Cellulose Acetate and Sulfonated Polysulfone Blend Ultrafiltration Membranes. II. Pore Statistics, Molecular Weight Cutoff, and Morphological Studies

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ABSTRACT: The determination of the pore size, porosity, number of pores, molecular weight cutoff (MWCO), and morphology of an ultrafiltration membrane is necessary for predicting the performance of a membrane for a specific application. For ultrafiltration membranes prepared from cellulose acetate and sulfonated polysulfone in the presence and absence of various concentrations of the additive poly(ethylene glycol) 600, pore statistics and MWCOs were determined in studies with dextrans of different molecular weights. Surface and cross-sectional morphologies of the membranes were analyzed with scanning electron microscopy at different magnifications. The pore size increased with increasing concentrations of sulfonated polysulfone and additive in the casting solution. Similarly, the MWCOs of the membranes ranged from 19 to 150 kDa, depending on the various polymer blend compositions and additive concentrations. Results from scanning electron microscopy provided qualitative evidence for the trends observed for the pore statistics and MWCO results. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 430–444, 2002; DOI 10.1002/app.10414

Key words: ultrafiltration; pore size; molecular weight cutoff; morphology; membrane characterization; membranes; separation techniques

INTRODUCTION

The molecular weight cutoff (MWCO), morphology, and pore statistics are the structural properties of membranes that are essential for the application of membrane processes for desired permeate qualities.[1] This article is one of a series examining ultrafiltration (UF) membranes based on cellulose acetate (CA) and sulfonated polysulfone (SPS) and their characterization and performance applications. The first part of this series concerns the preparation of blend membranes based on CA and SPS blend membranes at differ-ent polymer compositions in the absence and presence of various poly(ethylene glycol) 600 (PEG 600) concentrations and their characterizations in terms of compaction, pure water flux, membrane hydraulic resistance, and water content.

A broad variety of morphologically different polymeric membranes can be prepared with changes in parameters such as the compositions and concentrations of polymers, solvents, and additives.[2,3] The determination of morphological characteristics plays an important role in evaluating the performance of the membranes. The membranes usually consist of cylindrical pores perpendicular to the membrane surface, the sizes of which are represented by the pore size distribution. Only solute molecules smaller than the membrane pore diameter can be transported

through the membrane.[4] Most of the commercially available membranes are specified by their pore size or MWCO value,[5] which has been found to be an important parameter affecting the separation characteristics of the UF membranes.[6] The major methods available for the determination of pore statistics are bubble pressure breakthrough, mercury porosimetry, solute retention challenge, electron microscopy, adsorption-base methods, thermoporometry, permporometry, and NMR measurements.[7] Most descriptions involve a combination of these methods. In this investigation, the solute retention method and scanning electron microscopy (SEM) were used for determining the pore statistics because of their simplicity and their advantage in determining MWCOs.

Furthermore, the filtration characteristics of dextrans with different molecular weights can also be used to correlate MWCOs and pore statistics.[8] Several UF, microfiltration, and reverse osmosis membrane systems with different polymeric membranes have been evaluated for their pore statistics, MWCOs, morphologies, and formation mechanisms.[9–12] The MWCO of a membrane mainly indicates the size of the solute molecules that could be taken as the feed, the retention percentage of which is greater than 80%. Therefore, it has been considered a key parameter of membranes useful for a variety of pharmaceutical, food, and biotechnological applications.

Surface morphology, however, is a membrane surface phenomena that mainly describes the qualitative nature of the membranes. The cross-sectional morphology of membranes has been used to ascertain the types and structures of the pores, subsequently being helpful in identifying the roles of the membrane casting-solution composition and casting conditions in the mechanism of pore formation.[13]

The objective of this study was to determine the pore statistics, MWCOs, and morphologies of CA/SPS-based blend UF membranes and to discuss the results of the investigation in terms of the effects of the polymer blend composition and additive concentration. The characteristics of the CA/SPS blend membranes were also compared with pure CA, SPS, and polysulfone (PSf) membranes.

EXPERIMENTAL

Materials

Dextrans with molecular weights of 19, 42, 77, and 150 kDa were procured from Sigma–Aldrich

Co. (Milwaukee, WI) and stored at a suitable temperature before use. Sulfuric acid and phenol were procured from SRL Chemicals, Ltd. (Mumbai, India) and used as received for the analysis of dextrans. Liquid nitrogen was employed for drying the membrane samples for SEM analyses. Deionized and distilled water was employed for the preparation of dextran aqueous solutions.

Characterizations

Pore Statistics

The average pore radius $(\bar{R})$, surface porosity or porosity percentage (ϵ), and number of pores (n) of CA, CA/SPS, SPS, and PSf membranes were determined by UF of dextran polymers of different molecular weights. The molecular weight of a solute with solute rejection percentage (% SR) greater than 80% may be used to evaluate $\bar{R}$ with the following equations:

$$\%\mathrm{SR} = 1 - \frac{C_p}{C_f} \times 100$$

where C_p and C_f are the concentrations of the permeate and feed, respectively. The analysis of dextran was performed with a ultraviolet–visible spectrophotometer at $\lambda_{\max} = 485$ nm:

$$SR = 100\left(\frac{\bar{\alpha}}{\bar{R}}\right)$$

where $\bar{\alpha}$, the average solute radius, is constant for each molecular weight. Average solute radii, known as Stoke radii, can be evaluated according to the procedure developed by Sarbolouki.[8] From the values of % SR and $\bar{\alpha}$ derived from the Sarbolouki equation,

$$\bar{\alpha} = \frac{0.96M^{0.59} + 0.128M^{0.5}}{2}$$

$\bar{R}$ can be calculated. From the values of $\bar{R}$, ϵ for the membrane can be calculated with the slit model and, with membranes considered to be the symmetric skin type, with the following formula:[14]

$$\varepsilon = \frac{3\pi\eta J}{\bar{R}\Delta P} \times 100$$

where η is the permeate viscosity (0.01 cP with the permeate considered to be pure water), J is the flux of the solvent (water) in the presence of the solute (dextran; expressed in $cm^3/cm^2/s$), and ΔP is the applied pressure (345×10^3 Pa.

From the values of ϵ and $\bar{R}$, n can be calculated:

$$n = \frac{\varepsilon}{\pi \bar{R}^2}$$

MWCO

MWCO is a pore characteristic of membranes and is related to rejection for a given molecular weight of a solute. The molecular weight has a linear relationship with the pore radius or pore size of a membrane. In general, the MWCO of a membrane is determined by the identification of an inert solute, which has the lowest molecular weight and has a solute rejection of 80–100% in steady-state UF experiments.[6] Therefore, carbohydrate dextrans with molecular weights of 19, 42, 77, and 150 kDa were chosen, and their rejection percentage by the blend and pure membranes was determined by an analysis of the feed and permeate concentrations of dextran with an ultraviolet–visible spectrophotometer[15] at $\lambda_{max} = 485$ nm.

Morphological Studies

The top surfaces of CA/SPS blend membranes and CA, SPS, and PSf pure membranes were studied with SEM (Leica Streoscan, Cambridge, United Kingdom). The membranes were cut into pieces of various sizes and mopped with filter paper. These pieces were immersed in liquid nitrogen for 20–30 s and were frozen. Frozen bits of the membranes were broken and kept in a desiccator. These membrane samples were used for SEM studies. The membranes for SEM analysis were from pieces of the same composition that were used for other performance characterizations for qualitative emphasis and a comparison of the performance and pore statistics.

The samples were mounted on sample holders called studs and gold-sputtered to provide electrical conductivity to very thin layers of the polymeric membranes, and photomicrographs were taken in very high vacuum conditions operating between 15 and 25 kV, depending on the physical nature of the sample.[16] Various SEM images were taken at various magnifications for top-surface and cross-sectional views of the polymeric membranes. The locations for images on membrane surfaces were identified by careful observation of the membrane surface. However, uniformity in pore distribution was given importance in setting a location for image scanning.

RESULTS AND DISCUSSION

Pore Statistics

The determination of the pore size, porosity, and number of pores for the CA/SPS blend UF membranes, in the absence and presence of the additive PEG 600, with dextrans of different molecular weights is discussed. All the experiments were carried out three times for ensured reproducibility of the results. From the results, mean values for both the pore radius and porosity were calculated. Table I shows dextrans of different molecular weights, the rejection of which was greater than 80%, and their flux for pure CA and SPS membranes and for representative CA/SPS blend membranes.

Effect of the Polymer Blend Composition

The results of the analysis showed that when the SPS composition in the blend system was enhanced from 5 to 15%, the pore radius of the blend membranes also increased, very marginally, from 47.83 to 48.43 Å, as shown in Table II and Figure 1. The radius of the membrane pores increased linearly to 64.02 Å when the SPS composition reached 25%. Similarly, the porosity percentage also had an increasing trend with increasing SPS composition. However, the number of pores was 3.132×10^{-10} at a 5% SPS composition and gradually was reduced with increasing SPS. The increase in pore size and porosity might have been due to incompatibility between SPS and CA, leading to the formation of macrovoids[17] and enhanced hydrophilicity incorporated by the sulfonation of PSf. The decrease in the number of pores with increasing SPS composition might have been due to the availability of more SPS for the formation of big networks with CA, which, in turn, reduced the number of pores and the formation of larger sized pores, as evidenced by SEM analysis (Fig. 2).

Effect of the Additive Concentration

The addition of the water-soluble additive PEG to polymeric casting-solution systems can change

Table I   Percentage Rejection and Flux Properties of Dextrans for CA, CA/SPS Blend, and SPS Membranes

Blend Composition % (17.5 wt %)		PEG 600 (wt %)	Dextran Rejection (%)	Molecular Weight of Dextran (Da)	Flux of Dextran (L/m²/h)
CA	SPS				
100	0	0	81	19,000	13.56
95	5	0	81	42,000	14.23
85	15	0	80	42,000	22.67
75	25	0	83	77,000	41.54
0	100	0	80	77,000	76.88
100	0	2.5	88	42,000	44.36
95	5	2.5	80	42,000	49.32
85	15	2.5	80	77,000	60.19
75	25	2.5	85	77,000	56.45
0	100	2.5	84	150,000	125.71
100	0	5.0	90	77,000	52.52
95	5	5.0	80	77,000	59.36
85	15	5.0	88	150,000	98.14
75	25	5.0	87	150,000	120.60
0	100	5.0	80	150,000	154.80
100	0	7.5	88	77,000	77.15
95	5	7.5	89	150,000	87.25
85	15	7.5	86	150,000	138.75
75	25	7.5	88	150,000	133.46
0	100	7.5	80	150,000	192.20
100	0	10.0	86	77,000	82.10
95	5	10.0	88	150,000	99.50
85	15	10.0	84	150,000	180.56
75	25	10.0	88	150,000	176.25
0	100	10.0	78	150,000	197.40

[L/m²/h = 27.78 × 10^{-6} cm³/cm²/s]

the morphology of the resulting membranes. It is shown in Table II that, for a given polymer composition, when the PEG concentration was increased from 2.5 to 10 wt %, the membrane pore radius and porosity percentage also increased proportionately. However, the number of pores did not coincide with the trend of the porosity and pore radius. This confirms the role of the additive in the formation of pores and its interaction with the membrane material during gelation and membrane formation (Fig. 1).

Furthermore, at a given additive concentration, an increase in the SPS composition from 5 to 15 wt % increased the average pore radius. A further increase in the SPS composition to 25% reduced the pore radius, which is in good agreement with the flux results of the membranes shown in Table I. Similarly, when the SPS composition increased, the porosity of the membranes passed through a maximum. The lower porosity

at 25% SPS may be due to the aggregation of additive molecules with SPS and CA.

The data obtained for the number of pores have different magnitudes and trends than the data for the porosity and pore radius. The number of pores was higher at a lower additive concentration, decreased at 5 wt % PEG, and increased again at 10 wt % PEG. This opposite trend for the number of pores and the flux may be explained by the pores being smaller and the number being higher.

CA membranes as homopolymeric membranes had increasing pore radii with increasing additive concentration. The porosity also showed a similar trend that confirmed the flux and rejection properties of the CA membranes distinctly, as shown in Table I. However, the number of pores differed very much from the porosity because the system exhibited smaller pores in a higher number in comparison with other blends at 0 and 2.5 wt % PEG 600.

Table II   Pore Characteristics of CA, CA/SPS Blend, and SPS Membranes

Blend Composition % (17.5 wt %)		PEG 600 (wt%)	$\bar{R}^a$ (Å)	ε^a (%)	n ($\times 10^{-10}$)
CA	SPS				
100	0	0	30.70 (0.19)	0.0334 (0.0003)	11.318
95	5	0	47.83 (0.6)	0.0225 (0.0003)	3.132
85	15	0	48.43 (0.31)	0.0355 (0.0001)	4.820
75	25	0	64.02 (0.38)	0.0480 (0.0015)	3.560
0	100	0	68.02 (0.43)	0.0857 (0.0006)	5.901
100	0	2.5	44.03 (0.51)	0.0564 (0.0011)	12.553
95	5	2.5	48.43 (0.62)	0.0597 (0.0003)	4.049
85	15	2.5	65.56 (0.8)	0.0810 (0.0110)	5.725
75	25	2.5	65.56 (0.4)	0.0671 (0.0012)	5.213
0	100	2.5	94.19 (0.82)	0.1015 (0.0004)	3.644
100	0	5.0	60.46 (0.00)	0.0658 (0.0000)	5.740
95	5	5.0	65.56 (0.00)	0.0686 (0.0000)	5.089
85	15	5.0	89.90 (0.52)	0.0808 (0.0206)	3.263
75	25	5.0	82.54 (0.5)	0.1008 (0.0102)	3.881
0	100	5.0	97.67 (1.23)	0.1205 (0.0005)	4.024
100	0	7.5	61.84 (0.00)	0.0946 (0.0000)	7.881
95	5	7.5	88.89 (0.49)	0.0745 (0.0005)	3.002
85	15	7.5	92.00 (1.08)	0.1143 (0.0007)	4.303
75	25	7.5	89.90 (0.00)	0.1124 (0.0000)	4.430
0	100	7.5	98.90 (0.62)	0.1474 (0.0006)	4.802
100	0	10.0	63.27 (0.02)	0.0984 (0.0004)	7.930
95	5	10.0	89.90 (0.73)	0.0839 (0.0011)	3.307
85	15	10.0	94.19 (0.56)	0.1458 (0.0002)	5.233
75	25	10.0	89.90 (0.52)	0.1437 (0.0053)	5.862
0	100	10.0	101.43 (0.6)	0.1475 (0.0005)	4.968

[a] Numbers within parentheses represent standard deviation values.

Pure SPS membranes also exhibited similar behavior in their pore radius and porosity. However, the number of pores was higher for SPS membranes in the absence of the additive. The number of pores increased with the additive concentration increasing from 2.5 to 7.5 wt % (Fig. 3). The formation of pores became almost constant at 10 wt % PEG 600. This was due to the leaching of the additive from the membrane surface during gelation, and, in the absence of the additive, the pores were smaller, though their number was high (Table II).

For pure PSf membranes, the MWCOs of dextran, the rejection percentage of which was greater than 80%, and the flux of dextran are shown in Table III. The pore radius, porosity percentage, and number of pores all increased with an increase in the additive concentration in the membrane casting solution (Table III). This behavior confirmed the absence of any interaction between PEG and PSf molecules and resulted in the uniform nature of the formation mechanism, regardless of the additive concentration.

MWCO

The MWCO of a membrane is determined to specify the rejection behavior of the membrane. It corresponds to the molecular weight of the solute with a solute rejection greater than 80%.[18] The MWCO can generally be estimated with linear polymers such as PEG or poly(vinylpyrrolidone) or with spherical molecules such as bovine serum albumin. In this investigation, dextrans with molecular weights of 19, 42, 77, and 150 kDa were chosen because of the nonavailability of other dextran molecular weights for the estimation of MWCO. The rejection percentage of dextrans of various molecular weights for pure CA membranes, CA/SPS blend membranes, and pure SPS and PSf membranes, prepared in the absence and
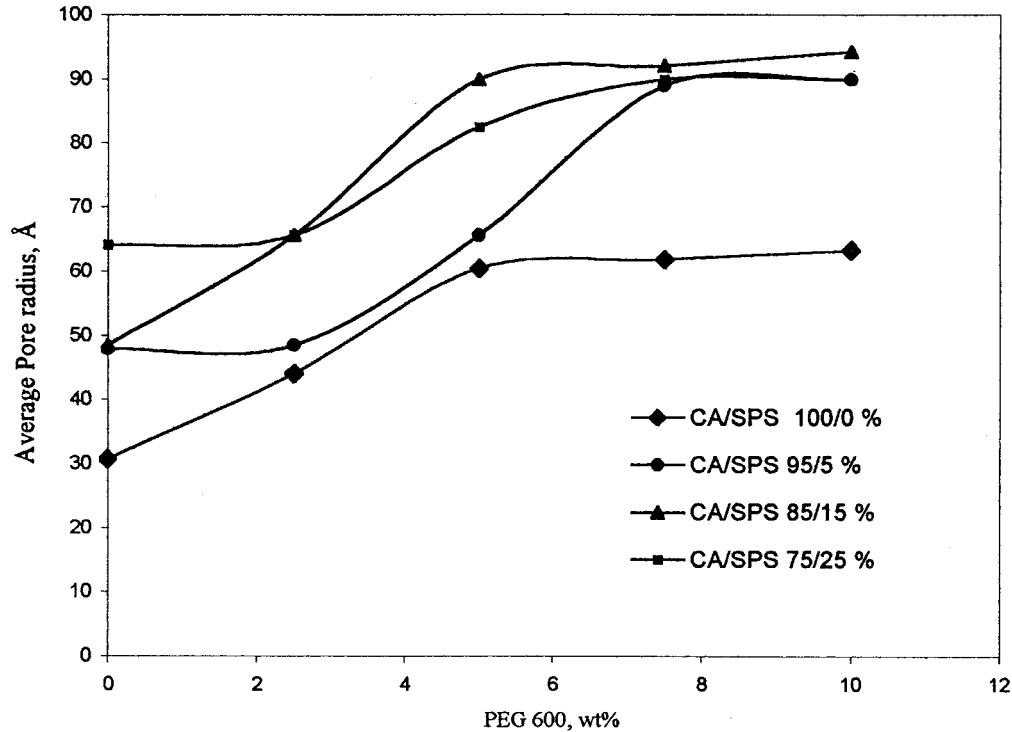
Figure 1 Effect of the PEG 600 concentration on the pore radius of CA/SPS blend membranes.

presence of PEG 600 (from 2.5 to 10 wt %) in a casting solution, were determined. Blend membranes with 95/5, 85/15, and 75/25 compositions were taken as representative samples for the study, and the results are shown in Table IV.

Role of the Polymer Blend Composition

From the experiments, we found that the pure CA membrane, without the additive PEG 600, had an MWCO between 19 and 42 kDa.

It is also evident from Table IV that the MWCO values were dependent on the polymer composition. Therefore, in the CA/SPS blend membranes, in the absence of the additive, as the SPS content increased, the MWCO value also increased from 42 kDa for 5% SPS to 77 kDa for 25% SPS. This result correlates well with the permeability results of the membranes shown in Table I.

The pure SPS membrane, without the additive, exhibited a higher MWCO value of 77 kDa, as shown in Table IV, and established the higher permeability values exhibited by the SPS membrane. The MWCO values of CA/SPS membranes at higher SPS contents were, however, larger than the value of the pure PSf membrane.

Role of the Additive Concentration

It was believed that the incorporation of the additive into the casting solution would alter the MWCOs of all the CA, CA/SPS, and SPS membranes. Therefore, for pure CA (100%) membranes, when the additive concentration was increased from 2.5 to 10 wt %, the MWCO values increased from 42 to 77 kDa.

Various additive concentrations had significant effects on the MWCOs of the CA/SPS blend membranes. It is evident from Table IV that, for a given blend composition, an increase in the additive concentration increased the MWCO linearly. Similar observations were also observed for the other two blend compositions.

Furthermore, for a given additive concentration of 2.5 wt %, as the SPS content in the blend increased, the MWCO also increased from 42 to 77 kDa. Corresponding increasing values were also observed for the 5 wt % additive concentration. However, for 7.5 and 10 wt % additive concentrations, the MWCOs for all the blend membranes were between 77 and 150 kDa. The determination of exact MWCOs was not carried out because of the nonavailability of dextrans of suit-
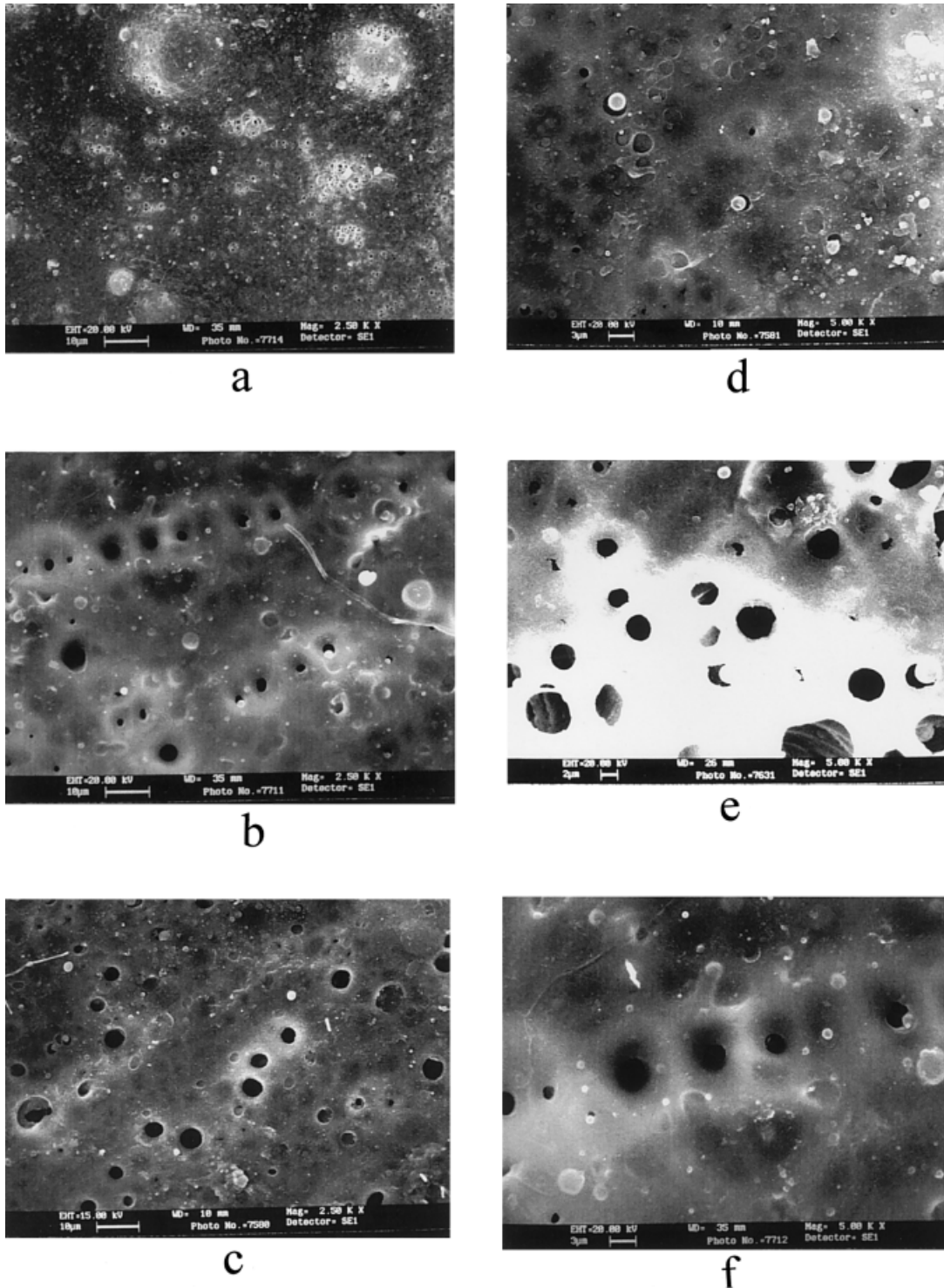
Figure 2 SEM micrographs of the top surfaces of CA/SPS blend membranes with various blend compositions and a 10 wt % additive concentration: (a) 95/5, (b) 80/20, and (c) 75/25 CA/SPS (original magnification, 2500×) and (d) 95/5, (e) 80/20, and (f) 75/25 CA/SPS (original magnification, 5000×).
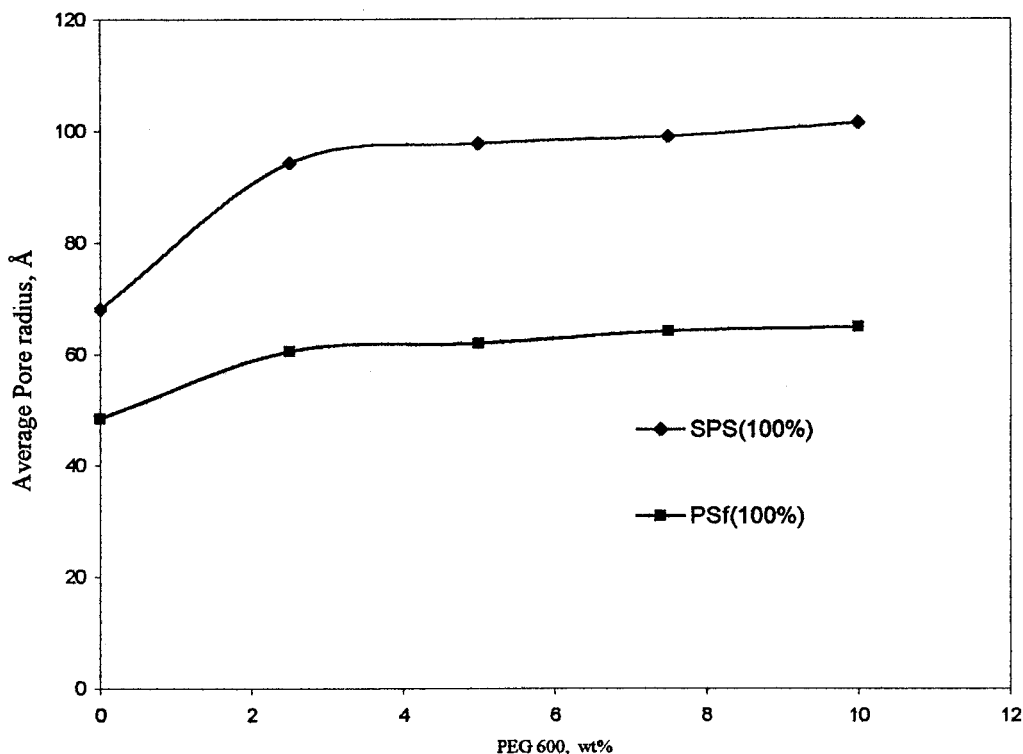
Figure 3   Effect of the PEG 600 concentration on the pore radius of pure SPS and PSf membranes.

able molecular weights. Furthermore, because the size of the PEG 600 molecule is linear and small, it did not have much influence in altering MWCO to a greater extent. Similar results have already been reported.[19]

The pure SPS membranes, however, exhibited MWCOs of 77–150 kDa at a 2.5 wt % additive concentration, increased to 150 kDa at a 7.5 wt % additive concentration, and remained constant even up to a 10 wt % PEG concentration in a casting solution. The CA/SPS membranes at

higher SPS contents had higher MWCOs than pure PSf membranes at corresponding additive concentrations (Table V).

Morphological Studies

The surface structure of a flat-sheet, UF membrane, that is, the skin of the membrane, is the most critical part, helping to identify the role of the membrane in the mechanism of permeation and rejection. SEM is an important and key tool

Table III   Dextran Rejection, Flux, and Pore Characteristics of PSF Membranes with a 17.5 wt % Polymer Concentration

Concentration of PEG 600 (wt %)	Dextran Rejection (%)	Molecular Weight (Da)	Dextran Flux (l/m²/h)	$\bar{R}^a$ (Å)	ε^a (%)	n ($\times 10^{-10}$)
0.0	80	42,000	19.74	48.43 (0.29)	0.0309 (0.0001)	4.1997
2.5	90	77,000	43.97	60.46 (0.68)	0.0553 (0.0005)	4.8192
5.0	88	77,000	53.20	61.84 (0.00)	0.0652 (0.0000)	5.4347
7.5	85	77,000	78.71	64.02 (0.78)	0.0936 (0.0008)	7.2747
10.0	84	77,000	83.83	64.78 (0.39)	0.0988 (0.0001)	7.4623

[a] Numbers within parentheses represent standard deviation values.

Table IV   MWCO of CA/SPS Blend Membranes with a 17.5 wt % Polymer Concentration

Blend Composition (%)		MWCO (kDa)				
		PEG 600 Concentration (wt % in Casting Solution)				
CA	SPS	0	2.5	5.0	7.5	10.0
100	0	19–42	42	42–77	77	77
95	5	42	42	77	77–150	77–150
85	15	42	77	77–150	77–150	77–150
75	25	77	77	77–150	77–150	77–150
0	100	77	77–150	77–150	150	150

for the determination of the morphology of the membranes. To attain high-performance membranes for specific applications, we must manipulate the morphological structures of the membranes.[20] Therefore, morphological studies of various sections of pure and blend membranes were performed with SEM.

CA Membranes

CA membranes in the absence and presence of 5 and 10 wt % PEG 600 were scanned, and the results are shown in Figure 4(a–e).

Figure 4(a–c) corresponds to the top surface of CA membranes with 0, 5, and 10 wt % additive at an original magnification of 5000×. In Figure 4(a), it can be observed that with 0 wt % additive, the pores are smaller and widely distributed. With increases to 5 and 10 wt %, the pore sizes also increase. This confirms the concept of the leaching of additive during gelation. Similar observations with polyvinylpyrrolidone as an additive have been made by other researchers.[21]

The finger-like structures shown in Figure 4(d,e) are cross sections of pure CA membranes with 0 and 10 wt % PEG 600 concentrations; they establish the asymmetric structure of the membranes. Similar finger-like observations have

been made by others for CA–inorganic salt membranes.[22]

The morphology exhibited by the CA membranes with and without PEG 600 also supports the important properties of the membranes (their flux and separation performance) prepared in the presence and absence of PEG 600, as shown in Table I.

CA/SPS Blend Membranes

The performance of CA/SPS blend membranes with various additive concentrations correlated well with membrane morphology. Figure 5(a–e) shows the top surfaces of CA/SPS blend membranes with 80/20 compositions at 0, 2.5, 5, 7.5, and 10 wt % additive concentrations. At 0 wt % PEG 600, CA/SPS blend membranes exhibit smaller pores distributed evenly. As the PEG 600 concentration increased in the casting solution, the pore size also increased linearly. This supports the observed experimental trend for dextran flux of the corresponding membranes shown in Table I.

The top surfaces of CA/SPS blend UF membranes with 95/5, 80/20, and 75/25 compositions at original magnifications of 2500× and 5000× at a constant additive concentration of 10 wt % in

Table V   MWCO of Pure PSf Membranes with a 17.5 wt % Polymer Concentration

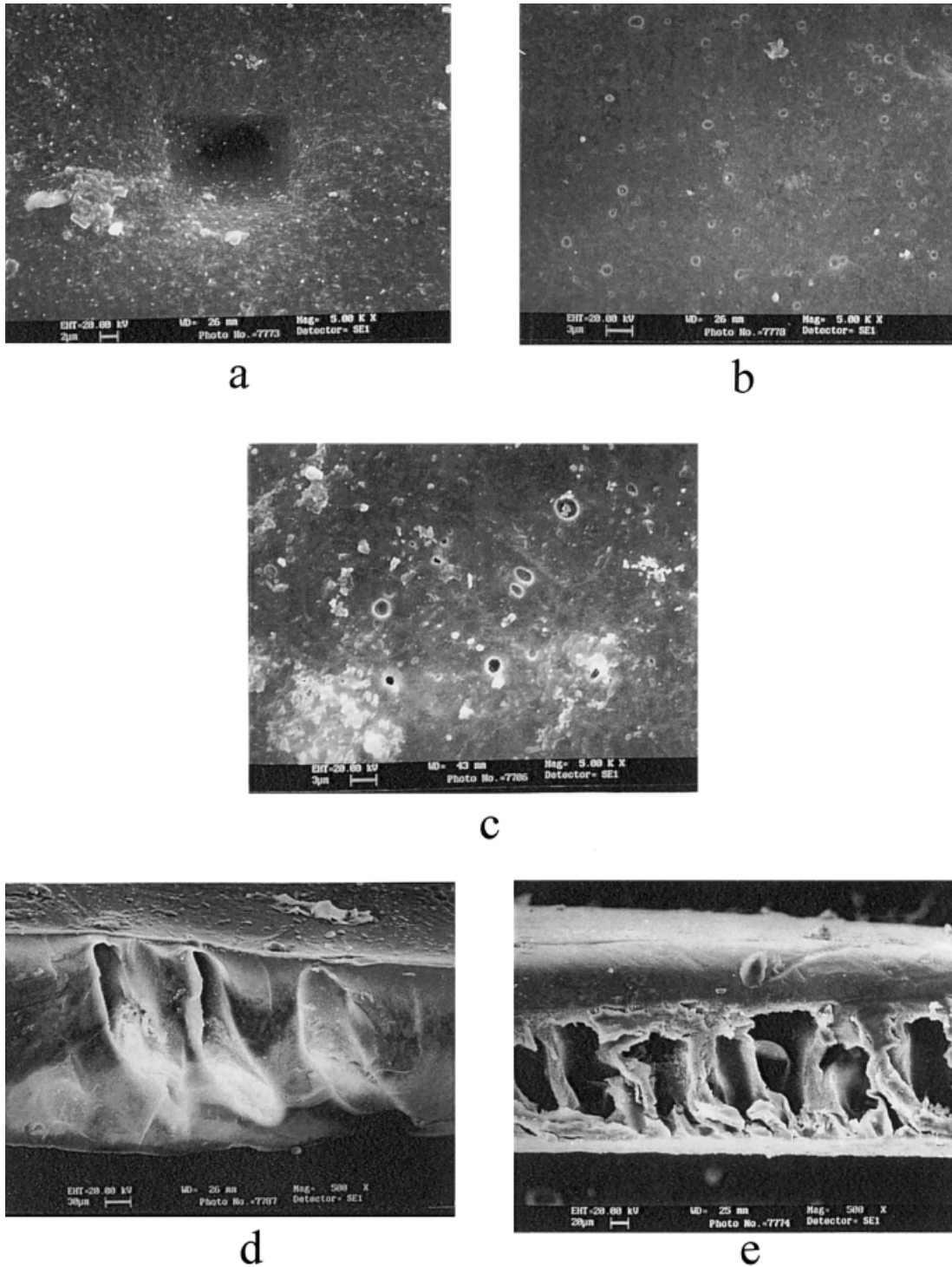| Composition (%) (Polymer Weight), (17.5 wt %)	MWCO (kDa)				
	PEG 600 Concentration (wt %)				
	0	2.5	5.0	7.5	10.0
PSf (100%)	42	77	77	77	77–150

Figure 4   SEM micrographs of CA (100%) membranes with different additive concentrations: (a) 0, (b) 5, and (c) 10 wt % PEG 600 (top surface; original magnification, 5000×) and (d) 0 and (e) 10 wt % PEG 600 (cross section; original magnification, 500×).

the casting solutions are shown in Figure 2(a–f), which reflects the effect of the polymer blend composition on the morphology. As the SPS composition in the blend increased to 20%, the number of pores also increased. A further increase in the SPS composition to 25% reduced the number of
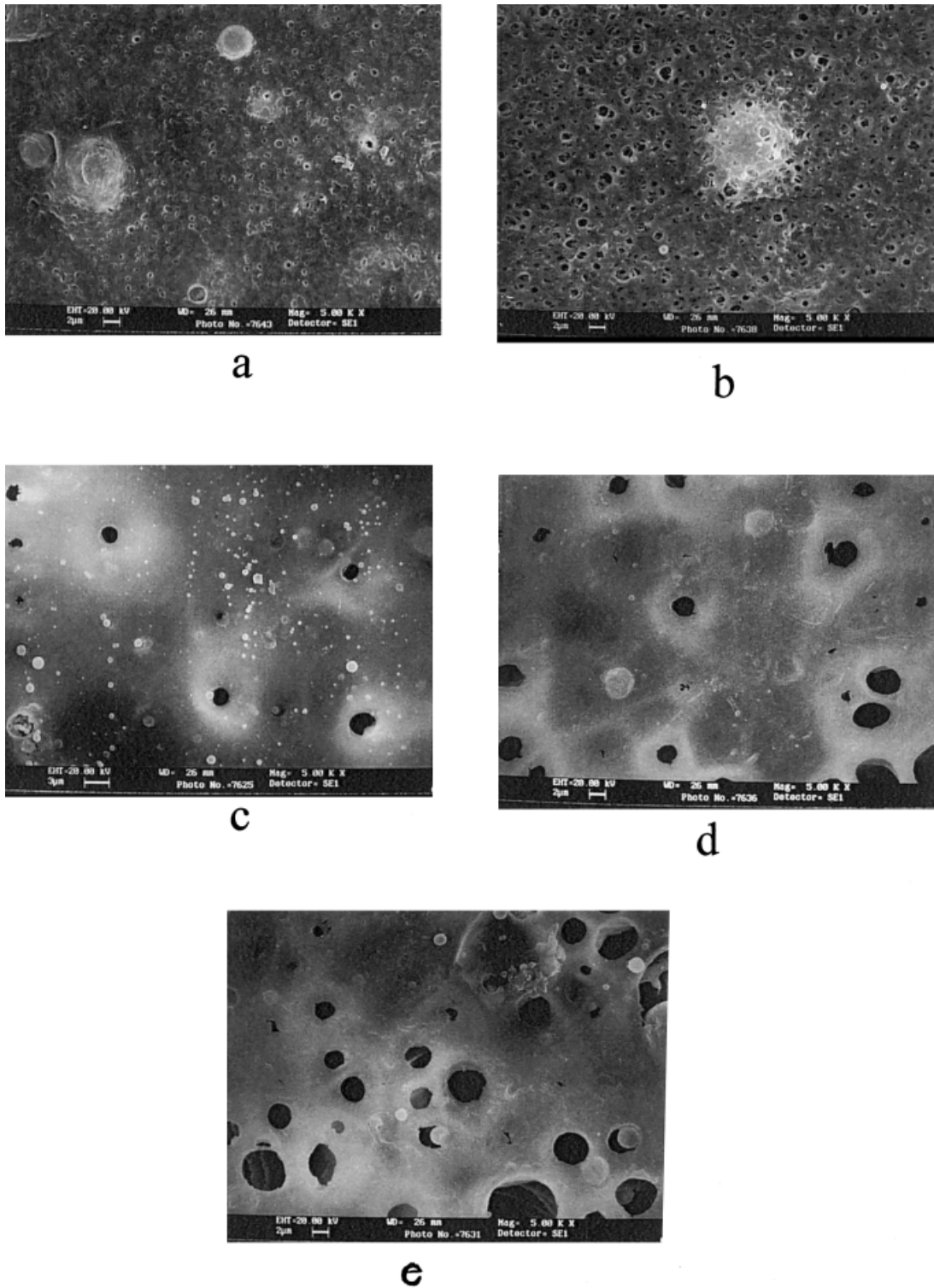
Figure 5 SEM micrographs of CA/SPS (80/20) blend membranes with different additive concentrations: (a) 0, (b) 2.5, (c) 5, (d) 7.5, and (e) 10 wt % PEG 600 (original magnification, 5000×).
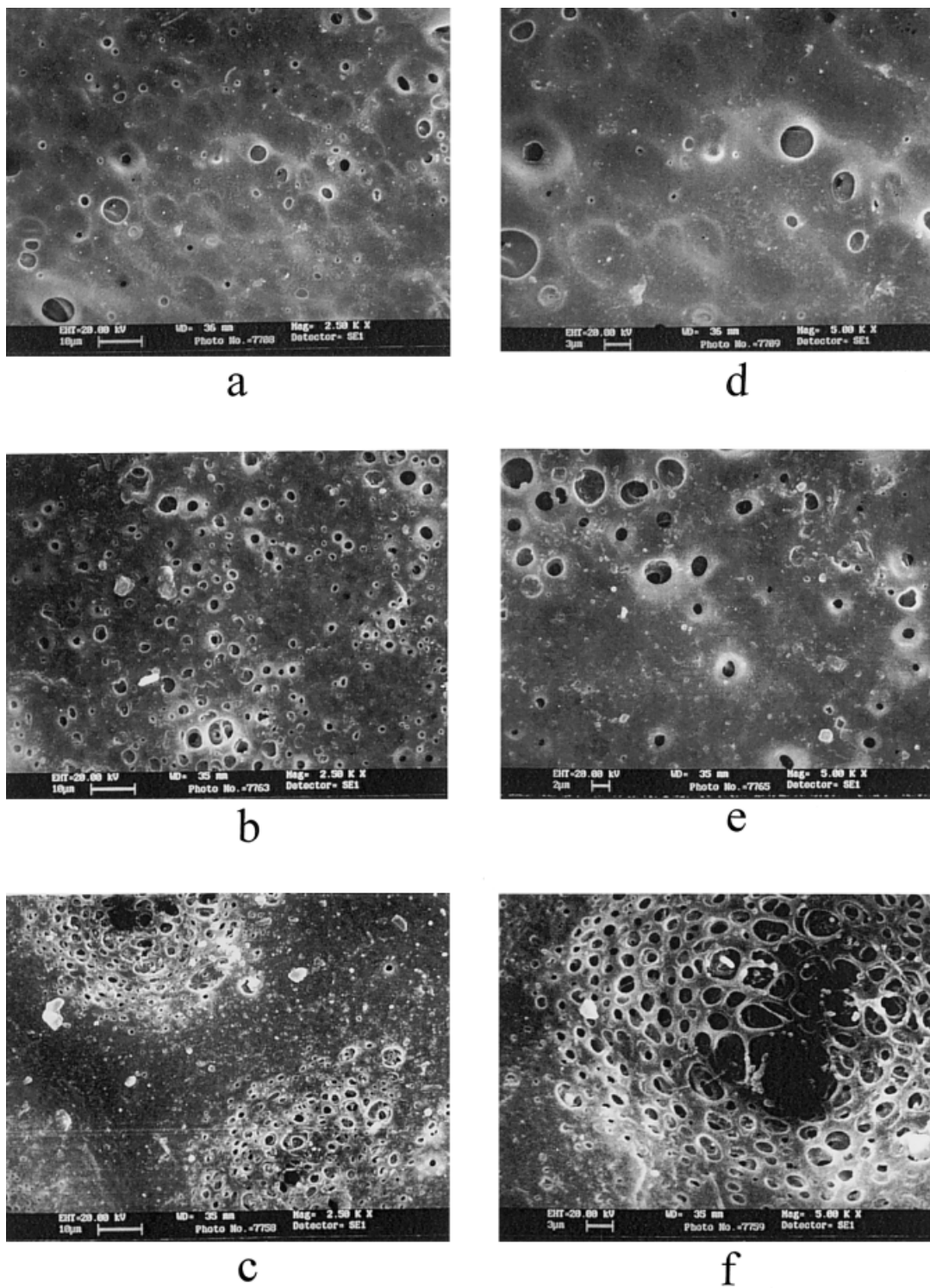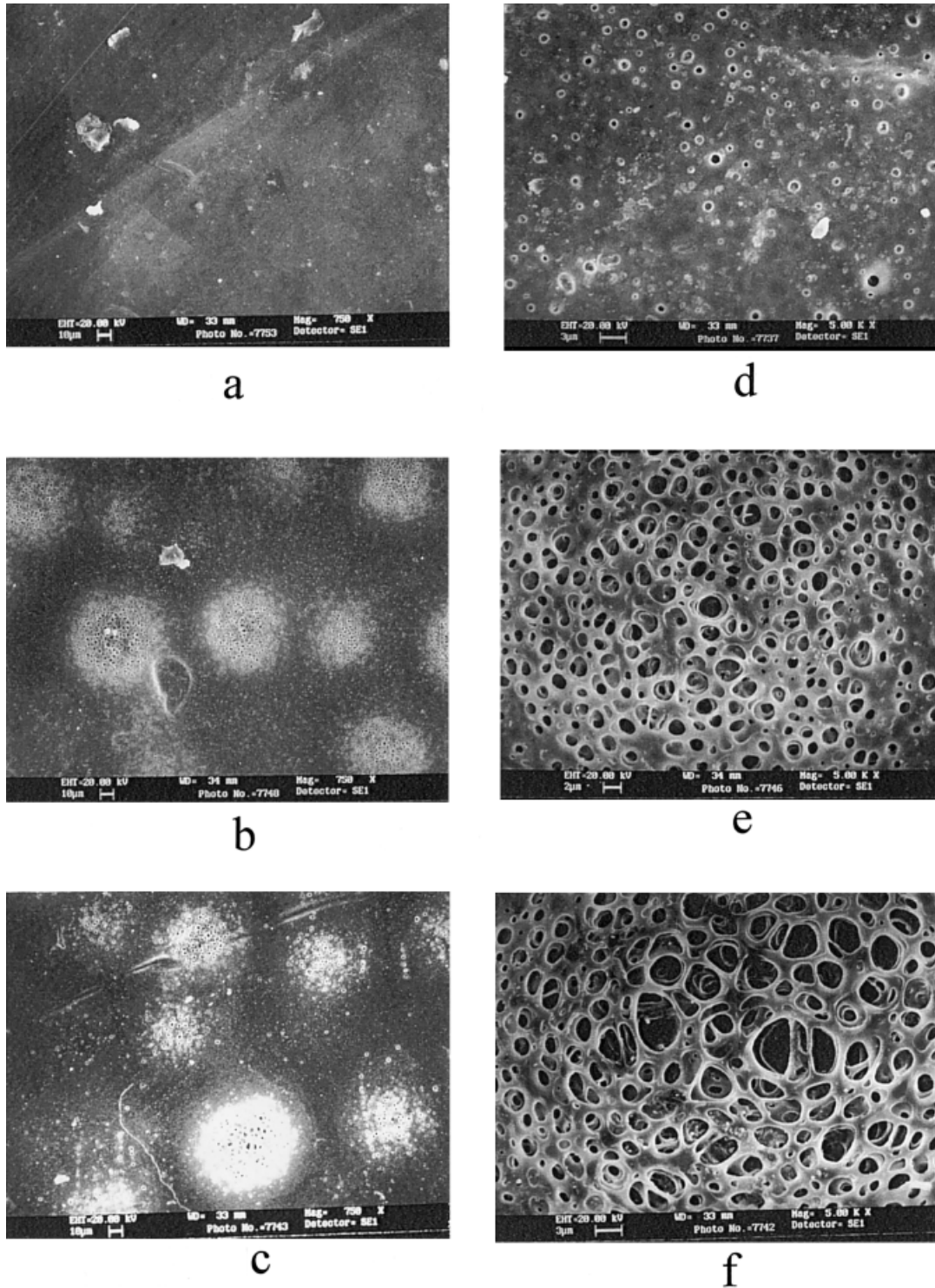
Figure 6 SEM micrographs of the top surfaces of SPS (100%) membranes with different additive concentrations: (a) 0, (b) 5, and (c) 10 wt % PEG 600 (original magnification, 2500×) and (d) 0, (e) 5, and (f) 10 wt % PEG 600 (original magnification, 5000×).

Figure 7 SEM micrographs of the top surfaces of PSf (100%) membranes with different additive concentrations (a) 0, (b) 5, and (c) 10 wt % PEG 600 (original magnification, 750×) and (d) 0, (e) 5, and (f) 10 wt % PEG 600 (original magnification, 5000×).

pores. These findings support the trend observed in the flux and separation of dextran shown in Table I. This unusual behavior, a decrease in the number of pores with an increase in the SPS composition in a blend beyond 20%, may be due to the presence of quantitatively sufficient amounts of both the macromolecular additive PEG 600 and a higher molecular weight SPS polymer, which can readily diffuse with respect to each other during gelation, resulting in phase separation.

Because PEG is soluble in water, the phase separation process was affected only by SPS that had been blended with the other higher molecular weight polymer, CA, leading to a delayed phase-separation process for the high molecular weight component CA in contrast to the relatively low molecular weight component SPS, creating two timescales of precipitation. The short timescale phase separation was responsible for creating the top layer of one membrane, which had a high nonsolvent content, whereas the composition was highly unstable in the longer timescale phase separation. Therefore, the delay in the demixing of the SPS polymer was not possible. Because demixing was not delayed, the polymer precipitation occurred rapidly, and the macrovoid formation was effectively hindered.[23] Furthermore, these morphological studies confirmed our experimental trends for the blend membranes. Similar results have also been found by other researchers.[24–26]

SPS and PSf Homopolymeric Membranes

Figure 6(a–f) represents the top surfaces of SPS (100%) membranes with 0, 5, and 10 wt % additives at original magnifications of 2500× and 5000×. Figure 6(a,d) clearly shows that at a 0 wt % additive concentration, the SPS membrane had lower porosity than those in the presence of the additive. Furthermore, SPS membranes had relatively higher porosity than PSf in the absence of the additive [Fig. 7(a,d)]. This confirms the incorporation of hydrophilic character into SPS.

With an increase in the additive concentration in a pure SPS casting solution from 0 to 5 wt %, both the membrane pore size and porosity increased. A further increase in the additive concentration to 10 wt % increased the porosity, and pores appeared as clusters, as shown in Figure 6(c,f). This might have been due to the existence of a higher amount of PEG in the casting solution, which promoted instability of the polymer composition and caused pore formation randomly over the membrane surface. These results correlated well with the experimental results observed in the pore statistical studies discussed earlier.

Figure 7(a–f) shows the top surfaces of the PSf (100%) membranes with 0, 5, and 10 wt % PEG 600 at original magnifications of 750× and 5000×. Figure 7(a,d), which represents PSf in the absence of the additive, shows the existence of uniform and scattered smaller pores. However, when the PEG 600 concentration was increased to 5 wt %, the pores agglomerated, resulting in clusters of pores [Fig. 7(b,e)]. A further increase in PEG 600 did not affect the pore cluster formation but increased the size of the pores markedly, as shown in Figure 7(c,f). This trend may be due to the leaching of excess PEG 600, present in the nascent membrane, during gelation. This morphology observation coincides well with the results obtained for pore characteristics. Similar observations have also been made by other researchers.[27]

CONCLUSIONS

Structural properties such as pore statistics, MW-COs, and morphologies of UF membranes prepared from CA and SPS with various compositions in the absence and presence of the additive PEG 600 at various concentrations were determined. MWCOs of the membranes were estimated with dextrans of different molecular weights (19–150 kDa) depending on the compositions of the polymers and concentrations of the additive, PEG 600. SEM analysis showed that in the blend membranes, the pore size increased with increasing SPS concentration. Moreover, the incorporation of the additive into the blend system changed the morphology of the membranes considerably. In all, the properties of the blend membranes were different than those of the homopolymeric membranes. In general, the additive PEG 600 played a major role in altering the structural properties of the resulting membranes.

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