Effect of Support Material on Ultrafiltration Membrane Performance

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ABSTRACT: Supported ultrafiltration (UF) membranes based on polyacrylonitrile were prepared by phase inversion method using nonwoven polyester fabric as support with different origin. The membrane preparation parameters, including dope solution composition and casting conditions, were kept same while changing the support fabric. Various analyses performed, viz. water flux, protein rejection, porosity, and membrane compaction indicated that the support used for UF membrane preparation affects the membrane properties to a great extent, and a right support need to be chosen for a preparation of membrane with desired properties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3389–3395, 2006

Key words: ultrafiltration; polyacrylonitrile; supported membrane; compaction; protein rejection

INTRODUCTION

Applications of ultrafiltration (UF) membranes in various areas like water treatment, pharmaceutical, chemical, dairy and food, paper, textile industry, etc. are rapidly growing, stressing the need for a surge on new membranes with improved properties. The membrane performance in terms of flux, rejection performance, fouling characteristics, stability under operating conditions, etc. becomes crucial for large scale applications. The membrane porosity (size and density) play a crucial role in depicting many of these properties. It is well-known that membrane porosity can be manipulated by systematically varying membrane preparation parameters like composition of coagulation bath and its temperature,[1,2] solvent[1] and nonsolvent used for polymer solution preparation,[1,3] concentration of the dope solution,[4–6] evaporation time,[7,8] presence of additives,[1,6,9–12] etc. The flat sheet-supported phase inversion membranes are usually prepared by coating a uniform layer of polymer solution onto a porous support, followed by gelation and precipitation. Although most of the UF membranes are prepared using a support fabric, effect of nature of the support material on properties of the UF membrane formed is weakly addressed. The effect of some preparative parameters on the structure, porosity, and UF membrane performance was studied.[13] The membranes with support and without support showed different performance, and the earlier type exhibited additional pores due to stretches.

In the present investigation, the polyester-based support materials with different origin (woven and nonwoven type) were used for making UF supported membranes. The use of nonwoven support is not reported in the literature. It was, thus, thought to investigate the membrane performance using this type of support as well. The effect of support on formed UF membrane was assessed by casting polyacrylonitrile (PAN) solution of same composition at identical conditions and analyzing their performance. Investigations of crucial membrane performance properties like water flux, rejection performance of proteins of different molecular weight, porosity determination by liquid–liquid displacement method, membrane compaction, and scanning electron micrographs of membranes casted onto different support put a light on the effect of support properties on the performance of formed UF membranes.

EXPERIMENTAL

Materials

Polyacrylonitrile (PAN) was received from IPCL (Vadodara, India) (MW = 75,000 g/mol). The nonwoven polyester fabric, Viledon—-H3160 and H1006 were procured from M/s. Frudenberg (Germany); Hollytex—-3329, 3324, and 3265 from Ahlstrom (USA); while woven PES-111 was procured from M/s. Frank Industrial Corporation (Baroda, India). The properties of these materials as supplied are given in Table I. *N,N*-Dimethyl formamide (DMF, analytical reagent grade) was procured from M/s. Merck-India,

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TABLE I
Support Material Properties as Provided by Suppliers

Support fabric	Weight (g m^{-2})	Thickness (mm)	Air permeability	Tensile strength	Elongation (%)	Water holding capacity (wt %)[a]	Bulk porosity of support (%)[a]
H3160	60	0.07	30 (dm^3 s^{-1} m^{-2}) (at 2 mbar)	210 N/50 mm	22	23.08	41.77
H1006	75	0.11	70 (dm^3 s^{-1} m^{-2}) (at 2 mbar)	125 N/50 mm	15	38.58	53.68
3329	96.5	0.13	5.1 cfm	CD 28 lbs in^{-1} MD 55 lbs in^{-1}	CD 72	24.15	49.57
3324	99.9	0.13	9 cfm	CD 28 lbs in^{-1} MD 60 lbs in^{-1}	CD 80	29.12	47.79
3265	81.2	0.13	20 cfm	CD 21 lbs yd^{-2} MD 65 lbs in^{-1}	CD 70	28.26	57.56
PES-111	112.6	0.18[a]	8–10 cfm	NA	NA	28.05	56.13

[a] The data generated by investigators NA: not available.

zinc chloride ($ZnCl_2$, GR grade) from M/s. Loba Chemie, while isobutanol from M/s. Qualigens fine chemicals. Bovine serum albumin (BSA, faction-V), lysozyme, and ovalbumin (grade-V) were obtained from M/s. Sigma chemicals (USA); while trypsin (from bovine pancrease) and pepsin were obtained from M/s. SRL chemicals. The DMF was dried over 4A-molecular sieves, while $ZnCl_2$ was purified by melt process. All other chemicals were used as received.

Membrane preparation

A dope solution of PAN in DMF was prepared by initially adding 26.6 g of $ZnCl_2$ to 637.4 g of DMF, stirring for 12 h in a dry atmosphere at ambient conditions. To this, 136 g of dry PAN powder was added and further stirred for 72 h. The formed solution was degassed to remove entrapped gases. The undissolved particles, if any, were removed by centrifugation at ~2700 rpm for 3 h. The membrane was prepared on a moving support using pilot scale continuous membrane casting facility at ambient conditions, while using water as the nonsolvent. The membranes were stored in 0.5% aqueous formalin solution at 4°C until use.

Membrane characterization

Water flux determination

Water flux of membranes was measured using (i) Amicon cell (11 cm^2 active area) in dead-end mode and (ii) rectangular cell (191 cm^2 active area) in cross-flow mode (Fig. 1) at 1 bar pressure. Initially, 100 mL of distilled water was allowed to permeate through the membrane to remove formalin, and then the water flux was measured. The measurements were repeated at least for 10 coupons by dead-end mode and four coupons by cross-flow mode. The average flux and percent variation is given in Table II.

Rejection analysis

The protein rejection performance [lysozyme (14 kDa), trypsin (23 kDa), pepsin (33 kDa), ovalbumin (43 kDa), and BSA (68 kDa)] was analyzed using 0.1% aqueous

TABLE II
Properties of Membranes Casted on Various Supports

Membrane identification	Support used	Physical observation of membrane		Bulk porosity of membrane (%)	Water flux, J_w (L m^{-2} h^{-1}) at 1 bar				$R_{Ovalbumin}$ (%)
					Dead end mode		Cross flow mode		
		Penetration through support	Presence of pinholes		Average (L m^{-2} h^{-1})	Variation (%)	Average (L m^{-2} h^{-1})	Variation (%)	
M-3160	H 3160	Negligible	No	60.49	36	34	51	–	85
M-1006	H 1006	Negligible	No	61.24	42	26	44	11	82
M-3329	3329	No penetration	No	57.01	70	29	77	7	80
M-3324	3324	No penetration	No	60.42	81	16	76	7	85
M-3265	3265	Very less	Yes	55.4	119	27	152	30	74
M-111	PES-111	Intermitant patches	Yes	57.86	196	29	213	31	53

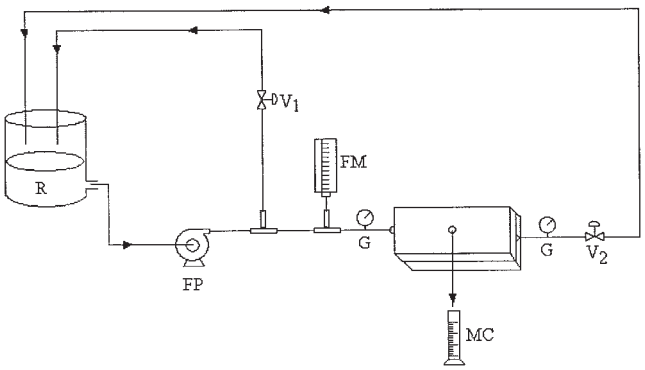

Figure 1 Schematic of compaction setup; R, reservoir; V1 and V2, control valves; G, pressure gauge; FP, feed pump; FM, flow meter; MC, measuring cylinder.

solution at 7.5 pH (McIlvaine buffer). The concentration of feed and permeate was determined by UV spectrophotometer at 280 and 260 nm wavelength. A minimum of six coupons were analyzed for rejection and the averaged data (variation ± 2%) plotted as in Figure 4. The percent rejection (%*R*) was calculated by using eq. (1).

$$\% \text{ R} = \left[1 - \left(\frac{C_p}{C_f}\right)\right] \times 100 \quad (1)$$

where, C_p is concentration of the permeate, while C_f is the feed concentration.

Pore size distribution analysis

Membrane porosity was determined by liquid–liquid displacement technique using water saturated isobutanol–water as a solvent pair.[14] The pore size and pore density were calculated using Cantor's eq. (2) and Hagen-Poiseuille's eq. (3).

$$r_{P_i} = \frac{2\sigma \cos\theta}{P_i} \quad (2)$$

$$n_i = \left(J_i - \frac{J_{i-1}P_i}{P_{i-1}}\right)\frac{8\eta l}{\pi P_i r_{p_i}^4} \quad (3)$$

where, r_{P_i} is the radius of the pore, θ is the polymer–water contact angle; n_i is the number of pores per unit area; η is the viscosity of water; l is pore length that is assumed to be equal to the membrane skin layer thickness of 1 μm; J_i correspond to the flux measured at the ith increment where the applied pressure is P_i.

Membrane compaction study

The schematic diagram of crossflow set up is shown in Figure 1. The membrane coupon was mounted in the cross flow UF cell. The water at 0.6 L/min was fed continuously to the cell at a desired applied pressure. The water flux was recorded at 30 min time interval. In all the cases, though a steady flux was obtained after ~2.5 h, the flux at the 4th hour was recorded as the flux at that applied pressure. At least three coupons were repeated for each membrane.

Membrane resistance

To determine the membrane resistance (R_m), pure water flux (J_w) was measured using a dead-end set up at various transmembrane pressures (ΔP) before compaction pressure. The membrane resistance (R_m) was determined as the inverse of slope of the graph of transmembrane pressure versus water flux using eq. (4).[15]

$$R_m = \frac{\Delta P}{J_w} \quad (4)$$

Determination of porosity of support material

The overall porosity of the support was determined by using the following eq. (5).[16]

$$\text{Bulk porosity } (\%) = \frac{V_m - V_p}{V_m} \times 100 = \frac{DA - (W_m/\rho_p)}{DA} \times 100 \quad (5)$$

where, V_m is the volume of the sample (equals to $D \times A$) and V_p is the volume occupied by the polymer (equals to W_m/ρ_p); A is the coupon area having thickness D and mass W_m of the support material; ρ_p is the density of the polyester.

Scanning electron microscopy

The membrane cross sections were investigated by scanning electron microscopy (SEM), Leica, Stereoscan, 440. The membrane specimen was prepared by fracturing at liquid nitrogen temperature, and then dried in vacuum oven at 40°C for 24 h.

Water holding capacity of support and the membrane

The support and membrane coupons of 5 × 5 cm^2 size were immersed in water for 24 h and weighed. These coupons were kept in vacuum oven at 60°C for 24 h and again weighed. The water holding capacity was calculated using eq. (6).[17] The measurement was repeated for three times, and data are averaged as given in Table I.

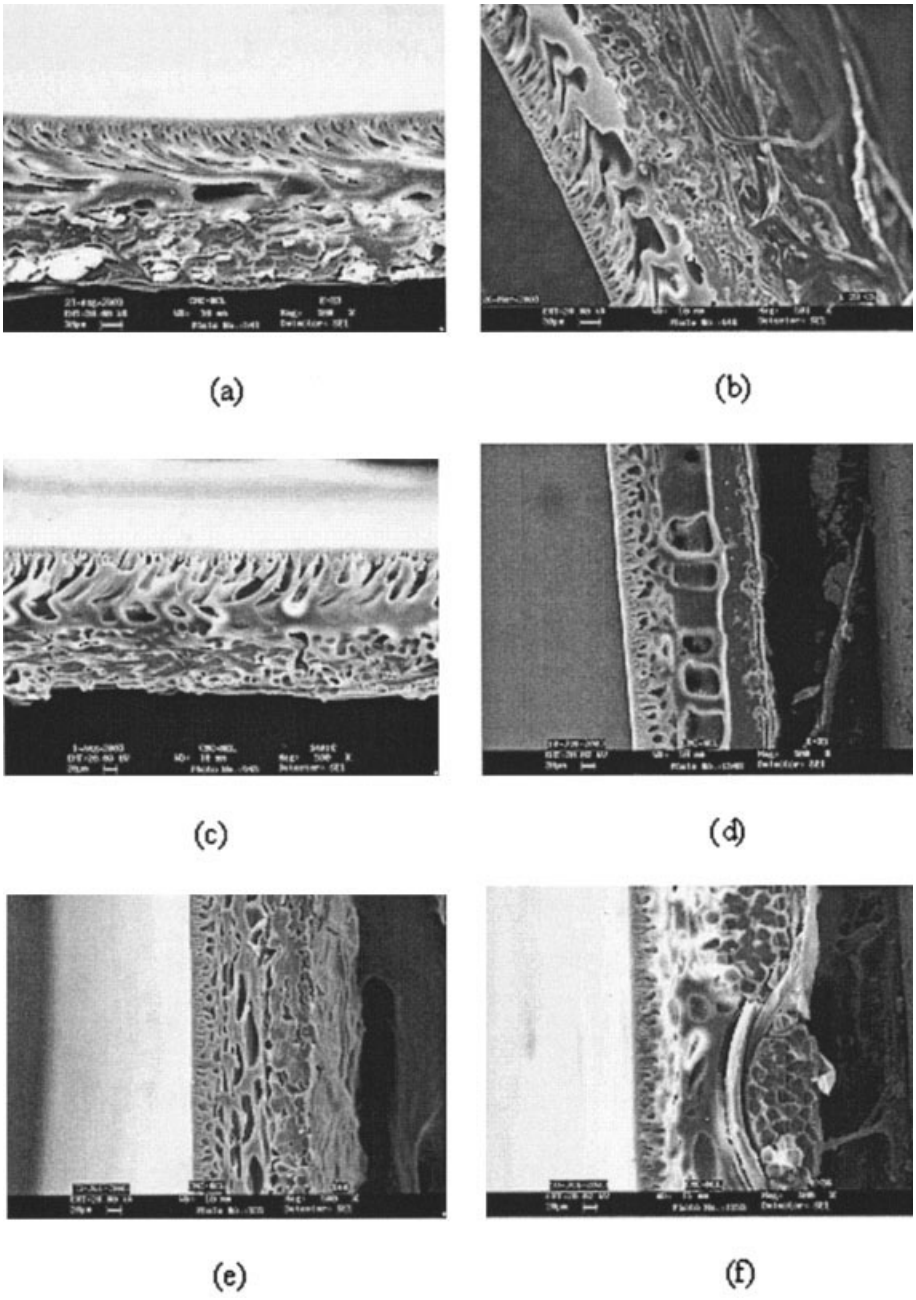

Figure 2 Scanning electron micrographs of cross sections of membranes casted on different supports; (a) M-3160, (b) M-1006, (c) M-3329, (d) M-3324, (e) M-3265, and (f) MPES-111.

$$\% \text{ Water content} = \frac{\text{wet sample weight} - \text{dry sample weight}}{\text{wet sample weight}} \times 100 \quad (6)$$

RESULTS AND DISCUSSION

In view of the objective of the present work of assessing the usefulness of various support materials, the membranes were casted on these supports by keeping all parameters viz., dope solution composition, casting conditions including air dry time, gelation and curing time, and temperature of respective bath the same. The variation in properties of membranes so prepared thus can be considered to result from the variation in support material used of different origin. The physical properties of the support materials used are given in Table I. The thickness for H3160 support was lowest, while for PES-111 it was the highest among the series used, as also reflected by their GSM value. The water holding capacity of all these polyester-based supports

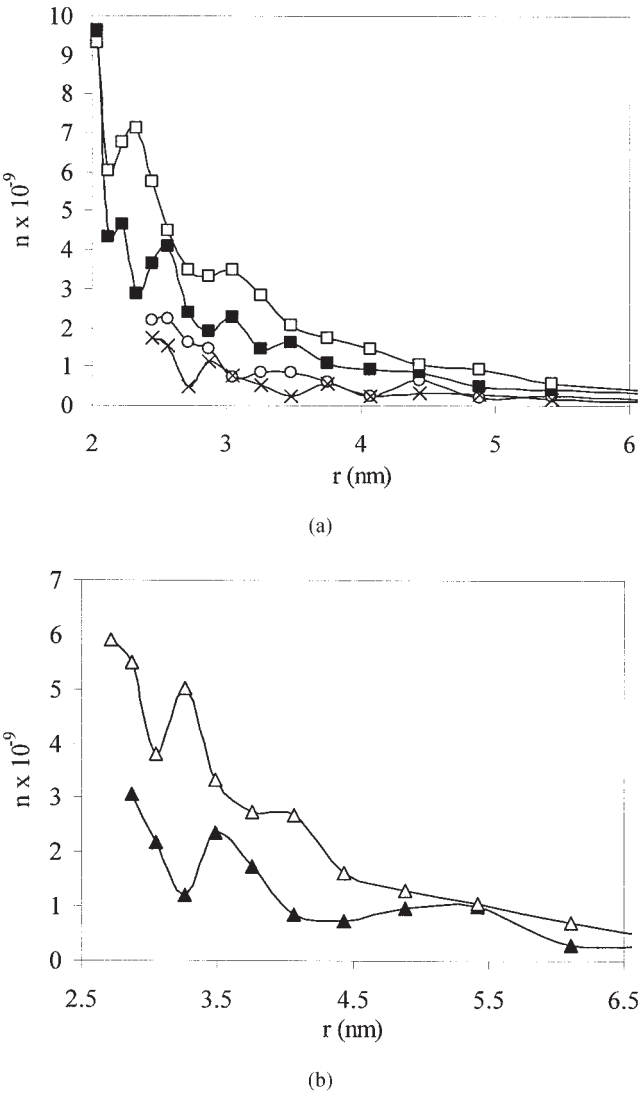

Figure 3 (a) Pore size distribution of membranes. (×), M-3160; (○), M-1006; (■), M-3329; (□), M-3324. (b) Pore size distribution of membranes. (△), M-3265; (▲), M-111.

did not match with the support porosity, probably due to the different processing during their manufacture. The membrane prepared using these supports had a total thickness of 250 ± 25 μm. The macroscopic observation of the membranes prepared using these supports indicate that except for M-3265 and M-111, other membranes did not exhibit noticeable defects. The penetration of the dope solution on the other side of the membrane was observed only for M-3265 and M-111, which was more severe for the latter case. An intermittent patches showing penetration of dope solution through the pores and the presence of pinholes in these cases indicated that the porosity of this support is higher for the used dope solution viscosity. Although this problem could have been solved by varying membrane casting parameters, but it was not attempted since the objective was to make membranes with identical conditions. The coupons for further analysis were selected from these membranes such that they contained no defects. The SEM analysis (Fig. 2) of the membrane cross section shows that all these membranes exhibit a structure having well-defined skin layer on the top as common to UF membranes.

The water flux (J_w) by dead-end mode showed lower water flux and higher variation than that of for cross-flow mode as anticipated (Table II). The J_w for membranes M-3160 and M-1006 was lower, followed by flux for M-3329 and M-3324. The flux for M-3265 and M-111 was on the higher side. Although the percent variation in flux looks on a higher side for dead-end mode, it is lesser for cross-flow mode (except for M-3265 and M-111) due to larger membrane area used in cross-flow case (17.4 times). The higher variation even in cross-flow mode for M-3265 and M-111 could be attributed to the larger pore size variations in the latter cases. This is evident from the pore size distribution curves (Figs. 3(a) and 3(b)), which shows that M-3265 and M-111 membranes exhibited wider pore size distribution than other cases. This is further supported by rejection analysis. All the membranes showed >90% rejection for BSA (Fig. 4), indicating their molecular weight cut off (MWCO) to be less than 68 kDa. An ovalbumin rejection was >80%, except for M-3265 (74%) and for M-111 (49%). Figure 4 also shows that rejection of other proteins (pepsin, trypsin, and lysozyme) was >40% for most of the cases at pH of 7.5. A good correlation (R^2 = 0.89) was also seen between water flux and ovalbumin rejection (Fig. 5), showing that though the casting parameters for all these membranes were same, pore size of the membranes casted on different support are different. Thus, the variation in flux is not only dependant on pore

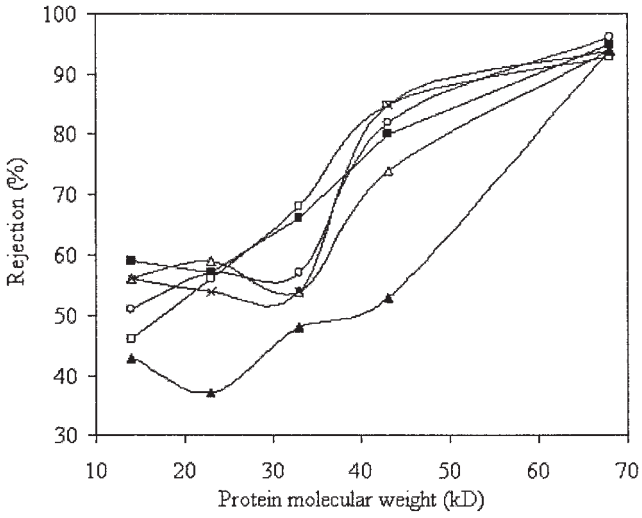

Figure 4 Rejection analysis of membranes using proteins of different molecular weight. (×), M-3160; (○), M-l006; (■), M-3329; (□), M-3324; (△), M-3265; (▲), M-111.

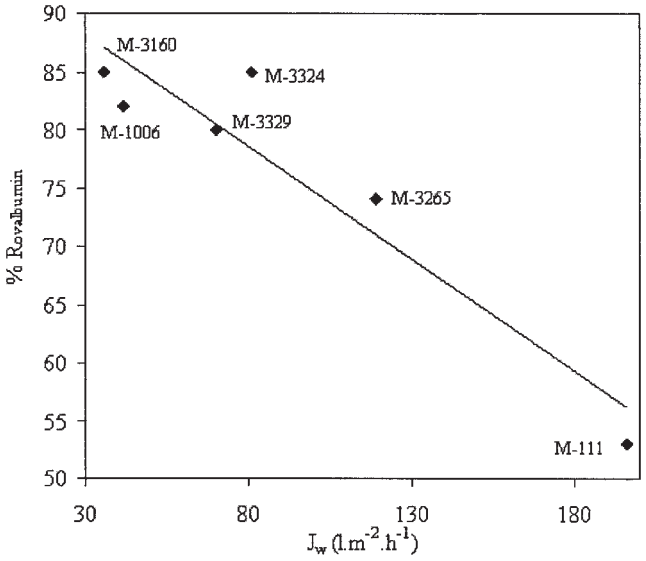

Figure 5 Relationship of water flux (J_w) and ovalbumin rejection for various membranes.

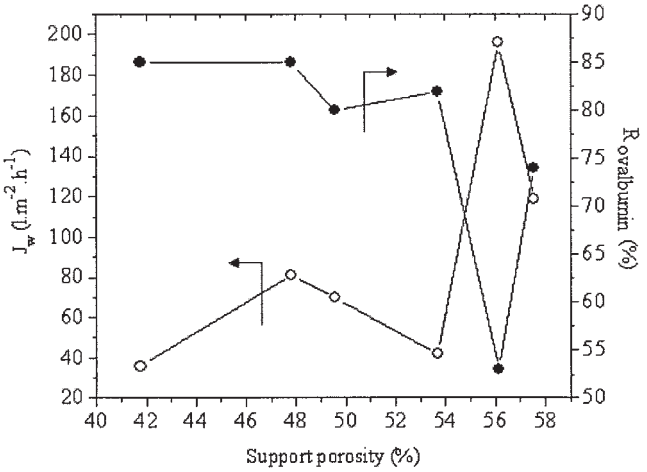

Figure 6 Variation in water flux (J_w) and ovalbumin rejection ($R_{ovalbumin}$) with support porosity.

size. The pore size distribution as calculated using eq. (3), and plotted in Figures 3(a) and 3(b). The membranes M-3329 and M-3324 showed more number of pores near to smaller pore size of ~2 nm. The membranes M-3160 and M-1006 showed their lowest pore size of 2.5 nm. Their pore density and surface porosity is also lower than other membranes. Thus, they exhibited lower water flux. In other words, the backing H1006 and H3160 produced tighter membranes. This is also supported by the membrane resistance as given in Table III. The membranes M-3160 and M-1006 exhibited the highest resistance in series. A graph for variation in water flux and ovalbumin rejection with support porosity shows that, if PES-111 is neglected, there is increase in permeation and decrease in rejection as the support porosity increases (Fig. 6). Although no correlation was found between membrane bulk porosity (obtained from wet and dry weights) and support porosity, membrane surface porosity increases with the support porosity (Fig. 7). This observation though looks attractive, other membrane characterization also need to be considered while selecting appropriate backing.

Membrane compaction

The membrane compaction analysis of these membranes was studied by compressing these membranes hydrostatically in cross-flow mode using setup as shown in Figure 1. Although there are various methods of studying compaction,[18–20] we chose to do the compaction hydrostatically, since this method is closer to real case application. Initially, the time required to obtain a constant flux at certain pressure was determined. For all the membranes and pressures studied, the flux became constant after ~2.5 to 3 h. The steady water flux after 4 h of applying particular pressure is plotted in Figure 8. It can be seen that the compaction pressure for PES-111 is lowest. The compaction pressure for other membranes is ≥4 bar. This distinctly conveys that membranes prepared using woven support PES-111 not only gets compacted more easily, but also the flux declines after compaction pressure. Although M-3265 exhibited flux nearer to this membrane, its compaction pressure is closer to the membranes casted using nonwoven supports. The support used for making M-3265 and M-111 have higher porosity compared with other supports as reflected from their porosity and air permeability. Although M-3265 have higher porosity, its compaction pressure is al-

TABLE III
Membrane Properties Determined by Pore Size Distribution and Compaction Analysis

Membrane	Pore density ($n \times 10^{10}$)	Surface porosity (%)	Compaction pressure (bar)	R_m (Pa m^{-1} s^{-1})
M-3160	0.7	0.30	4	1.54×10^{10}
M-1006	1.3	0.45	5	1.35×10^{10}
M-3329	7.9	1.55	4	7.54×10^{9}
M-3324	6.8	1.77	5	4.73×10^{9}
M-3265	2.1	1.01	4	4.75×10^{9}
M-111	4.2	1.96	2	2.47×10^{9}

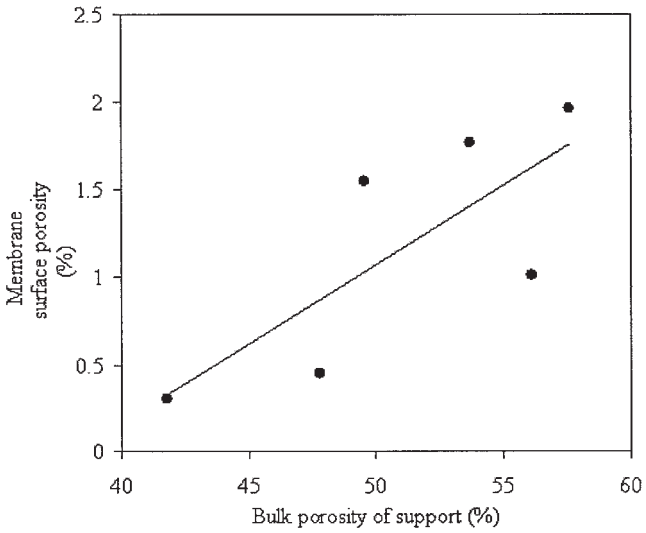

Figure 7 Variation of membrane surface porosity with bulk porosity of the support material.

most double than that of M-111. The flux of M-3160 and that of M-1006 remained almost similar at all pressures. Although the flux of M-3329 and M-3324 are identical at 1 bar, the difference increases at higher pressure. On this basis and also M-3324 having good rejection performance, appreciable pore density, surface porosity, and lesser membrane resistance, the support 3324 appears to be a better choice than any of the supports investigated.

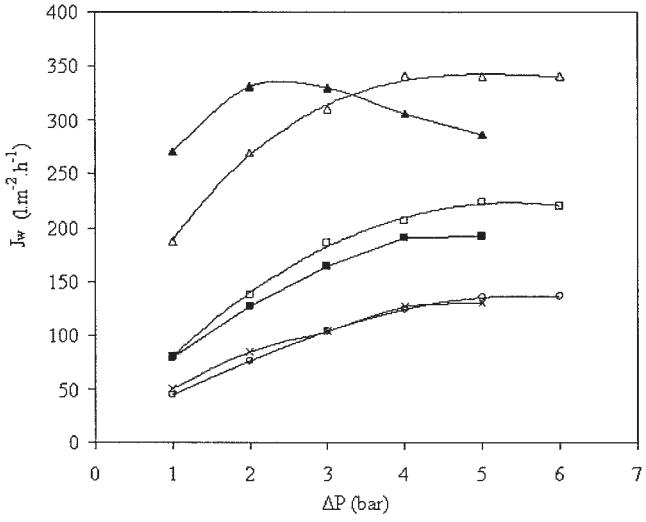

Figure 8 Variation of average water flux (J_w) with transmembrane pressure (ΔP) for membranes prepared with different backing. (×), M-3160; (○), M-1006; (■), M-3329; (□), M-3324; (△), M-3265; (▲), M-111.

CONCLUSIONS

Although the PAN-based UF membranes were prepared on various support materials by keeping membrane preparation conditions similar, the membrane characterization elaborated the suitability of these supports. Although two broad types, woven and nonwoven supports, were investigated, the membrane casted on the earlier one exhibited higher water flux, but showed poorer rejection and compaction behavior. This membrane also contained defects generated during its formation. Among the membranes prepared using nonwoven supports, M-3265 has highest water flux, but the membrane contained certain defects. The M-3324 had intermediate water flux but excellent membrane forming capacity, high rejection, and showed good resistance to compaction than other membranes.

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