}{W_2} \times 100$$

where W_1 and W_2 are the wet and the dry weight at 105°C of the membrane, respectively.

Preparation of Membrane

Sulfuric acid-based casting solutions were prepared from all the 6 polymers. After casting on a smooth, clean glass plate the membranes were quickly immersed in a water bath for gelation. After 30 min, the membranes were taken out and washed thoroughly with water and preserved in distilled water. No heat treatment was given to the membrane.

Ultrafiltration Test

Prior to ultrafiltration experiments, all membranes were subjected to pressurization at 75 psig for 30 min with distilled water. Subsequent to this pressurization, experiments with whole milk, papain (10%), Na-alginate (0.1% and 0.25%), egg albumin were carried out and permeates were detected by different test methods as shown in Table II.

Table II Methods of Detection and Molecular Weight of Some Solutes

Solute	Average M_w	Method for its Detection
Whole milk (milk protein)	15,000	N ₂ -estimation
Papain (10% solution)	20,000	Sugar refractometer
Egg albumin (1.0% solution)	65,000	NaCl/Na ₂ SO ₄ precipitation
Na-alginate (0.10 and 0.25% solution)	150,000	Acetone/alcohol precipitation

RESULTS AND DISCUSSION

In the present studies an unusual polymer-solvent system has been used for making the porous membrane. The membrane is not asymmetric in nature as it gives 10% salt rejection when tested with sodium chloride solution. The polymer membranes were cast according to the phase inversion method. An air exposure from 10 s to 1 h yielded an identical porous membrane, except the sulfuric acid absorbs the atmospheric moisture and creates incipient ge-

Table I Polyurea-amides from Different Acid Chlorides, Diamines and Diisocyanates

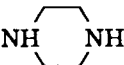

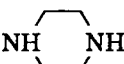
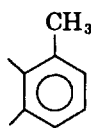
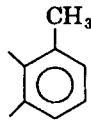


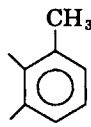
Polymer No.	Acid Chloride	Diamine	Diisocyanate	Softening Point, °C	Reduced Viscosity, η_{red}
1	—(CH ₂) ₄ —	—(CH ₂) ₆ —	—(CH ₂) ₆ —	245	1.36
2	—(CH ₂) ₄ —		—(CH ₂) ₆ —	400	1.04
3	—(CH ₂) ₄ —		—(CH ₂) ₆ —	217	0.72
4	—(CH ₂) ₄ —			225	1.50
5	—(CH ₂) ₄ —	—(CH ₂) ₆ —		210	0.50
6				315	0.98

Table III Composition, Characterizations, and Performance of Polyurea-Amide Membranes

Polymer No.	Membrane Casting Composition		Casting Solution Viscosity, Cp	PWP Flux, GFD	NaCl Performance		Strength at Break, kg/cm ²	Porosity %	Dimensional Shrinkage %
	Polymer Wt %	Conc. H ₂ SO ₄ Vol %			Flux, GFD	R NaCl %			
1	40	60	15,000	120	120	10	60.5	75.21	17.3
2	40	60	15,000	110	105	10	73.9	73.01	20.1
3	45	55	10,500	205	200	0	Membrane brittle	70.10	10.2
4	30	70	16,500	82	80	9	80.3	69.12	20.2
5	45	55	9,000	27	27	0	Membrane brittle	68.73	14.5
6	25	75	15,000	80	75	8	35.2	76.75	15.5

Membrane gelation in 20°C water; as-cast membrane thickness 150 μm. Feed: 5000 ppm sodium chloride solution; operating pressure: 600 psig.

Table IV Effect of Gelation Media on the Dimensional Shrinkage and Porosity

Gelation Media	Dimensional Shrinkage, %	Pure Water Flux, GFD	Porosity, %
Ice water 2°C	10.5	123	75.7
Water 25°C	20.1	110	73.0
Methanol 50% in water	18.3	108	72.0
0.1N H ₂ SO ₄ 25°C	5.7	130	80.3

Table V Solvent Resistance of Polyurea-Amide Membrane^a Made of Polymer No. 2

Solvent	Dissolve	Swelling	Unaffected
Dioxane	-	-	+
Acetone	-	-	+
Tetrahydrofurane	-	-	+
Chloroform	-	-	+
Sulfolane	-	+	-
Dimethyl formamide	-	+	-
Dimethyl acetamide	-	+	-
N-Methyl pyrrolidone	-	+	-
0.1N H ₂ SO ₄	-	-	+
0.1N NaOH	-	-	+
98.08% H ₂ SO ₄	+	-	-

^a (+) Yes; (-) No.

lation of the upper surface of the membrane. Thus, the porous structure is produced during the gelation process with the rapid exchange between sulfuric acid and water. This assumption is supported by our earlier investigation on a polyurea-sulfuric acid-

based porous membrane which was developed for ultrafiltration applications.⁹

The addition of any organic additives, i.e., polyethylene glycol, tetrahydrofuran, triethyl phosphate, and methyl cellosolve ranging from 1.0–10.0% into

Table VI Rejection of High Molecular Weight Solutes by Polyurea-Amide Membrane

Polymer No.	Rejection, %				
	Whole Milk	Papain 10%	Egg Albumin 1.0%	Na-alginate	
				0.1%	0.25%
Operating Pressure, psig					
	65	70	50	50	50
1	100	80	100	100	100
2	100	70	100	100	100
3	100	80	100	100	100
4	100	75	90-95	100	100

the acid-based solution kept at 5°C has no effect on the membrane porosity. Heat treatment from 70–95°C has no effect on the membrane porosity. Thus, the membrane produced has a highly porous structure.

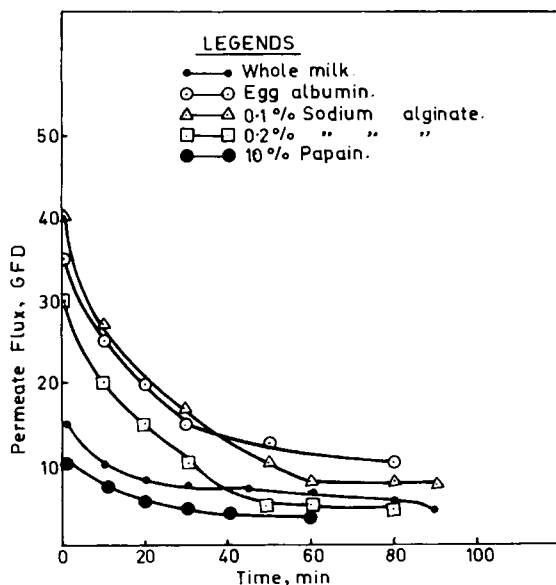
Optimization of Membrane Casting Composition

Optimized casting compositions of the polymers and the reverse osmosis characteristics of the resulting membranes are shown in Table III. Casting solution viscosity and the mechanical strength of the membrane were adopted as criteria to develop the membrane compositions. Since polymers 3 and 5 have very low solution viscosities, higher concentrations in the casting compositions were used. The mem-

branes made from these polymers are very brittle. Membranes with a good mechanical strengths could be produced from polymers 1, 2, 4, and 6. The membrane, as it gels very quickly in water, shrinks in size. To reduce the dimensional shrinkage membranes of polymer 2, they were gelled in different media as shown in Table IV. Dilute sulfuric acid (0.1 N) is the suitable gelation medium for this membrane as the dimensional stability and the porosity of the membrane could be improved.

Solvent Resistance of the Membrane

A few circles of each polymer membranes were kept immersed in organic solvents for 1 week. Membrane circle's diameter remained the same, except for the membrane swelling which has been noted in amide type of solvents. The results are shown in Table V for the membrane of polymer 2.

**Figure 1** Permeate flux as a function of time.

Ultrafiltration of Some Solutes

From the indicated studies it is confirmed that polyurea-amide membrane finds a better application in ultrafiltration. Being a very porous structure, membranes are expected to produce high permeate rates and high rejection for high molecular weight solutes. Membranes of polymers 1, 2, 4, and 6 were examined for the concentration process as shown in Table VI. The composition of the membrane used is according to the polymer concentration shown in Table III. A typical permeate flux vs. time curve for different solutes is presented in Figure 1 for the polymer 2 membrane. All the membranes showed exactly similar behavior though not identical in view of minor variations in porosity, and pore size, etc. The nature of the curves is similar, showing an initial rapid decrease in flux, followed by a slow and gradual

decline as the concentration of the solute increases with time.

The flux rate is recoverable to some extent in ultrafiltration experiments by flushing the membranes with water at nominal operating pressure after the UF experiment is complete. Even after flushing the membranes repeatedly, the original water permeability could not be obtained in these membranes.

CONCLUSIONS

Six types of polyurea-amides have been synthesized and characterized for their use in RO/UF applications. It is possible to produce porous structure in polymer membrane using acidic solvent, i.e., sulfuric acid. The resulting membrane is not an asymmetric type but rather a porous gelled-structure membrane.

REFERENCES

1. T. Matsuura, P. Blais, and S. Sourirajan, *J. Appl. Polym. Sci.*, **20**, 1515 (1976).
2. T. Matsuura and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, **17**, 419 (1978).
3. D. W. Krevelen Van, *Properties of Polymers*, Elsevier, Amsterdam, 1976.
4. P. Blais, in *Reverse Osmosis and Synthetic Membranes*, S. Sourirajan, Ed., National Research Council, Canada, Ottawa, 1977, Ch. 9.
5. J. E. Cadotte, R. S. King, R. J. Majerle, and R. J. Patterson, *International Synthesis in the Preparation of Reverse Osmosis Membranes*, Paper presented at the 179th Annual ACS Meeting, Houston, TX, March, 1980.
6. M. Kurihara, N. Harumiya, T. Tonomura, and M. Nakasatomi, *Desalination*, **38**, 449 (1981).
7. M. Kurihara, Y. Nakagawa, H. Takeuchi, N. Kanamaru, and T. Tonomura, *Desalination*, **46**, 101 (1983).
8. P. W. Morgan, *Condensation Polymers by Interfacial and Solution Methods*, Wiley-Interscience, New York, 1965.
9. S. V. Joshi and A. V. Rao, *J. Appl. Polym. Sci.*, **28**, 1457 (1983).

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