

Pervaporation of chloroform-acetone mixtures through DCP crosslinked poly (ethylene-co-vinyl acetate) membranes

M N Muralidharan^a & S Anil Kumar^{b*}

^aDepartment of Chemistry, M P M M S N Trust's College, Shoranur, Palakkad, India

^bDepartment of Chemistry, N S S College, Nemmara, Palakkad, India

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Membranes of poly (ethylene-co-vinyl acetate) crosslinked with dicumyl peroxide (DCP) were prepared. The permeation characteristics in the pervaporation process were examined using chloroform-acetone mixtures. The DCP modified membranes exhibited chloroform permselectivity. The sorption characteristics, effects of feed concentration and crosslinking density on pervaporation were also examined. The separation was found to be maximum at high concentrations of chloroform in the feed mixture. The maximum separation and flux were found to be associated with a moderate amount of crosslinking agent in the membrane. As the crosslinking density was increased, flux and selectivity were found to decrease.

Keywords: Pervaporation, poly (ethylene-co-vinyl acetate), dicumyl peroxide

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In 1970s and 1980s, membrane methods of separating liquids and gases became an exceedingly important and dynamically developing field¹. Even today, the membrane separation processes are getting more and more importance in chemical industries because of low cost, easy maintenance, stability in hostile environments², low energy and material consumption, the continuous nature of the process, simplicity and flexibility of control. The ability of polymers to selectively solubilise and transport the molecules of gas, vapour, liquid and sometimes solute through its solid phase has made them the most preferable material for membrane separation process.

Pervaporation is the most developed membrane separation method which is widely in use today. This method could attract the attention of specialists in chemical and related fields like biochemical and petrochemical industries as an energy saving and environmentally friendly technology. The main advantage that makes this method an outstanding one is that it can be used to separate any liquid mixture in all concentration ranges³⁻⁷. Pervaporation is the selective evaporation of a component from a liquid mixture through a membrane. Pervaporation differs from other membrane separation methods in the fact that the material transported through the membrane undergoes a phase change. The method is basically a

solution-diffusion process. The driving force for the transport is the concentration difference across the membrane due to pressure difference. When in contact with the feed mixture, the membranes swell and work as a pseudo liquid immobilised layer. At first, the component molecules get adsorbed at the upperside of the membrane and then diffuse to the other side. On the other side, utilising a minimum energy of enthalpy of vaporisation, a phase change occurs and the vapour is removed and then condensed. Fig. 1 shows the schematic representation of the pervaporation process.

Pervaporation can be used for dehydration of organic solvents and removal of organics from aqueous streams. Additionally, pervaporation has emerged as a good choice for the separation of heat sensitive products.

Many works have been reported on the separation of binary liquid mixtures by this technique. Huang and Lin⁸ studied the separation of binary liquid mixtures of aqueous alcohol solution and established some characteristics of permeation. Yoshikawa *et al.*⁹ separated lower alcohol-water mixtures using both cross linked and uncrosslinked polybutadiene membranes. They found that cross linked polymer permeated lower alcohols in preference to water. Mulder *et al.*¹⁰ prepared a blend of poly (acrylic acid) and poly (vinyl alcohol) and used it as membrane.

*For correspondence (E-mail: anugraha_anil@yahoo.co.in)

They established that the selectivity depends on both blend composition and feed composition. Kumar *et al.*² studied the effect of cross links on pervaporation by cross linking poly (ethylene-co-vinyl acetate) with dicumyl peroxide (DCP) and benzoyl peroxide (BP)². They established that, for maximum flux and selectivity, there should be an optimum amount of cross linking agent. Rajagopalan *et al.*¹¹ used pervaporation for the separation of methyl anthranilate from grape essences with poly dimethoxyl siloxane-polycarbonate membranes and followed the effect of the process parameters on separation. Cox and Baker¹² used pervaporation for the treatment of wastewater contaminated with organics and found it more cost-effective than other treatment options. Pervaporation is well suited for the recovery of VOCs with medium to high volatility, from small to medium sized aqueous streams containing 200 to 50,000 ppm dissolved organic compounds. Since the feed water is typically heated to relatively low temperatures (40 to 60°C), pervaporation is ideal for the recovery of high value, thermally labile compounds such as flavour and aroma chemicals from water¹³. An *et al.*¹⁴ used membranes of PVC/EVA blends for the separation of benzene-cyclohexane mixtures. Matsui and Paul¹⁵ used ionically crosslinked poly(*n*-alkyl acrylate) membranes for the separation of toluene/*i*-octane mixtures.

In this article the pervaporation of chloroform-acetone mixtures through poly(ethylene-co-vinyl acetate) membranes is reported. This membrane was selected because of the close solubility parameter of chloroform and poly (ethylene-co-vinyl acetate), easy preparation of the membranes, and good mechanical properties.

Experimental Procedure

Materials and methods

Poly (ethylene-co-vinyl acetate), EVA (Pilene 1802), used was supplied by Polyolefin Industries Limited, Chennai, India. The basic characteristics of

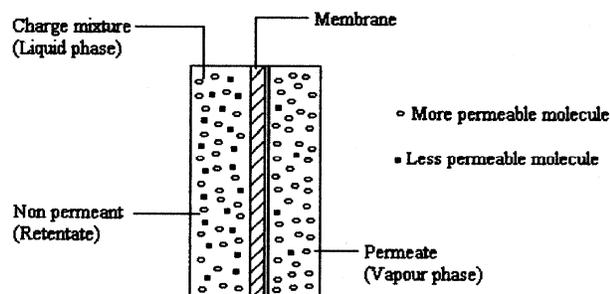


Fig. 1—Schematic representation of the pervaporation process.

the co-polymer are given in Table 1. The cross linking agent used was dicumyl peroxide (DCP) (40% activated). The solvents used were chloroform and acetone. All the solvents used were distilled twice before use.

Preparation of membranes

Cross linked poly (ethylene-co-vinyl acetate) (EVA) membranes were prepared. EVA was crosslinked by peroxide technique¹⁶ using dicumyl peroxide (DCP) as the cross linking agent. Samples with different loadings of DCP were also prepared. The formulations of mixtures are given in Table 2.

EVA granules were sheeted out in a two roll mixing mill having friction ratio 1:1.4. During mixing, dicumyl peroxide was added. The cure characteristics of the samples were studied in a Goettfert rheometer. Knowing their cure characteristics, the samples were cured to their optimum cure time at 170 °C in a hydraulic press under a pressure of 25 tonnes. The thickness of each membrane was ~ 120 µm. The membranes are designated as D₁, D₂, D₄ and D₆ according to the DCP content where the subscript numbers represents the grams of DCP used per 100 g polymer.

Solvent uptake experiments

Solvent uptake experiments were carried out to find the solubility parameters of chloroform and acetone. Samples of previously weighed dry EVA membranes (D₁) were kept soaked in equal volumes of chloroform and acetone for 48 h. Then membranes

Table 1—Characteristics of Poly(ethylene-co-vinyl acetate) (EVA)

Properties	
Molecular weight(M_w)	20,000
Vinyl acetate (Wt. %)	18.0
Meltflow index (g/10min)	2.0
Vicat softening point (°C)	59.0
Tensile strength at break (MPa)	14.0
Elongation at break (%)	750.0
Density (g/cc)	0.937
Intrinsic viscosity (dL/g)	0.170
Tg	-10°C

Table 2—Composition of the membranes

Wt. of polymer(g)	Wt. of DCP(g)	No. of moles of DCP	Representation of the sample
100	1	0.0015	D ₁
100	2	0.0030	D ₂
100	4	0.0060	D ₄
100	6	0.0090	D ₆

were taken out and weighed within 25 s. The weight differences between the dry and soaked samples were calculated for both the solvents to find in which solvent polymer swells more. The experiment was repeated for the mixture of the two solvents in different compositions with D₁, D₂, D₄ and D₆ membranes.

The solvent uptake ratios of the polymer samples (D₁, D₂, D₄ and D₆) in different compositions of chloroform-acetone mixture were calculated using the equation

$$S = (W_s - W_d)/W_d$$

where W_d denotes weight of dry membrane and W_s denotes weight of solvent swollen membrane.

Pervaporation experiment

A schematic representation of the pervaporation process is represented in Fig. 2. The permeation cell assembled from two half cells of column couplers made of glass, fastened together by bolted clamps. The capacity of each half cell was about 100 mL and the effective surface area of the membrane was 19.3 cm². The membrane was supported on a finely porous stainless steel plate. Vacuum at the downstream side was maintained by using Hindhivac (Ed-6). A pressure of 3.5 to 4 mm of Hg was applied. Such a lower pressure was maintained because pervaporation experiments are generally conducted with higher vacuums in order to attain appropriate flux and selectivities. The membrane was soaked in the mixture for 24 h and then kept in the pervaporation cell for about 2 h for each run to reach equilibrium conditions before collecting the permeate. The permeated vapours were completely condensed in a trap placed in a Dewar flask cooled to -40°C using ice-calcium chloride mixture. Complete condensation was effected by placing two traps in series. The experiments were carried out with membranes having different DCP loadings. Different feed compositions were also used. All the experiments were conducted at room temperature.

The permeate and feed compositions were analysed by a Gas Liquid Chromatograph (Shimadzu GC14B, Japan). The column used was BP-1 (Capillary) and the detector was FID (Flame Ionization Detector). Helium was used as the carrier gas and hydrogen and compressed air were used for the flame in FID. The injection port was maintained at a temperature of 240°C, column temperature at 50°C and detector temperature was at 250°C.

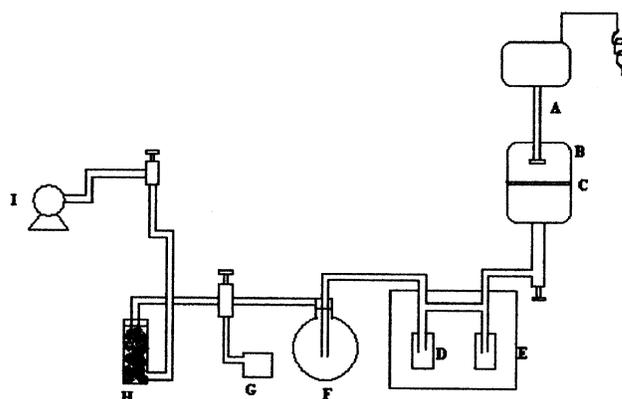


Fig. 2—Schematic diagram of pervaporation apparatus (a) Stirrer, (B) Permeation cell, (C) Membrane, (D) Collection traps, (E) Dewar flask, (F) R B flask, (G) Pressure gauge, (H) Moisture trap and (I) Vacuum pump.

The performance of the membrane in pervaporation was characterised by permeation rate or flux (J) and selectivity α_{ij} .

The selectivity is given by

$$\alpha_{ij} = (Y_i/Y_j) / (X_i/X_j)$$

where Y_i and Y_j are weight fractions of the components in the permeate, X_i and X_j are weight fraction of the components in the feed, i is the more permeating solvent and j is the less permeating solvent. The permeation rate or flux is the amount of component permeated in unit time and per unit cross section area of the membrane. The flux is expressed as g/m²h.

Results and Discussion

Solvent uptake characteristics

From the solvent uptake experiments it was found that the polymer (D₁) swells more in chloroform. This is because the solubility parameter of the polymer is close to that of chloroform.

The solvent uptake ratios of the polymer samples (D₁, D₂, D₄ and D₆) in different compositions of chloroform-acetone mixture were calculated. The degree of solvent uptake of modified poly (ethylene-co-vinyl acetate) membranes with different DCP loadings in the binary mixtures of chloroform-acetone used in this study are represented in Fig. 3.

When binary mixtures of chloroform and acetone with different compositions were used to find the solvent uptake ratio of D₁, D₂, D₄ and D₆ membranes, it was found that, in all the cases, as the chloroform

composition increases, the solvent uptake ratio also increases. It was seen that the solvent uptake ratio decreases in the order $D_1 > D_2 > D_4 > D_6$ for all compositions of chloroform. This is because, when the amount of crosslinking agent increases, the polymer matrix becomes very rigid and thus the solvent uptake is decreased. Thus, a lower solvent uptake ratio is observed for high amounts of crosslinking agent.

Performance of the membrane

Pervaporation of a binary mixture of chloroform and acetone containing 50% each was carried out through DCP crosslinked (D_1) EVA membrane. It was expected acetone to permeate more because of its lower molecular size. However, from the experiment, it was observed that DCP modified EVA shows more selectivity towards chloroform than acetone. The selectivity factor was greater than unity. This can be explained by considering two factors, the polarity and solubility parameters. EVA is polar in nature. Chloroform is more polar than acetone. Thus, in this case, it is not the molecular size that accounts for the permeation of molecules, but the polar-polar interaction of chloroform and EVA and the comparability in their solubility parameters enables chloroform to permeate more freely than acetone through DCP modified EVA membranes.

The polymer-solvent interaction is the most important factor that determines the effectiveness of the membrane. Earlier, it was reported that unmodified EVA membranes showed acetone selectivity from a mixture of carbon tetrachloride and acetone². But in this study, when EVA was modified with DCP, membrane showed more selectivity towards chloroform than acetone. In the case of virgin EVA which is more crystalline in nature, the compact crystalline regions does not allow the bigger size chloroform molecules to pass through even though there is more interaction. Hence, the smaller size acetone molecule permeates more. But the flux and selectivity are very low.

When EVA was crosslinked with DCP, the crosslinking introduced C-C networks thereby reducing the crystallinity and increasing the porosity. This is illustrated schematically in Fig. 4. When the porosity increased, the bigger size chloroform molecules could permeate without any hindrance through the polymer matrix. Thus higher flux and selectivity were observed.

The selectivity and flux were calculated for D_1 for different compositions of chloroform-acetone

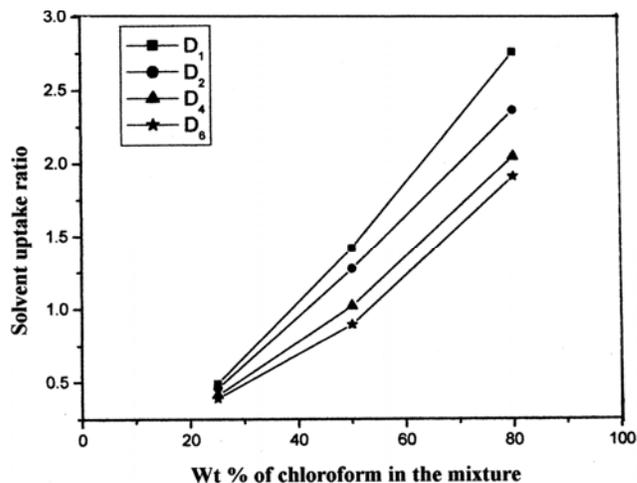


Fig. 3—Dependence of solvent uptake ratio on the amount of CHCl_3 in the mixture of chloroform-acetone for EVA membranes with different DCP loadings.

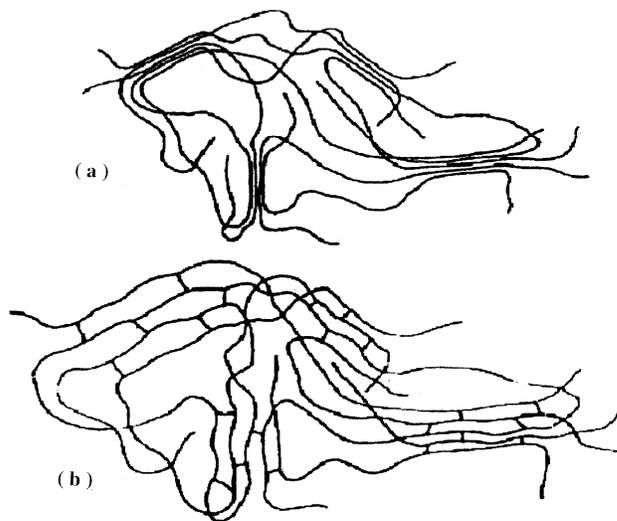


Fig. 4—Schematic representation of the morphology of (a) neat (unmodified) and (b) crosslinked (modified) EVA.

mixtures. In all compositions, selectivity was greater than unity and high values for flux were also obtained. Thus, the performance of DCP crosslinked EVA is appreciably good enough for the pervaporation of chloroform acetone mixtures.

Effect of feed composition

When different feed compositions of chloroform and acetone were used for the pervaporation through DCP crosslinked (D_1) EVA membrane, it was observed that, as the chloroform content is increased in the feed, the percentage composition of chloroform in the permeate is also increased. From the solvent

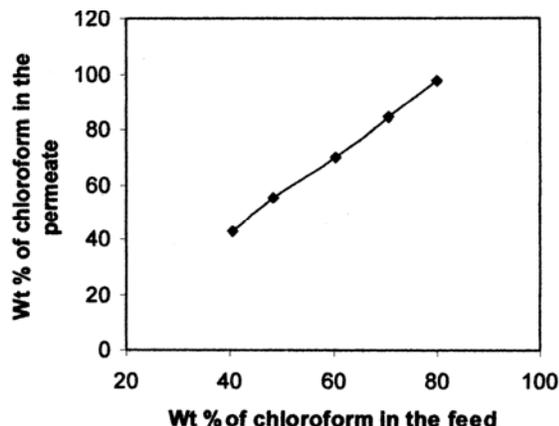


Fig. 5—Effect of feed composition on pervaporation of chloroform-acetone mixtures through D_1 membrane.

uptake experiments it is seen that, the solvent uptake is more at high compositions of chloroform due to the close solubility parameters of chloroform and EVA. The same reason can be assigned for the more permeation of chloroform at high proportion of chloroform in the feed. This trend is represented in Fig. 5.

The flux and selectivity were calculated for different feed compositions. The permeation rate (flux) increased with the increase in chloroform composition in the feed mixture (Fig. 6). With the increase in chloroform concentration in the feed mixture, free volume of the membrane increases due to plasticization, and hence the rate increases. The high flux values are quite reproducible.

The D_1 membrane exhibited an increasing selectivity with increasing concentration of chloroform in the feed mixture (Fig. 7). There was only a small increase in the selectivity at lower concentrations but a very large increase at higher concentrations of chloroform in the feed mixture.

Effect of crosslinks on pervaporation

The influence of number of moles of DCP used in the membrane on pervaporation of a 70 wt % chloroform containing mixture was followed using D_1 , D_2 , D_4 and D_6 membranes. The amount of chloroform permeated decreased in the order $D_1 > D_2 > D_4 > D_6$ (Fig. 8).

The values of flux and selectivity also decreased with increase in number of moles of crosslinking agent (DCP) in the membrane (Figs 9 & 10).

The crystallinity of virgin EVA can be reduced by modifying with DCP thereby making it more flexible and more permeable to chloroform. But, as the

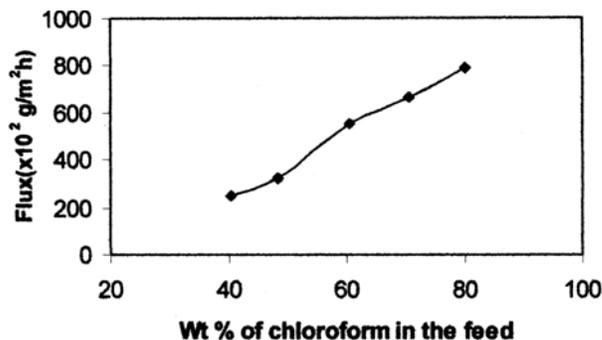


Fig. 6—Effect of feed composition on permeation rate for D_1 membrane.

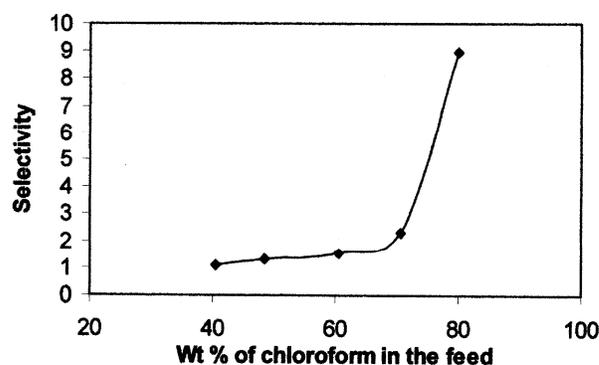


Fig. 7—Effect of feed composition on selectivity for D_1 membrane.

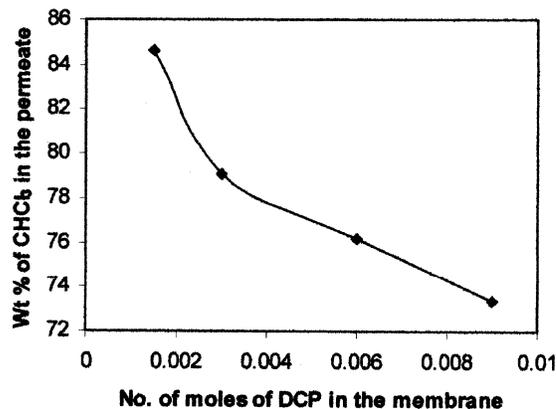


Fig. 8—Effect of number of moles of DCP in the membrane on pervaporation.

amount of DCP increases, the number of crosslinks in the polymer matrix also increases. The increased crosslinking density reduces the flexibility of polymer and the membrane become more rigid and the permeation of the molecules become more difficult. Thus, flux and selectivity decreases. As the amount of DCP increases the reduction in crystallinity is offset by the increase in crosslinks. Hence the permeability,

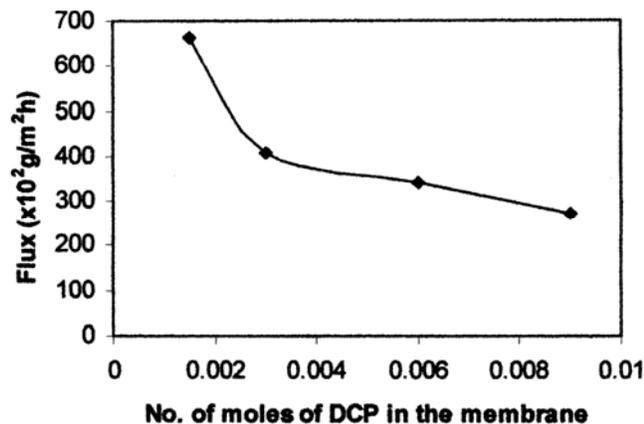


Fig. 9—Effect of number of moles of DCP in the membrane on permeation rate.

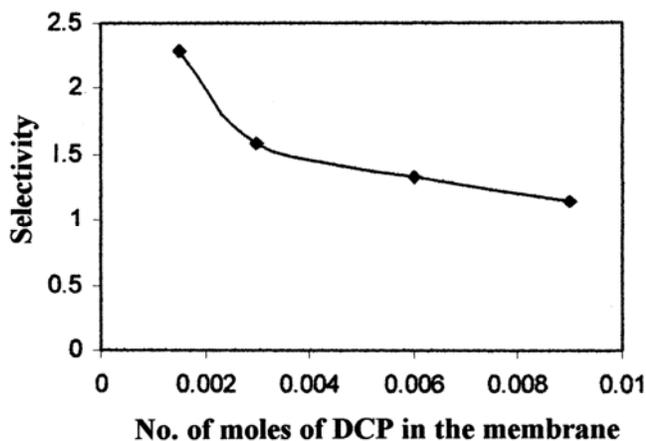


Fig. 10—Effect of number of moles of DCP in the membrane on selectivity.

flux and selectivity decrease in the order $D_1 > D_2 > D_4 > D_6$. From the observations it is clear that, for maximum flux and selectivity poly (ethylene-co-vinyl acetate) must be crosslinked with moderate amounts of DCP i.e., 1 g (0.0015 moles) of DCP per 100 g of polymer.

Conclusion

Poly(ethylene-co-vinyl acetate) membranes crosslinked with dicumyl peroxide exhibit chloroform selectivity from chloroform-acetone mixtures. As the amount of chloroform in the feed composition increases, both rate and selectivity increase. The values of flux and selectivity were found to decrease with the increase in the amount of crosslinking agent (DCP) in the membrane. High values for flux and selectivity were observed for an optimum amount of crosslinking agent (0.0015 moles of DCP per 100 g of polymer). The high values for flux and selectivity assures the effectiveness of DCP modified EVA membranes in pervaporation separation studies.

References

- 1 Volkov V V, *Russ Chem Bull*, 43(2), Feb (1994).
- 2 Anil Kumar S, Gedam P H, Kishan Prasad V S, Kumaran M G & Sabu Thomas, *J Appl Polym Sci*, 60 (1996) 735.
- 3 Schauer J, *J Appl Polym Sci*, 53 (1994) 425.
- 4 Sun F & Ruckenstein E, *J Membrane Sci*, 90 (1994) 275.
- 5 Hu C M & Chiang W Y, *J Appl Polym Sci*, 42 (1992) 1829.
- 6 Schauer J & Bleha M, *J Appl Polym Sci*, 46 (1992) 1807.
- 7 Park H C, Meertens R M, Mulder M H V & Smolder C A, *J Membrane Sci*, 90 (1994) 265.
- 8 Huang R Y M & Lin V T C, *J Appl Polym Sci*, 12 (1968), 1268.
- 9 Yoshikawa M, Wano T & Kitao T, *J Membrane Sci*, 89 (1993) 23.
- 10 Mulder M H V, Kruijtz F & Smolders C A, *J Membrane Sci*, 11 (1982) 349.
- 11 Rajagopalan N & Cheriyan M, *J Membrane Sci*, 104 (1995) 243.
- 12 Cox & Baker R W, *Industrial Wastewater*, (January/February 1998), 35.
- 13 Athayde A L, Baker R W, Daniels R, Le M H & Ly J H, *CHEMTECH*, (January 1997), 34.
- 14 An Q F, Qian J W, Sun H B, Wang L N, Zhang L & Chen H L, *J Membrane Sci*, 222 (2003) 113.
- 15 Matsui S & Paul D R, *J Membrane Sci*, 235 (2004) 25.
- 16 Anil Kumar S, Sabu Thomas & Kumaran M G, *Polymer*, 38(18) (1997) 4629.