

## PREPARATION AND PROPERTIES OF A COMPOSITE CHARGED MEMBRANE\*

D.A. NOORDEGRAAF AND C.A. SMOLDERS\*

*Chemical Technology, Twente University of Technology, P.O. Box 217,  
7500 AE Enschede (The Netherlands)*

AND

R. DE BOER AND D.J. ROMIJN

*Netherlands Institute for Dairy Research (NIZO), Ede (The Netherlands)*

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### SUMMARY

In order to develop a low pressure desalination membrane with fixed ionic charges, we made use of the normally unwanted crosslinking tendency in preparing the polyelectrolyte poly(styrenesulfonate) by sulfonation of polystyrene. After dipcoating a poly(sulfone) or poly(phenylene oxide) UF membrane with a dilute solution of this polyelectrolyte in water in the presence of some free sulfuric acid and silversulfate, fixation and cross-linking of the coating polymer took place by a heat treatment.

Different membrane properties could be obtained by varying the pore size of the supporting UF membranes, and by variation in the coating polymer (M.W., concentration) and sulfuric acid concentration. We found that fluxes sometimes decline drastically in comparison with the original pure water flux; salt rejection values (at 1.5 g/l NaCl concentration and 0.5 MPa) never are very high ( $\leq 60\%$  for monovalent anions). The most important potential application for these membranes lies in their non-fouling properties.

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## INTRODUCTION

Although charged membranes from different materials have been developed in the past for RO and UF applications, the lack of charged membranes having an asymmetric structure, as for instance in composite RO membranes, is an important reason why charged membranes rarely are put into practice [1–5]. Only few composite charged membranes came beyond the stage of laboratory curiosity [6, 7]. Asymmetric, charged membranes will favour water permeability in two ways: i) only a thin top layer forms the barrier for water transport, ii) the thin layer can have more open structure, as long range electrostatic repulsion forces are responsible for salt rejection [8].

We developed a composite charged membrane by forming a thin layer of poly(styrenesulfonate) (PSA) on top of an ultrafiltration membrane. The membrane was prepared by dipcoating an UF membrane in a poly(styrenesulfonate) solution in water in the presence of free sulfuric acid and silversulfate, followed by heat treatment. The result was a membrane showing moderate salt rejections (up to 60% for monovalent ions) and reasonable fluxes at low pressure (10–50 l/m<sup>2</sup>.h at 0.5 MPa).

We examined the influence on the final membrane properties of a variation in composition of the coating solution, the pore size in the top layer of the support membrane and the molecular weight of PSA. Preliminary results obtained with yet another method of introducing charged groups on the top layer of an UF membrane are presented. Ultrafiltration experiments with cheese whey were carried out with the prepared membranes in order to investigate their non-fouling properties.

## EXPERIMENTAL

### *Ultrafiltration support membranes*

Support membranes were cast from solutions containing either 15 wt% polysulfone or 12.5 wt% polysulfone and 12.5 wt% methoxymethanol in N,N-Dimethylformamide (DMF). Films of 0.15 mm thick were cast on a glass plate and coagulated in demineralized water with 2 wt% DMF and 0.5 wt% sodiumlaurylsulfate. Membranes from poly-(2,6 dimethyl-1,4 phenylene oxide), (PPO) were cast from a solution containing 10 wt% PPO in trichloroethylene/1-octanol mixtures (weight ratio 78/22). Films of 0.15 mm thick were coagulated in methanol during half an hour [9]. Polysulfone was P3500 obtained from Union Carbide, PPO was kindly supplied by General Electric.

### *Poly(styrenesulfonates)*

Samples of poly(styrenesulfonate) were obtained from Polyscience Inc. and from Serva; molecular weight of these samples were 6,000,000 and 100,000 respectively. Samples of polystyrene with different molecular

weights were prepared by emulsion polymerization of styrene with various amounts of initiator (dibenzoylperoxide), or by cationic polymerization in different solvents, according to the method of Pepper [10]. Polystyrene was sulfonated to a degree of 70–90% with sulfurtrioxide-triethylphosphate complex, as described by Turbak [11]. PSA samples with molecular weights ranging from 20,000 to 300,000 were obtained.

#### *Preparation of the charged membranes*

The support membranes were dipcoated with PSA by immersion in a 1–4 wt% solution of PSA in water with 1–2 wt% sulfuric acid and 0.005 wt% silversulfate. Excess coating solution was drained and the back of the membrane was rinsed with fresh water. Fixation took place by heat treatment at 150°C during half an hour. Crosslinking through the formation of sulfon bridges then occurs. Sulfonated PPO membranes were prepared by first stepwise exchanging water in the membrane with sulfolane, followed by sulfonation with a sulfurtrioxide solution in sulfolane at 50°C.

#### *Reverse osmosis and ultrafiltration experiments*

Unless otherwise indicated RO and UF experiments were performed with an Amicon “dead end” test cell model 401, also described in [12]. The test cell has a 400 ml feed solution volume and an effective membrane area of 37.4 cm<sup>2</sup>. The applied pressure was 0.5 MPa and the aqueous feed solution contained 1.5 g/l NaCl. Rejection of salt was measured conductometrically,  $R = (C_{\text{feed}} - C_{\text{permeate}})/C_{\text{feed}} \times 100\%$ , where  $C$  stands both for concentration and for conductivity.

Two different UF test cells with a circulation system were used. One system was Amicon TCF-10 Thin Channel Feed system with an effective membrane area of 39.2 cm<sup>2</sup> and a feed solution volume of 600 ml. Recirculation is made possible through a shallow spiral channel above the membrane. The second system consisted of a rectangular channel ultrafiltration cell with two pumps, one for circulation and one for pressurizing the feed. A diagram of the system is shown in Fig. 1.

## RESULTS AND DISCUSSION

During aromatic sulfonation sulfone formation easily takes place [13, 14]. In sulfonation of polyvinylaromatics this leads to a crosslinking reaction and the formation of water insoluble products [15]. The crosslinking reaction is shown in Fig. 2. This, often undesirable, crosslinking tendency can be used in a positive way for the purpose of introducing fixed charges in a membrane. If an ultrafiltration membrane is dipped in a coating solution containing polystyrenesulfonate (PSA), sulfuric acid and silversulfate as a catalyst, pulled out of the coating solution and heat treated in an oven at 150°C during

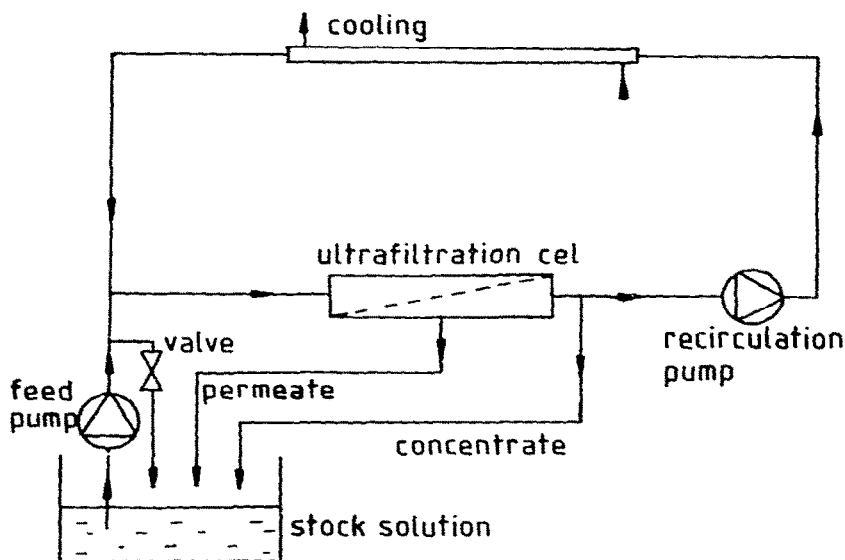


Fig. 1. Diagram of the recirculation cell.

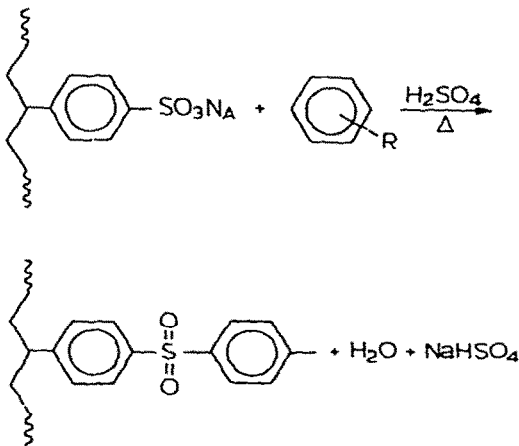


Fig. 2. Crosslinking reaction of polyvinylaromatics by sulfuric acid.

half an hour, PSA will be crosslinked and water insoluble. Crosslinking with the support membrane materials polysulfone and PPO, which contain aromatic rings, will also occur. The result is a membrane with fixed ionic charges.

We established the ionic nature of the membrane by filtrating salt solutions with different concentrations of NaCl and solutions with monovalent as

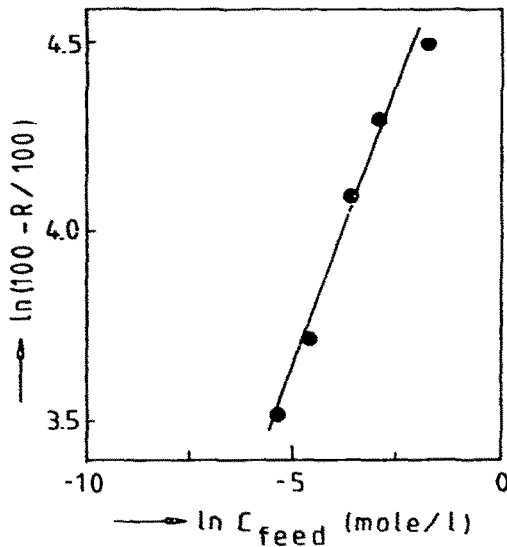


Fig. 3.  $\ln(100 - R/100)$  versus  $\ln C_{\text{feed}}$ .

TABLE I

REVERSE OSMOSIS WITH SOLUTIONS CONTAINING MONO- AND DIVALENT ANIONS AT 0.5 MPa

Flux l/m <sup>2</sup> h	Rejection %	Concentration of feed solution g/l	Salt used
11	40	1.5	NaCl
11	90	1.5	Na <sub>2</sub> SO <sub>4</sub>

well as divalent anions. In Fig. 3 it is shown that we find a linear relationship if we plot  $\ln(100 - R/100)$  versus  $\ln C_{\text{feed}}$ , which is in agreement with the results of Thomas for charged membranes [16]. From Table I it is seen that the rejection for a divalent anion is much higher than for monovalent anions, which also is behaviour that is expected for charged membranes [17]. The membrane used in the above measurements is prepared from a polysulfone support membrane, cast from a casting solution of 15 wt% polysulfone in DMF, and a coating solution with 2 wt% PSA (MW  $10^5$ ), 2 wt% sulfuric acid and silversulfate.

In Table II the results are shown of a varying concentration of PSA and sulfuric acid in the coating solution. Essentially the same results were found if the concentration of PSA is varied from 1 to 4 wt% and that of sulfuric acid from 1 to 2 wt%. This indicates that the relatively low flux found is not due to a gel layer in front of the membrane for then a decreasing water permeability with increasing PSA concentration is to be expected. A concentration of PSA lower than 1 wt% results in an irregular top layer. This causes further lowering of the flux as parts of the membrane where no PSA is present are not rewetted after the heat treatment when the membrane is put into operation at low pressure. A lower flux is also measured, if the concentration of sulfuric acid in the coating solution exceeds the concentration of PSA. The amount of sulfuric acid in the remaining thin layer of PSA after evaporation of water then becomes high and the support membrane is seriously damaged, which results in a low flux (see also Table V).

When the concentration of PSA exceeds 4 wt%, the crosslinking of PSA becomes ineffective and the top layer is washed off the membrane when it is put into operation and rejection will be low. As the acid content in the top layer is low in this case, the support membrane is less damaged and the flux is high.

We have tried to introduce a higher charge density on the membrane (resulting in a higher salt rejection) by decreasing the polymer coil dimensions. If PSA is dissolved in methanol/water mixtures the decreased dissociation of the polyelectrolyte could result in smaller coil dimensions [18, 19]. Table III shows the results if support membranes are coated with PSA dissolved in water/methanol mixtures. The table shows that changing the conformation

TABLE II  
MEMBRANE PROPERTIES WITH VARIATION OF COATING SOLUTION  
COMPOSITION

PSA wt%	H <sub>2</sub> SO <sub>4</sub> wt%	Flux l/m <sup>2</sup> h	Rejection %
0.5	1	5	53
1	2	5	39
1	1	13	39
2	2	18	43
4	2	13	40
5	1	60	20

Polysulfone support membrane cast from a 15 wt% solution in DMF, dipcoated with PSA (M.W. 100,000) from an aqueous solution. Feed 1.5 g/l NaCl, pressure 0.5 MPa.

of PSA mainly affects the flux and not rejection. The charge density has not increased, probably due to the fact that the crosslinking density is low. PSA can swell after its fixation on the membrane to proportions which it normally has in water. This results in an unchanged charge density. Possibly only a higher crosslinking density of PSA, using different coating techniques or crosslinking reactions, will lead to a higher charge density on the membrane.

The flux is influenced positively which can be attributed to the rewetting of the smaller top layer pores in the support membrane, after the crosslinking step at 150°C. Since the polymer is deposited in a denser conformation, it can also enter the smaller pores of the top layer. Without PSA none of these pores are wettable, and no water transport through the pores can take place at the low pressure applied.

The above results indicate that variation of the pore size in the membrane top layer or variation of molecular weight (i.e. radius of gyration) of PSA will affect the membrane properties, as, for instance is also the case in the formation of dynamic membranes [21]. This is shown in Table IV. The table gives the results of RO experiments when two membranes from two casting solutions containing different concentrations of polysulfone (resulting in different pore sizes [20]) are coated with PSA of different molecular weight.

The table shows that when a support membrane with a relatively low pure water permeability is used membrane properties improve when lower molecu-

TABLE III  
DIPCOATING SUPPORT MEMBRANES WITH SOLUTIONS CONTAINING  
METHANOL

Compositions of the coating solution	1 wt% PSA (M.W. 50,000) 1 wt% sulfuric acid 87 wt% methanol 11 wt% water silver sulfate		2 wt% PSA (M.W. 50,000) 2 wt% sulfuric acid 96 wt% water	
Membrane properties	Flux 1/m <sup>2</sup> h	Rejection %	Flux 1/m <sup>2</sup> h	Rejection %
	20	58	18	55
	35	48	24	39
			10	51
			12	50

Polysulfone support membrane cast from a 15 wt% solution in DMF. Feed 1.5 g/l NaCl, pressure 0.5 MPa.

TABLE IV

MEMBRANE PROPERTIES AS A FUNCTION OF MEMBRANE PORE SIZE AND OF PSA MOLECULAR WEIGHT AT 0.5 MPa

Pure water permeability of the support membrane*				
	Initial l/m <sup>2</sup> h	Steady state l/m <sup>2</sup> h	Initial l/m <sup>2</sup> h	Steady state l/m <sup>2</sup> h
	4000	600	400	200
Molecular weight PSA × 10 <sup>-3</sup>	Flux l/m <sup>2</sup> h	Rejection %	Flux l/m <sup>2</sup> h	Rejection %
6000	17	51	12	43
300	36	40	8	54
100	33	39	13	39
50	68	27	18	51
26	75	30	21	50
20	—	—	22	57
8	80	16	26	38

\*High flux support membrane from a casting solution with 12.5 wt% polysulfone, 12.5 wt% methoxyethanol and low flux membrane from 15 wt% polysulfone, both in DMF. Initial pure water permeability measured after 5 minutes of operation, steady state pure water permeability measured after 3 hours of operation at 0.2 MPa. Coating solution was 1 wt% PSA, 1 wt% H<sub>2</sub>SO<sub>4</sub>, Ag<sub>2</sub>SO<sub>4</sub> in water. Feed 1.5 g/l NaCl, pressure 0.5 MPa.

lar weight PSA is applied. When PSA with low molecular weight is deposited on a support membrane with a relatively high pure water permeability, flux increases and rejection drops. The polymer molecule is too small to fill completely the larger pores, so membrane resistance will decrease and salt slip become possible. However, the flux remains relatively low in spite of the decreasing additional membrane resistance. A reason for this is the deterioration of the membrane during the heat treatment by sulfuric acid. This deterioration of the support membrane is demonstrated in Table V.

In the experiments shown in Table V polysulfone and PPO ultrafiltration membranes are immersed in water with 0.5 wt% sulfuric acid, dried at 150°C during half an hour and rewetted with methanol before testing. It appears that PPO membranes have a better resistance to sulfuric acid at an elevated temperature. The flux decline (pure water permeability) for polysulfone is



TABLE V

PPO AND POLYSULFONE MEMBRANE PROPERTIES AFTER INTRODUCTION OF CHARGES BY VARIOUS METHODS

Membrane type	Flux l/m <sup>2</sup> h	Rejection %	Test conditions
PPO, untreated	200	—	0.2 MPa, Amicon 401
Polysulfone, untreated	170	—	0.2 MPa, Amicon 401
PPO, heat treated with sulfuric acid*	140	—	0.5 MPa, Amicon 401
Polysulfone, heat treated with sulfuric acid*	50	—	0.5 MPa, Amicon 401
PPO, coated with PSA M.W. 300,000**	54	33	0.5 MPa, Amicon 401 1.5 g/l NaCl
PPO, coated with PSA M.W. 50,000**	200	5	0.5 MPa, Amicon 401 1.5 g/l NaCl
PPO, sulfonated with SO <sub>3</sub> in sulfolane	290	12	0.4 MPa, recirculation cell***, 1.0 g/l NaCl

\* Immersion of the membrane in 0.5 wt% sulfuric acid, heat treated at 150°C during half an hour, rewetted with methanol.

\*\* Coating solution: 1 wt% PSA, 1 wt% sulfuric acid, silver sulfate.

\*\*\*See experimental.

larger than for PPO membranes. PPO membranes also show higher fluxes when coated with PSA because of its better resistance to sulfuric acid, especially when low molecular weight PSA is used. This is also shown in Table V.

The final example in Table V reports one of the results of another promising technique of introducing charges in ultrafiltration membranes. At 50°C SO<sub>3</sub> dissolves in sulfolane and readily sulfonates PPO. In this way PPO membranes can be sulfonated under mild conditions. No flux decline occurs in this treatment and the membrane has a small salt rejection. A disadvantage of this method is the complication that water reacts vigorously with sulfur trioxide, so that water has to be exchanged stepwise by sulfolane before the actual sulfonation.

#### *Ultrafiltration of cheese whey with charged membranes*

Cheese whey is a complicated solution of the following composition: proteins 0.6–0.7 wt%, nitrogen in non-protein form 0.1–0.2 wt%, lactose 5.0 wt%, lactic acid 0.2 wt%, salts 0.5 wt%, TDS 6.4–6.7 wt%. The isoelec-

tric point of whey protein is at a pH of 4.6 [22]. Above this pH the proteins are negatively charged and below this pH positively. The charge on the protein is expected to become important when ultrafiltration is carried out with charged membranes.

In our experiments we used a high flux support membrane coated with PSA (coating solution 1 wt% PSA, M.W. 26000, 1 wt% sulfuric acid, silver sulfate). The feed was either decalcified, de-ionized or pasteurized whey brought to a pH of 2.5 or 6.5. The initial concentration of calcium is 0.82, 1.9 or 37.8 mg/100 ml, respectively. The test cell was an Amicon circulation cell model TFC-10. The applied pressure was 0.3 MPa, the temperature 50°C. The results are shown in Fig. 4.

In all cases the highest fluxes are found when whey is ultrafiltered at pH is 2.5, thus when the proteins bear positive charges. The high flux abruptly decreases after prolonged ultrafiltration. This occurs after removal of about 300 ml water, which means a concentration factor of 2. Apparently this is

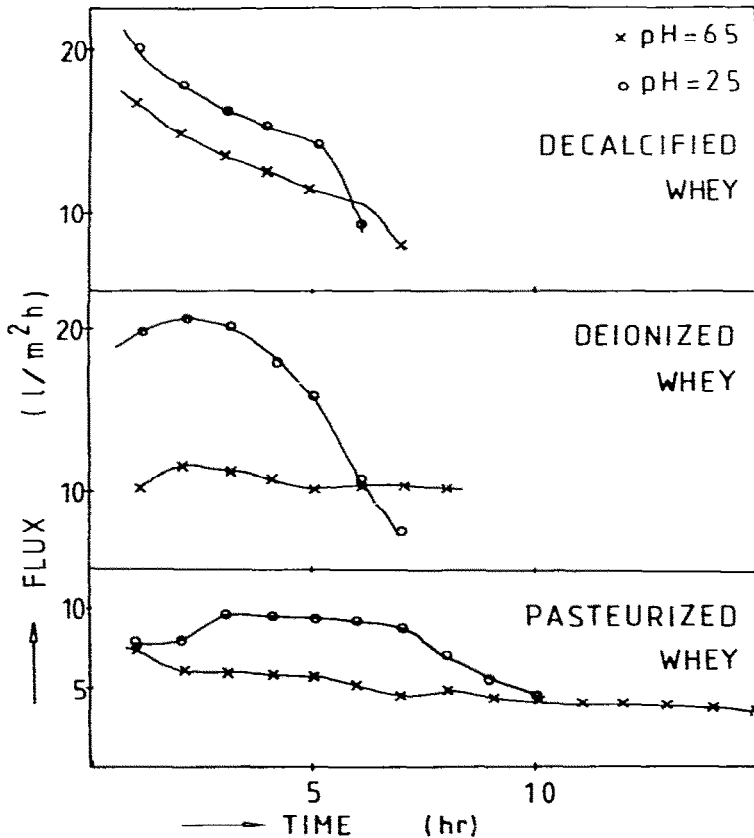


Fig. 4. Ultrafiltration of decalcified, deionized and pasteurized cheese whey at 50°C and 0.3 MPa.

the limit of dewatering in this case. The flux at  $\text{pH} = 6.5$  remains nearly constant or decreases slowly. Differences in flux between the various feeds are caused by the concentration differences in calcium ions and their precipitates, e.g. calcium phosphates. For a lower calcium content a higher flux is found.

It is surprising that in the ultrafiltration of cheese whey the higher fluxes are measured when whey protein is positively charged. One would expect that the attraction between a positively charged protein and a negatively charged membrane would result in a dense gel layer which would give a low flux. Apparently this is not the case. Of course, in both cases whether the protein is charged negatively or positively, a gel layer will be formed due to insufficient back diffusion and a charged membrane may influence only the initial stage of gel layer formation. In this initial stage negatively charged protein in contact with a negatively charged membrane will tend to rearrange in order to minimize electric repulsion, whereas positively charged protein will adhere to the membrane in a disorderly manner. In Fig. 5 this is schematically shown. We think that as a result of this process the gel formation formed by negatively charged protein will block the surface pores of the membrane more efficiently than positively charged protein does and thus causes a lower flux through the charged membrane.

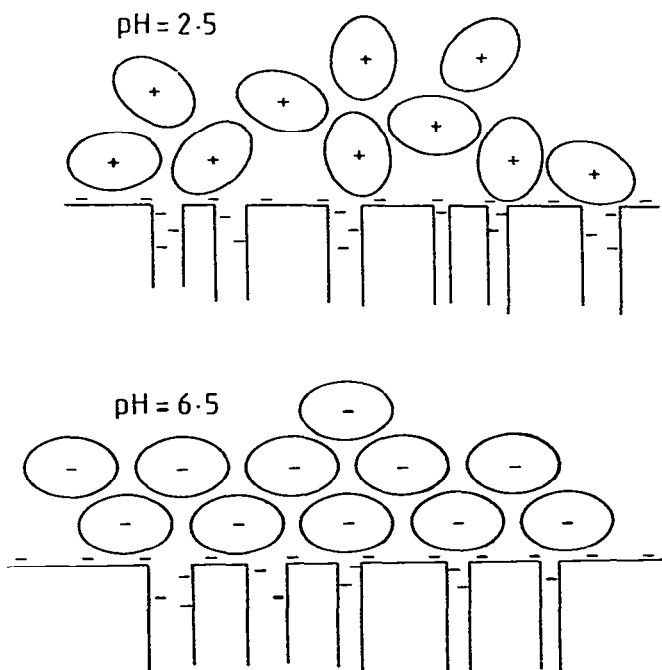


Fig. 5. Schematic representation of gel layer formation with a negatively charged membrane and cheese whey protein at different pH.

We are still in the process of further investigation to understand the mechanism of fouling by cheese whey. Future research will also be focused on direct sulfonation of ultrafiltration membranes and different crosslinking techniques for PSA.

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