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Preparation of a new class of polymeric composite membranes and their application in pervaporation

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The preparation of composite membranes consisting of thin films of polymeric networks sustained by thicker porous supports is described. The structure of the membranes was observed with the aid of a scanning electron microscope. The membranes were tested in a vacuum pervapouration unit with a water–ethanol solution containing 10 wt % alcohol. Free dense films of the same polymeric networks were also prepared in order to compare their pervapouration performance with that of composite membranes.

1. Introduction

Pervapouration is, in brief, a membrane process for separating the components of a liquid mixture on the basis of their different solubility and diffusivity in the membrane [1]. The mass transport through the membrane is achieved by maintaining a reduced total pressure on the permeate side of the membrane (vacuum pervapouration).

The heart of the process is the membrane, which should provide both a high permeate flux and a high selectivity, this latter being defined in terms of the separation factor $\alpha_{i,j}$ as [2]

$$\alpha_{i,j} = \frac{(C_i/C_j)^{\mathrm{P}}}{(C_i/C_j)^{\mathrm{F}}} = \frac{C_i^{\mathrm{P}}/C_i^{\mathrm{F}}}{C_j^{\mathrm{P}}/C_j^{\mathrm{F}}} \qquad (1)$$

where C_i^{P} and C_i^{F} are the concentrations of the preferentially permeating species, i, in the permeate, P, and in the feed, F, respectively.

Permeate flux depends on membrane thickness. A decrease of the latter causes an increase of the former but makes the membrane difficult to handle. To overcome this problem composite membranes are prepared. They consist of a thin, dense (non-porous) film, which represents the "true" membrane, supported by a thicker porous sublayer which provides both mechanical strength and handling property and does not practically affect either flux or selectivity.

Composite membranes for pervaporation are usually prepared by one of the following methods [3]:

(a) interfacial polymerization of reactive monomers on the surface of the support,

(b) dip-coating of the support in a polymer solution and drying, or

(c) dip-coating of the support in a reactive monomer or pre-polymer solution and thermal curing.

A new method for the preparation of composite membranes is described and preliminary results on some of their properties, structure and pervapouration performance is reported. The method involves the use of the radiation curing technique for obtaining thin films of polymeric networks coated on a porous support.

The radiation curing technique is gaining relevance in the field of coatings and microelectronics [4]. The main advantages of this technique are: (a) solvent use is avoided; (b) a fast curing reaction and solid film formation are easily obtained; (c) homogeneous films are formed whose thickness can be controlled in a wide range; and (d) the physical and chemical properties of the film can be changed with continuity by using reactive oligomers with different structures, and mixtures of them and functionalized monomers or oligomers [5, 6].

2. Experimental procedure

2.1. Materials

The porous supports used were of two types:

(a) polyvinylidene fluoride (PVDF) microfiltration symmetric membranes with an almost even porosity (pore size > 0.2 µm) all over the membrane cross-section (Fig. 1), and

(b) polyvinylidene fluoride or polysulphone (PSF) asymmetric ultrafiltration membranes with a porosity increasing across the membrane from top (pore size

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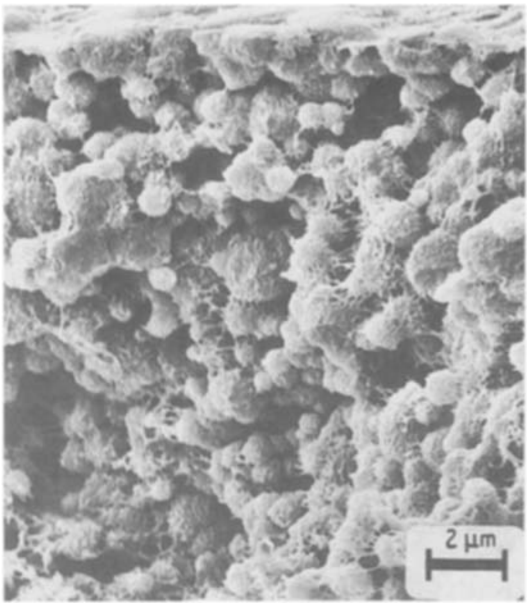

Figure 1 Scanning electron micrograph of the cross-section of a PVDF symmetric membrane (type (a) support).

< 0.05 µm) to bottom (pore size > 0.2 µm) as shown in Fig. 2.

The methods of preparation of porous supports are described elsewhere [7–9].

The reactive oligomers used were mainly of two types:

(a) tripropylene glycol diacrylate (B10), and

(b) an oligomer containing polydimethyl siloxane blocks linked by urethane groups and terminated with acrylic double bonds (B11).

2.2. Composite membranes and free dense film preparation

Sheets of the porous supports were coated with liquid mixtures containing reactive oligomers and irradiated by means of a u.v. lamp. Formulations having viscosities in the range 40–400 mPa s were mixed with 3 wt % of a photoinitiator (2.2 dimethoxy-2-phenylacetophenone) and applied on the porous support with a calibrated wire-wound applicator in order to obtain a film thickness in the range 5–50 µm. The system was then irradiated by means of a 500 W medium-pressure mercury lamp (Helios Italquartz) at a distance of 20 cm, working in a pure nitrogen atmosphere. An irradiation time suitable for obtaining the maximum hardness value of polymeric film was used. After curing, the system was subjected to thermal treatment at 60–80 °C for 8 h to obtain relaxation of the internal stresses in the polymer film: this treatment was shown to also reduce microdefects and film inhomogeneities due to the shrinkage occurring during the photopolymerization process.

Free dense films obtained by using the above formulations were also prepared in order to characterize the material properties and swelling behaviour. They were prepared by coating a glass or Teflon plate with the liquid mixture, irradiating it with the u.v. lamp, peeling the film from the plate and completing the curing process of the free film. In all cases, after u.v. irradiation, the gel content of the free film was > 98 wt %.

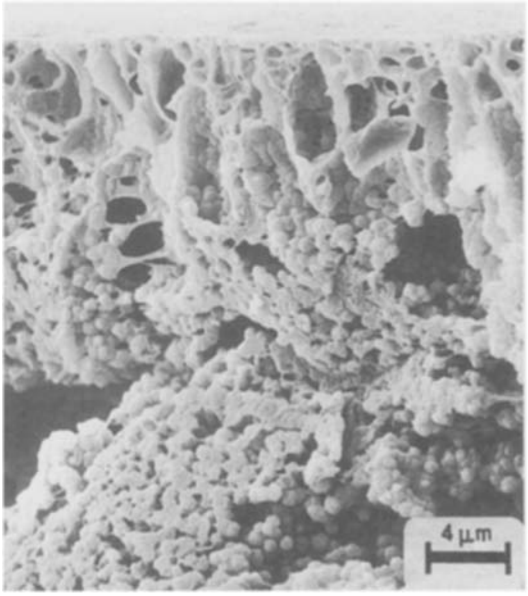

Figure 2 Scanning electron micrograph of the cross-section of a PVDF asymmetric membrane (type (b) support).

2.3. Composite membrane and free dense film characterization

The structure of the cross-section of the membranes was examined with the aid of a Cambridge Stereoscan 250 MK2 scanning electron microscope (SEM). The specimens were obtained by fracturing the membranes at liquid nitrogen temperature and coating with gold.

The flux and selectivity of both membranes and free dense films were evaluated at 30 °C with a laboratory vacuum (1–2 mm Hg) pervaporation unit fed with a water–ethanol solution containing 10 wt % alcohol. The surface in contact with the feed solution was 10 cm^2. The analysis of the permeate and feed composition was carried out with a gas chromatograph fitted with a Porapak Q 8/100 column.

Contact angle measurements were carried out at 20 °C on free dense films by using an Erma G-1 contact angle meter.

Equilibrium swelling data were obtained by a gravimetric method. Samples of free dense films were immersed in the liquid at 20 °C. After 1 h the films were removed from liquid, gently pressed between two sheets of filter paper and weighed. The procedure was repeated at intervals of 2 h until the degree of swelling was constant with time. In all cases equilibrium swelling was attained in 10 h.

Dynamic mechanical analysis was performed on the free dense films by using a Rheovibron Instrument DDV-II at 110 Hz. The maximum values of tanδ obtained with the two aforementioned oligomers occurred in the range 40–70 °C. These values can be considered as an indication of the glass temperature of the film obtained.

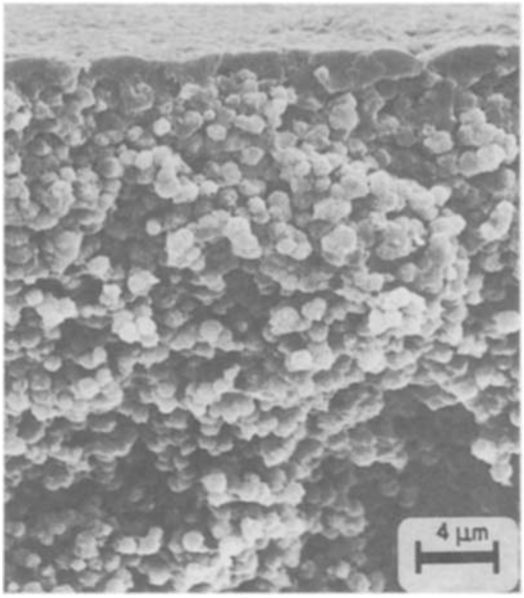

Figure 3 Scanning electron micrograph of the cross-section of a composite membrane obtained from B10 reactive oligomer and PVDF symmetric membrane (type (a) support).

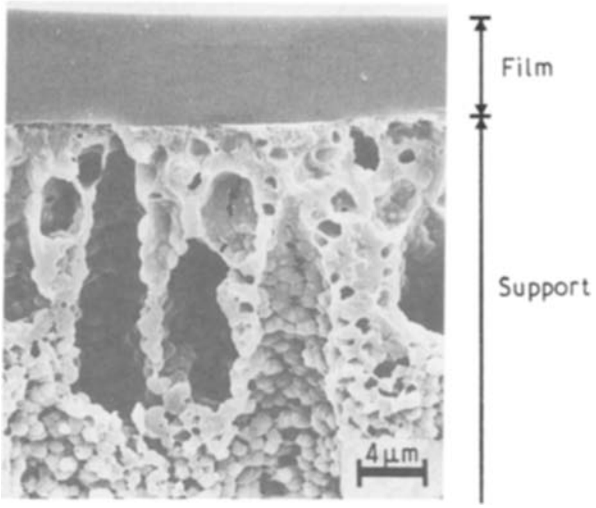

Figure 5 Scanning electron micrograph of the cross-section of a composite membrane obtained from B10 reactive oligomer and PVDF asymmetric membrane (type (b) support).

3. Results and discussion

Figs 3 and 4 show SEM micrographs of membranes obtained by applying, on type (a) supports (Section 2.1), layers of reactive oligomer B10 by using applicators able to supply a nominal thickness of 4 and 24 µm, respectively. The contrast between the two figures is striking. In Fig. 3 the surface of the resulting system appears rough and no dense film on the support is observed. This is due to the penetration of the applied layer into the pores of the support. In order to obtain continuous film formation it was necessary to apply a layer with a nominal thickness of 10 µm.

By using less porous supports of type (b), the penetration of the applied layer into the pore was considerably reduced. This is demonstrated in Figs 5 and 6, which show SEM micrographs of membranes obtained by applying the reactive oligomer (B10) on supports having approximately the same porosity but different chemical natures (PVDF in Fig. 5 and PSF in Fig. 6). In both Figures the interface between the dense film and the support is easily distinguishable, but only in the case of PVDF (Fig. 5) does the adhesion of the dense film appear good. The results so far obtained do not allow us to give a clear explanation of the adhesion behaviour of the different systems; this needs to be further investigated.

Similar behaviour was observed by using the other reactive oligomer (B11).

Table I lists the results of contact angle and equilibrium swelling measurements. A qualitative correlation is found between contact angle and swelling value, since the lower the former the higher the latter. The tabulated values suggest that ethanol–film interactions are higher than water–film ones.

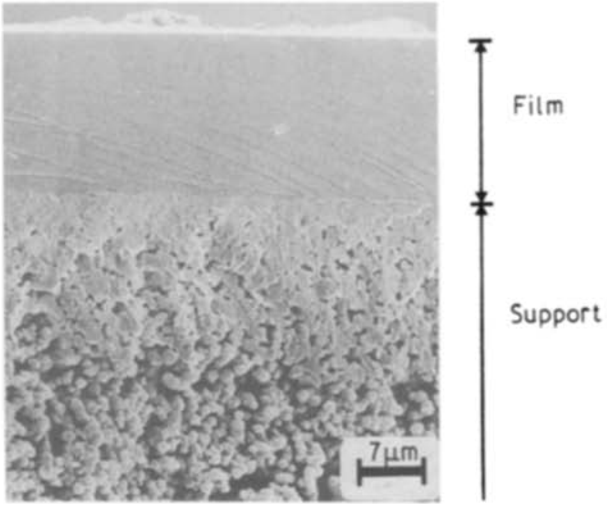

Figure 4 Scanning electron micrograph of the cross-section of a composite membrane obtained from B10 reactive oligomer and PVDF symmetric membrane (type (a) support).

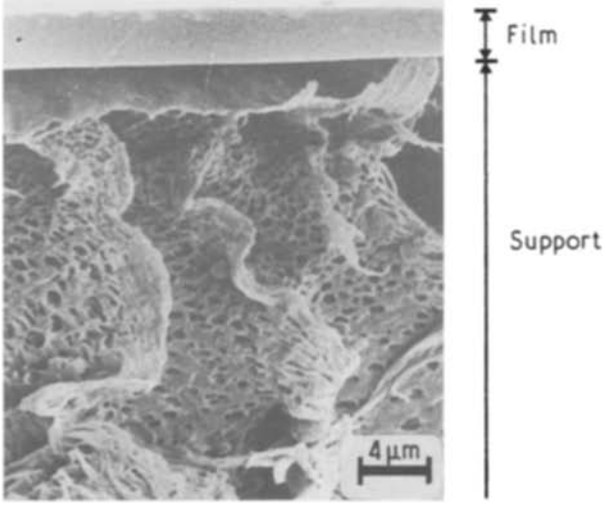

Figure 6 Scanning electron micrograph of the cross-section of a composite membrane obtained from B10 reactive oligomer and PSF asymmetric membrane (type (b) support).

TABLE I Equilibrium swelling and contact angle data at 20 °C of free dense films obtained from different reactive oligomers

Type of reactive oligomer	Film properties			
	Contact angle (deg)		Equilibrium degree of swelling (wt %)	
	Water	Ethanol	Water	Ethanol
B10	60	8	5.8	7.2
B11	97	34	0	4

TABLE II Pervaporation performance of dense free films and composite membranes obtained from different reactive oligomers and a PVDF asymmetric membrane (type b) support

Film or membrane type	Type of reactive oligomer	Film or membrane properties		
		Thickness (μm)	Selectivity[a]	Flux $(\mathrm{l\,m^{-2}\,h^{-1}})$
Free dense film	B10	60	2.1	0.40
	B10	30	2.1	0.76
	B11	60	2.8	0.08
	B11	30	2.5	0.20
Composite membrane (supported dense film)	B10	18	1.1	2.4
	B11	18	1.6	0.58

[a] $\alpha_{\text{ethanol}} = \left(\frac{\text{wt \% water (feed)}}{\text{wt \% water (permeate)}}\right)\left(\frac{\text{wt \% ethanol (permeate)}}{\text{wt \% ethanol (feed)}}\right)$

Table II compares pervapouration data obtained from both free dense films and composite membranes. The data indicate that the alcohol preferentially passes through the membrane. This fact is in qualitative agreement with the results reported in Table I. In addition it appears that by decreasing the thickness of the free dense films the permeate flux increases almost proportionally, whereas the selectivity only slightly decreases. From Table II it is also apparent that the selectivity of the composite membranes is lower than that expected on the basis of free dense film data, whereas the flux is higher. This is probably due to a higher level of microdefects in the supported films with respect to the free ones.

Efforts are in progress to control either film coating deposition or rate of polymerization in order to improve the homogeneity of the supported films.

4. Conclusions

The radiation curing technique has been proven useful for obtaining composite membranes. The success of the method depends on a proper choice of the support as far as its porosity and its chemical nature are concerned. The control of microdefects in the supported dense film during its formation seems of paramount importance in order to optimize membrane selectivity.

Acknowledgements

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