Available online at www.sciencedirect.com
SCIENCE DIRECT®
European Polymer Journal 40 (2004) 2153–2159
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Synthesis, characterization and thermal studies on cellulose acetate membranes with additive

G. Arthanareeswaran [a], P. Thanikaivelan [b], K. Srinivasn [a], D. Mohan [a,*], M. Rajendran [a]

[a] *Membrane Laboratory, Department of Chemical Engineering, AC College of Technology, Anna University, Chennai 600 025, India*
[b] *Centre for Leather Apparels and Accessories Development, Central Leather Research Institute, Adyar, Chennai 600 020, India*

Received 30 January 2004; accepted 27 April 2004
Available online 26 June 2004

Abstract

Cellulose acetate (CA) membranes are used in ultrafiltration applications, although they show low chemical, mechanical and thermal resistance. In order to prepare membranes with improved properties, modification of cellulose acetate with polyethelene glycol (PEG 600) has been attempted. In this study, CA has been mixed with PEG 600 as an additive in a polar solvent. The effects of CA composition and additive concentration given by a mixture design of experiments on membrane compaction, pure water flux, water content and membrane hydraulic resistance have been studied and discussed. The efficiency of protein separation by the developed CA membranes have been quantified using model proteins such as pepsin, egg albumin (EA) and bovine serum albumin (BSA). The thermal stability of the developed membranes prepared with PEG 600 additive has also been investigated using thermogravimetric analysis and differential scanning calorimetry.

Keywords: Cellulose acetate; Ultrafiltration; Membranes; Thermal studies; Protein rejection; Additive

1. Introduction

Efficient separation processes are needed for the whole spectrum of industrial sector. These include food and pharmaceutical industries to obtain high-grade products [1–3], supply of high-quality water for communities and industries [4] and removal or recovery of toxic or valuable components from various industrial effluents [5–7]. With the advent of membrane technology, separation, concentration and purification have become industrially viable unit operations due to its high efficiency of separation. Further, low energy of operation, spatial requirements, simplicity of operation using modern compact modules as well as recycling and reuse of chemicals and water promote membrane processes as a promising technique in separation processes. The heart of the process, membrane, plays a key role in dictating the applicability and efficiency of the process.

The first generation cellulose acetate (CA) membranes yield low flux and are susceptible to chemical and bacteriological agents [8]. The performance of CA may be improved by mixing it with appropriate additives to fulfill new requirements and associated membrane properties. The phase separation (inversion) method is one of the most popular methods used to produce porous polymeric membranes. Polyethylene glycol (PEG) has been widely used in the field of controlled drug release [9]. In this study, PEG (MW 600) was used as a plasticizer as well as a pore-forming agent and incorporated into CA membrane preparation. Various combinations of CA and additive have been derived using

* Corresponding author. Tel.: +91-442-220-3530; fax: +91-442-235-2642.
E-mail address: mohantarun@yahoo.com (D. Mohan).

0014-3057/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2004.04.024

mixture design of experiments concept [10]. The membrane compaction, pure water flux, water content, membrane resistance (R_m) and protein rejection have been determined. Characterization of prepared membranes for thermal behavior has also been made and discussed.

2. Experimental

2.1. Materials

Commercial grade CA was procured from Mysore Acetate and Chemicals Company Ltd., India. Analar grade *N*,*N*′-dimethyl formamide (DMF) from Qualigens Fine Chemicals, Glaxo India Ltd. was sieved through molecular sieves (Type-4 Å) for removing moisture and stored in dried condition prior to use. Other solvents such as acetone and methanol as well as surfactant, sodium lauryl sulphate (SLS), were purchased from Qualigens Fine Chemicals Ltd., India, which were of analytical grade. PEG 600 was procured from Merck (India) Ltd., and used as such, as an additive for the whole study. Sodium monobasic-phosphate anhydrous and sodium dibasicphosphate heptahydrate were procured from CDH Chemicals Ltd., India and used for the preparation of phosphate buffer solutions in protein analysis. Proteins viz., bovine serum albumin (BSA), $M_w = 69$ kDa and pepsin, $M_w = 35$ kDa were purchased from SRL Chemicals Ltd., India. Egg albumin (EA), $M_w = 45$ kDa was obtained from Council of Scientific and Industrial Research (CSIR), Bio-Chemical center, New Delhi, India. Deionized and distilled water used for all the studies.

2.2. Blending of polymers

The varying combinations of CA was dissolved with PEG 600 [10] in a polar solvent, DMF, under constant mechanical stirring at a moderate speed of rotation in a round bottom flask for 3–4 h at 40 °C. The homogeneous solution obtained was allowed to stand for at least 3 h in air tight condition to get rid of the air bubbles.

2.3. Membrane preparation

The preparation method was the same as that of the ''phase inversion'' method employed in the earlier work [11]. The casting environment viz., relative humidity ($35 \pm 2\%$) and temperature (10 ± 2 °C) was maintained for the preparation of membranes with better physical properties such as homogeneity, thickness and morphology. The thickness of the membranes was maintained at 0.22 ± 0.02 mm and verified with a micrometer having precision of 0.01 mm. The casting and gelation conditions were kept constant through out, since the thermodynamic conditions would largely affect the morphology and performance of the resulting membranes [12]. Prior to casting, gelation bath of 2 l consisting 2.5% (v/v) DMF, to reduce the rate of liquid–liquid demixing and macrovoid, and 0.2% (wt basis) SLS, to reduce surface tension at the polymer–non-solvent interface, in distilled water was prepared. The membranes were prepared by casting using doctor blade on the glass plate and maintaining the desired thickness by adjusting the height of the doctor blade and fixing an oil sheet paper at both ends of the doctor blade. After casting, the solvent present in the cast film was allowed to evaporate for 30 ± 5 s, and the cast film along with glass plate was gently immersed into the gelation bath for at least 1–3 h for complete precipitation and formation of membranes. The membranes were removed from the gelation bath and washed thoroughly with distilled water to remove DMF and surfactant. The membranes were subsequently stored in 0.1% of formalin solution to prevent microbial growth.

2.4. UF set up

The UF experiments were carried out in a batch type, dead end cell (UF cell-S76-400-Model, Spectrum, USA) with a diameter of 76 mm, fitted with a Teflon coated magnetic paddle. This cell was connected to a compressor with pressure control valve and gauge through a feed reservoir.

2.5. Membrane characterization

2.5.1. Compaction

The prepared membranes were cut into desired size needed for fixing it up in the ultrafiltration kit of 38.5 cm^2 area and initially pressurized with distilled water at 414 kPa for 6 h. The water flux was measured at every 1 h. The flux generally declines initially and attained steady state after 4–5 h of compaction. The prepressurized membranes were used in subsequent ultrafiltration experiments at 345 kPa [13].

2.5.2. Pure water flux

Membranes after compaction, were subjected to pure water flux estimation at a transmembrane pressure of 345 kPa. The permeability was measured under steady state flow. The pure water flux was determined [14] using Eq. (1).

$$J_w = \frac{Q}{A \cdot \Delta T} \tag{1}$$

where J_w = water flux, 1 $m^{-2}\,h^{-1}$; Q = quantity of permeate, l; A = membrane area, m^2; ΔT = sampling time, h.

2.5.3. Water content

Water content of the membranes was obtained as follows. The membranes were soaked in water for 24 h and weighed after mopping with blotting paper. These wet membranes were placed in a vacuum oven at 75 °C for 48 h and the dry weights were determined. The percent water content was derived [15] by Eq. (2).

$$\%\text{Water content} = \frac{\text{Wet sample weight} - \text{dry sample weight}}{\text{Wet sample weight}} \times 100 \quad (2)$$

2.5.4. Membrane hydraulic resistance (R_m)

To determine membrane hydraulic resistance (R_m), the pure water flux of membranes were measured at different transmembrane pressures (ΔP) viz., at 69, 138, 207, 276 and 345 kPa, after compaction. The resistance of the membrane, R_m, was evaluated from the slope obtained [16] by plotting water flux versus transmembrane pressure difference (ΔP), using Eq. (3).

$$R_m = \frac{\Delta P}{J_w} \quad (3)$$

2.5.5. Protein rejection studies

Molecular weight cut-off (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. Therefore, proteins of different molecular weights such as trypsin (20 kDa), pepsin (35 kDa), EA (45 kDa) and BSA (69 kDa) were chosen for the estimation of MWCO. All the protein solutions were prepared individually at a concentration of 0.1 wt% in phosphate buffer (0.5 M, pH 7.2) using deionized and distilled water and used as standard solutions and filtered through each membrane individually. The permeate protein concentration, collected over measured time intervals, was estimated using UV-Visible spectrophotometer (Shimadzu, Model UV-160A) at a wavelength of 280 nm. The percentage rejection was calculated [17] using Eq. (4).

$$\%SR = 1 - \left(\frac{C_p}{C_f}\right) \times 100 \quad (4)$$

where, C_p and C_f are the concentrations of permeate and feed solutions, respectively. The permeate fluxes of all protein solutions as a function of PEG was also determined.

2.6. Thermal studies

2.6.1. Thermo gravimetric analysis (TGA)

The TGA was carried out using a STA 409PC Seiko Instruments Inc., thermal analysis instrument. A sample of 3 mg of membranes was dried at 100 °C to remove moisture for 30 min, and then programmed from 30 to 600 °C at a rate of 20 °C/min under the nitrogen atmosphere.

2.6.2. Differential scanning calorimetry (DSC)

DSC measurement of prepared membranes was carried out using a Seiko Instruments Inc. DSC 5200 series differential scanning calorimeter at a heating rate of 10 °C/min under nitrogen atmosphere. The glass transition temperature, T_g, was calculated at the intersection of the tangents to the corresponding DSC curve.

3. Results and discussion

A series of membranes using combinations of CA and PEG 600 have been prepared based on mixture design concept of design of experiments procedure [10] in order to improve the performance with respect to water flux, membrane resistance, etc. The various combinations of CA and additive, as shown in Table 1, were derived using Design Expert software [10]. This study probes the role played by additive on the pore formation as well as membrane performance such as pure water flux, hydraulic resistance, water content and separation of proteins.

3.1. Membrane compaction

The compaction was aimed to make membranes with rigid pore structure and size, which could further yield reproducible results in characterization and performance evaluation. The developed membranes were hydrostatically compressed at 414 kPa pressure for 5 h to get constant flux. During compaction, initially the

Table 1
Combinations of CA, solvent and PEG 600 for the preparation of membranes[a]

Membrane no.	CA (%)	Solvent (%)	Additive (%)
1	15	82.5	2.5
2	20	77.5	2.5
3	25	72.5	2.5
4	21.25	72.5	6.25
5	15.5	78	6.5
6	10	82.5	7.5
7	17.5	72.5	10

[a] Derived from design of experiments.

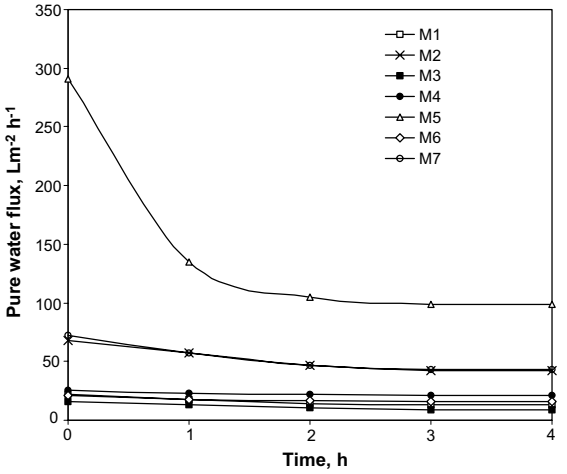

Fig. 1. Effect of time on pure water flux of CA membranes with PEG 600.

pure water flux was found to be high and declines gradually and reaches a steady state after 3 h for all the membranes, as shown in Fig. 1. This initial reduction in flux may be due to the fact that the membrane pores are being compacted leading to uniform pore size and steady state water flux.

3.2. Pure water flux

The effect of additive concentration on pure water flux of CA membranes was investigated, which is shown in Fig. 1, in order to find the possible improvement in the efficacy of the membranes. It is seen that the pure water flux is increasing upon increase in the concentration of additive. This fact is clearly demonstrated from the values obtained for M1 and M5 membranes. The corresponding pure water flux values are 13.5 and 98.7 $Lm^{-2} h^{-1}$. The increase in additive concentration increases the water flux because greater number of pores formed [18]. It is observed that membranes, corresponding to M2, M5 and M7, prepared from cellulose acetate with 2.5%, 6.5% and 10% PEG 600 showed a steady state pure water flux of 42.6, 98.7 and 43.6 $Lm^{-2} h^{-1}$. It seems that the increase in the concentration of PEG 600 does not increase the pure water flux linearly. This may be due to the change in the concentration of CA as well as solvent.

3.3. Water content

The pore former, PEG 600, concentration in casting solution of cellulose acetate was increased from 2.5 to 10 wt% and the water content of the membranes is shown in Table 2. It is found that the addition of PEG 600 to casting solution of pure cellulose acetate enhances the water content of the membranes. This is clearly evidenced from the values obtained for M1 to M3 membranes, where increase in the CA concentration decreases the water content at a constant additive concentration. A similar trend is also obtained for M4 to M6, where the additive concentration is increased slightly while the CA concentration is decreased significantly resulting in increased water content in the resultant membranes. This increase in water content may be due to the addition of PEG 600 to casting solution, which gets leached out upon gelation leading to formation of pores and becomes the domain of water molecules [19]. It is also possible that the PEG is hydrophilic that could attract water molecules inside the membrane matrix. Thus, the water content of 75.15% at 0 wt% PEG 600 [20] has attained a maximum of 87.22% at 7.5 wt% PEG 600 and 10% CA.

Table 2
Water content of the prepared membranes

Membrane no.	Water content (%)
1	80.33
2	77.51
3	76.22
4	78.05
5	80.95
6	87.22
7	78.46

3.4. Membrane hydraulic resistance (R_m)

Membrane hydraulic resistance is the intrinsic resistance of the membrane determined using pure water as feed [21]. It is an indication of the tolerance of the membranes towards hydraulic pressure. It is determined by subjecting the membranes to varied pressures (69–414 kPa) and measuring the pure water flux of the membranes. Thus, the R_m values for the membranes were deduced from the inverse of the slope of a plot of the transmembrane pressures versus pure water fluxes [22]. The pure water fluxes of the membranes were measured at transmembrane pressures of 69, 138, 207, 276, 345 and 414 kPa. The plot of transmembrane pressures versus pure water fluxes is shown in Fig. 2. In general, the pure water flux is increasing with the increase in transmembrane pressure. This is because the increase in the operating pressure increases the driving force for permeation of water. More particularly, the CA and PEG 600 combinations corresponding to M5 offers better hydraulic resistance compared to any other membranes, which may be due to the increased additive content in a most favorable CA concentration. This result is in agreement with that of pure water flux experiments. The R_m of the membranes were calculated from the slope of the plot and given in Table 3. It is seen that

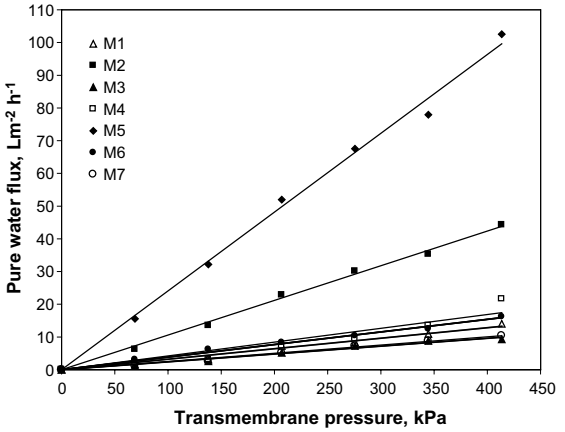

Fig. 2. Effect of transmembrane pressure on pure water flux of CA membranes with PEG 600.

Table 3
Membrane hydraulic resistance of the prepared membranes

Membrane no.	R_m
1	31.15
2	9.44
3	39.84
4	23.70
5	4.15
6	25.97
7	9.66

the R_m of M5 is the lowest in comparison to other membranes indicating that the pure water flux would be higher, which is in agreement.

3.5. Protein rejection studies

Studies on the rejection of proteins such as BSA, EA and pepsin through the prepared membranes at 345 kPa TMP is important in order to find the role of additives. The pH of the individual feed solution was kept constant at 7.2, since a change in pH may increase the adsorptive fouling of the membranes [23]. Furthermore, intermolecular forces between protein molecules and membranes will predominate and affect the efficiency of membranes if the pH of the solution changes [24]. The permeate flux of proteins such as BSA, EA and pepsin through the developed membranes is shown in Fig. 3. It is seen that the permeate flux of all the proteins is increased significantly when higher PEG 600 is added to CA (M7). Typically, a maximum flux of 900 $Lm^{-2} h^{-1}$ is obtained for pepsin among the selected proteins. The fluxes for BSA and EA are 864 and 790 $Lm^{-2} h^{-1}$, respectively. This may be due to that the presence of PEG 600 in the casting solution favors the formation of larger sized

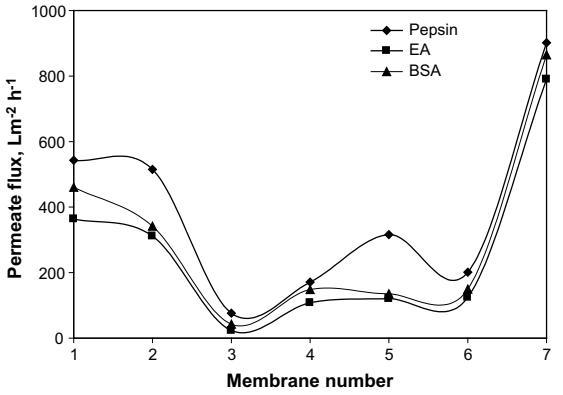

Fig. 3. Permeate flux of various proteins passed through CA membranes with PEG 600.

pores on the skin layer, during the gelation process of the membrane through leaching [25]. However, when the wt% of CA is increased from 15% to 25% at a constant additive input (2.5 wt%), the permeate flux of all the proteins decreases significantly.

While considering the percentage rejection during the separation of proteins an inverse trend is observed as seen in Fig. 4 in comparison to the permeate flux values. Higher wt% of PEG 600, which had shown a higher flux, provides lower rejection of proteins in the range of 33%–40%. Membranes (M1 to M3) prepared using increasing percentage of CA with a constant wt% of additive (2.5%) show increasing percent rejection of all the proteins on contrary to permeate flux values. M4, prepared using 21.25% CA and 6.25% PEG 600, offers maximum rejection of proteins. The corresponding rejection of BSA, EA and pepsin is 77%, 64% and 49%, respectively. Since none of the prepared membranes provide a

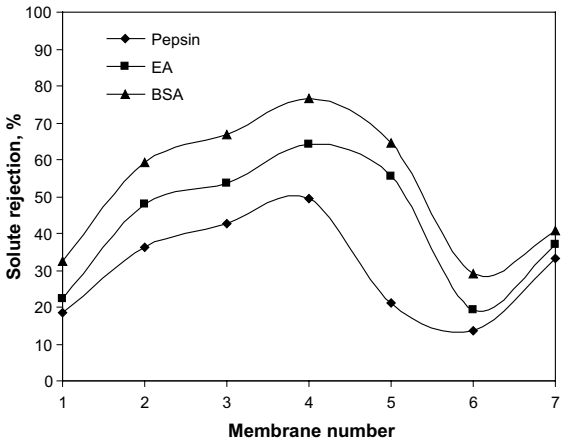

Fig. 4. Percentage rejection of various proteins separated through CA membranes with PEG 600.

rejection in the range of 80–100%, the MWCO of the membranes could not be arrived. In general, BSA is found to have higher rejection among the proteins studied. The order of percentage rejection is BSA > EA > pepsin. This may be due to the decreasing molecular weights of BSA, EA and pepsin, which is 69, 45 and 35 kDa, respectively.

3.6. Thermal Studies

3.6.1. Thermo gravimetric analysis (TGA)

The TGA curves of all the prepared membranes are shown in Fig. 5. In general, it is seen that the degradation of all the cellulose acetate based membranes occurs in three steps. The first step, from the room temperature (30 °C) to ~330 °C, represents the volatilization of the volatile matter and/or the evaporation of residual absorbed water. The second step, starts at ~330 °C and ends at ~450 °C, represents the main thermal degradation of the cellulose acetate chains. The third step, starts at ~450 °C, symbolizes the carbonization of the degraded products to ash. These three steps may correspond to the steps suggested by Chatterjee [26], representing the thermal degradation of the cellulose based materials. Further, it can also be observed that the thermal stability of CA is slightly modified by the presence of additives. It has been reported that the degradation of CA starts at 260 °C without any additives [27]. In this study, it is seen that some of the combinations of CA and PEG 600 results in increased thermal stability. More particularly, membranes M1, M4, M5, M6 and M7 show improvements in thermal degradation starting at as high as 300 °C compared to the value for pure CA. It should be noted that the effective additive content per unit percentage of CA is higher in all these membranes. In other words, membranes M2 and M3 have lower PEG 600 wt% per unit percentage of CA.

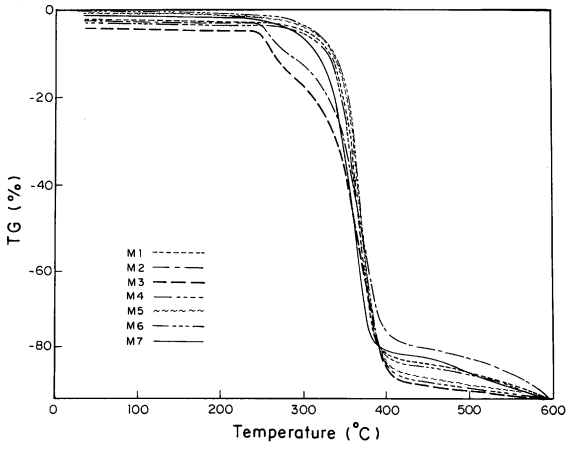

Fig. 5. TGA curves of various CA membranes with PEG 600.

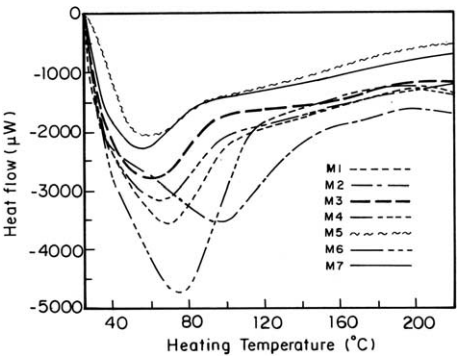

Fig. 6. DSC thermograms of various CA membranes with PEG 600.

3.6.2. Differential scanning calorimetry (DSC)

DSC curves of the CA/PEG 600 membranes prepared in this study are shown in Fig. 6. The glass transition temperature (T_g) is generally used to interpret membrane structure when employing a thermal analysis on a membrane [28]. A higher T_g indicates that membrane possesses more free volume fraction, therefore, a looser structure and vice versa. It is reported that pure CA membrane exhibits a T_g of ~55 °C [29] without any additives. It is interesting to note that the endothermic peak shifts to higher temperature region, if higher additive is added. Typically, for M6, which has the highest additive (0.75 wt%) per unit percentage of CA, the T_g is ~100 °C. On the whole, membranes M2, M3, M4, M6 and M7 possess T_g greater than 60 °C. In general, all the membranes show broad endothermic peaks. M3 has more endothermic heat flow (~−4750 μW) compared to all other membranes. The differences seen in the endothermic heat flow could be due to the differences in the CA and PEG 600 contents as well as packing density among the different membranes.

4. Conclusion

Various membranes with CA and PEG 600 have been prepared using mixture design of experiments concept for enhancing ultrafiltration membrane characteristics such as pure water flux, water content and membrane hydraulic resistance. It is found that the CA composition, the presence of hydrophilic additives (PEG 600) and their concentration play a key role in changing the membrane characteristics since the resulted membranes possess changes in porosity and pore size. Protein rejection studies reveal that the increase in additive concentration has a direct influence on the permeate flux

as well as percentage rejection values. It is seen that PEG 600 has significant role in altering the thermal properties, especially thermal stability, of the developed membranes. There seem to be a positive linear relation between the additive concentration and T_g, although the percentage of CA has some influence.

References

[1] Bemberis I, Neely K. Chem Eng Prog 1986;82:29.
[2] Ahner N, Gottschlich D, Narang S, Roberts D, Sharma S, Ventura S. Sep Sci Technol 1993;28:895.
[3] Bhattacharjee C, Datta S. Sep Sci Technol 1996;31:95.
[4] Rosberg R. Desalination 1997;110:107.
[5] Slater CS, Ahlert RC, Uchrin CG. Desalination 1983;48:171.
[6] Potnis SP. Chem Weekly 1992;7:137.
[7] Huang YC, Koseoglu SS. Waste Manage 1993;13:484.
[8] Staude E, Breitbach L. J Appl Polym Sci 1991;43:559.
[9] Cleek RL, Ting KC, Eskin SG, Mikos AG. J Control Release 1997;48:259.
[10] Arthanareeswaran G, Muthukumar M, Thanikaivelan P, Rajendran M, Mohan D. J Appl Polym Sci, submitted for publication.
[11] Machado PST, Habert AC, Borges CP. J Membr Sci 1999;155:171.
[12] Barth C, Gonclaves MC, Pires ATN, Roeder J, Wolf BA. J Membr Sci 2000;169:287.
[13] Kutowy O, Sourirajan S. J Appl Polym Sci 1975;19:1449.
[14] Osada V, Nakagawa I. Membrane science and technology. New York: Marcel Dekker Inc.; 1992.
[15] Tamura M, Uragami T, Sugihara M. Polymer 1981;22:829.
[16] Bhattacharya D, McCarthy JM, Grieves RB. AICh J 1974;20:1206.
[17] Malaisamy R, Mohan D, Rajendran M. Polym Int 2003;52:412.
[18] Wang D, Li K, Teo WK. J Membr Sci 1995;98:233.
[19] Taiping H, Shenghua D, Lingying Z. Water Treat 1991;6:51.
[20] Mahendran R, Malaisamy R, Mohan D. Eur Polym J 2004;40:623.
[21] Cheryan M. Ultrafiltration handbook. Lancaster: Technomic Publ Co.; 1986.
[22] Kesting RE. Synthetic polymeric membranes. New York: McGraw-Hill Book Company; 1971.
[23] Persson KM, Gekas V, Tragardh G. J Membr Sci 1995;100:155.
[24] Brinck J, Jonsson AF, Jonsson B, Lindau J. J Membr Sci 2000;164:187.
[25] Koehler JA, Ulbricht M, Belfort G. Langmuir 1997;13:4162.
[26] Chatterjee PK. J Polym Sci 1968;6:3217.
[27] Lucena MC, Alencar AEV, Mazzeto SE, Soares SA. Polym Degrad Stab 2003;80:149.
[28] Fritzsche AK, Cruse CA, Kesting RE, Murphy MK. J Appl Polym Sci 1990;39:1949.
[29] Shieh JJ, Chung TS. J Membr Sci 1998;140:67.